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Polyketone Blends with Various Added Materials

A Screening Evaluation

R. G. Lutz

Technical Progress Report **WRC 155–88**
Project No. 62177

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Polyketone Blends with Various Added Materials

A Screening Evaluation

Technical Progress Report **WRC 155–88**

Project No. 62177
CARILON® Polymers – Exploratory

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ABSTRACT

This report presents the results of an extensive study in which the effects of twin screw mixing conditions and a representative sampling of additives were screened for their physical and chemical effects on polyketone terpolymer. About 100 extruder runs, using about 65 different additives were carried out.

Processing and blending were carried out in a co-rotating, twin screw mini-extruder. The products were examined to varying degrees for any possible effects on the polyketone component in oven, melt and ozone stability, processing efficiency, crystallinity, color, flame retardancy, added phase dispersion size, compatibility, second order transitions, crosslinking and barrier characteristics.

The most important goal of this work, to find a solution to the oxidative stability problem with polyketone, unfortunately was not met. However, many potentially useful leads were uncovered and most of the findings can be useful in the guidance of further work with polyketone. Many cases of improvements in oven and melt stability and in processability were found, along with ways to alter various physical properties. Also found were flame retardant, controlled crosslinking agents and unexpected effects of processing variables.

Technical Progress Report WRC 155–88

Polyketone Blends with Various Added Materials

A Screening Evaluation

by

R. G. Lutz

INTRODUCTION

POLYKETONE AS AN ENGINEERING THERMOPLASTIC

CARILON® polymers, or polyketone (PK), seem to have physical property sets and projected costs that make them potentially useful in most applications which are presently being served by the entire class of conventional engineering thermoplastics (ETP). PK's have an impressive array of good physical properties, in many respects combining some of the best qualities of conventional crystalline and amorphous polymers—high modulus and good stress crack resistance. There seems no doubt that many engineering markets may become vulnerable to penetration or take-over by PK.

Chemical instability in PK, both in the melt and in the solid state, is the area long recognized as the strategic Achilles' heel of polyketone. It presents a serious challenge to the possibility of widespread acceptance of this family of polymers in the marketplace. Ultimately, control of the profits from this new class of material may fall into the hands of those who discover and patent the key routes to stability, rather than of those who have lead the way in synthesis, production and product application.

Improved melt stability will be required if PK's are to be handled much as conventional thermoplastics are. Severe chemical stress will be imposed on the polymer immediately after synthesis, when it is melt processed into nibs. One or more additional melt processing steps normally will be required, before the polymer is finally placed into use. Tactical selection of high molecular weight polymers clearly would require improved melt stability over the level found in early PK evaluation.

In the event that a level of melt stability cannot be achieved that is commensurate with the processing requirements of those PK's that have marketable properties, a variety of unconventional fabrication techniques offer fallback positions, should they be required. However, such advanced methods of forming polymers into objects only circumvent melt processing degradation and still do not address the more critical problem of long term service life. It is the latter which could absolutely restrict the range of PK applications.

Stabilization of solid PK articles against oxidative degradation clearly will be required at levels far above those found in the neat polymer. It has become apparent through the work of KSLA and of WRC that stabilization through the use of conventional free radical traps and peroxide decomposers is not likely to achieve the stability levels found in existing commercial ETP's, which reach as high as UL 150°C (UL continuous service life).[1] Presently, the UL oven life for the best stabilized versions of PK stands no higher than around 80°C. This is well below a reasonable target of 100°C, which is the lower range for conventional ETP's.

The search for new stabilizing chemistry or techniques specific to PK therefore is of the highest strategic priority and should be persued along a broad front. One such approach is through melt blending, the subject of the screening study reported here.

There are two other shortcomings to PK's, each of which involves susceptibility to changing modulus at ambient temperature. These are a tendency to absorb water, which also changes specimen dimensions, and a small but significant second order transition near ambient temperature. Both are intrinsic and physical, rather than chemical in nature. They seem less critical than chemical stability, although they will play some role in the suitability of PK for many applications.

The consequences of moisture absorption have always been the most serious shortcoming of high modulus nylons. In PK's, the level of equilibrium water pick-up at saturation and ambient temperature is about 3%. That is half to one third of that found in nylon 66 and 6. However, this is still much higher than is found in other ETP's like PC, PBT, PAcetal, *etc.*

None of the other thermoplastics commonly used in engineering applications have a transition in the vicinity of room temperature. Although in PK the change in properties as the β-transition temperature is traversed is not large, the slope in modulus-temperature is significantly greater than arises purely from thermal expansion. Further, the temperature position of the transition is affected by the level of water absorbed. If unaccounted for, this can sometimes make the results from testing at ambient conditions seem ambiguous.

These characteristic, physical problems are intrinsic to the bulk amorphous phase of PK. The most likely approach to their modification, short of chemical changes in the polymer structure, is through the use of compatible additives. As with stabilization, the present melt blending screening study is a first, empirical attempt to address this area of PK modification.

The development of the widest range of specific applications for PK certainly will require some modification of the polymer beyond stabilization. One of the most likely routes to tailoring property sets is through polymer blending. This approach is commonly used for toughening and hybridization of polymer properties. Ultimate physical properties were not obtained in these experiments because of the poor quality of the base polyketone available for use at the onset of the study.

STABILIZATION

Polyketones degrade in the melt by crosslinking leading ultimately to the formation of coke-like, black residues. In the solid state, PK's are subject to thermal and ultra-violet oxidative property loss, and possibly have a susceptibility to ozone as well. All of these problems are of such magnitude that they will need to be solved to some extent before PK can play a significant role in the marketplace. Like other successful polymers when they were first discovered, polyketone needs major development in these areas. There are many different avenues that potentially might lead to adequate stabilization.

Oxidative free radical degradation of conventional polymers generally commences only after an induction period, the length of which can be prolonged by the presence of radical trap inhibitors. Thereafter, rapid and increasingly complex chemical pathways are followed. Although such radical chemistry also can be expected to occur in PK, experience showed from the beginning that the decay of properties with oxidative time-temperature appears to be much more complex. This is illustrated in Figure 1, where no clear induction period is in evidence. (E/Eo is ultimate elongation relative to the initial level, approximately 400%.)

Lack of the usual induction time during oxidative stress of PK also was clear in certain DSC oxidative induction time experiments (OIT) run by D. L. Handlin, in which the results bore no resemblance to the usual course found with hydrocarbon polymers.

Attempts to optimize the inhibition of radical reactions in CARILON polymers using conventional inhibitors such as hindered phenols at relatively low concentrations is being pursued by KSLA and by outside contract. This approach did not constitute a goal of the work being reported here.

For PK's, in addition to conventional radical reactions, there will be unique degradation pathways that are intrinsic to the polyketone molecular structure. This chemistry will be quite different from that found in more familiar polymers. For example, melt stability was shown by E. P. Smith, WRC, to be extremely

sensitive to poisoning by brief, casual prior contact of the powder with certain glass substrates at ambient conditions. The presence of traces of alkali metals was then shown by E. J. Smutny, WRC, to have similar effects.[2] Both result in rampant crosslinking.

PK degradation problems indeed appear to involve several different reaction pathways, including but not limited to oxidative radical reactions initiated either by peroxides or radiation. Oven life is benefited by hindered phenol free radical traps, but as mentioned earlier, does not appear to clearly follow an induction period.

Such species as the enol form of the keto group may undergo condensation reactions, thus also participating in degradation chemistry.[3] It also seems likely that crossover between radical and ionic reactions will occur, the consequences of which will further obfuscate the critical mechanisms.

The complexity of PK degradation chemistry tends to defy detailed prediction of the predominant pathways, often confounding direct chemical additive intervention. Ketones generally are in equilibrium with their enol forms and are subject to a number of different ionic type reactions, including solvation and condensation, catalyzed by acids and bases. The consequences of such reactions are apparent in PK. Crossover between radical and ionic pathways also may be catalyzed. Chemical reaction with an unsuspected degradation path intermediate also might be possible. Model ketone compound studies by R. Q. Kluttz have attempted to identify new chemical approaches to stabilization.

The action of catalysts and initiators may well play an important role in the degradation chemistry of PK. For example, convincing evidence has been found that crosslinking in the melt is heterogeneous,[4] implying some type of local catalysis. Although the actual state of contaminating reactivity sites in CARILON polymers, as we presently know them, is unknown, such postulated chemical agents constitute a prime target for stabilizing activity in the blends screening study.

Ozone is always present in urban air, especially in the summer months, and indeed has been measured at very high levels inside the WRC laboratory. It therefore will be present, uncontrolled, in the atmosphere of all of the usual tests, including oven aging. Possibly worse, it will have the opportunity to react with PK powder each time a sample is exposed to the ambient air. It seems unlikely that O_3 is involved in the batch-to-batch variations of PK samples since most are now extruded prior to contact with air.

The most direct stabilization approach, of course, will be through the addition of chemical reagents. In addition, however, a more subtle, but still possibly very promising approach to stabilization is through the melt blending of substances which may offer indirect stabilization opportunities that are quite unique in their mode of action.

Blended components can be thermodynamically compatible, partially compatible or incompatible. Soluble, or miscible additives could operate by some combination of direct chemical involvement and by altering the effective acidity or basicity of the environment. Compatible components also could interact with PK segments or with certain degradation products by solvation-like interaction. These interactions in turn could result in a change in enolization equilibrium or some other chemical characteristic. Such effects might influence initiation or the subsequent course of degradation. Clearly, there is a possibility of either aggravating or alleviating degradation problems through compatible additives.

Unfortunately, intensive mixing of polymer melts does not necessarily result in solubilization of polymeric components that are thermodynamically compatible under the conditions of blending. For example, polystyrene and PPO, polymers that are miscible in all proportions, are very difficult to dissolve completely simply by melt mixing. Therefore, a determination that separate phases exist in a blended mixture does not in itself constitute proof of incompatibility.

Incompatible phases do not offer the possibility of directly altering the PK physical-chemical environment at the chain segment level in the same way that miscible components do. The exception, of course, would be at the interfaces between phases, normally affecting no

more than a minute portion of the material, depending simply on the interdispersion morphology.

On the other hand, for incompatible combinations the twin screw mixer acts as a very efficient fluid contactor, or extractor, during the brief passage of molten polymer. Undiscerned harmful or beneficial components might be either introduced or removed by that kind of efficient phase contacting. Incompatible phases might react with, sequester or partition out degradation promoting or catalytic components. By that type of physical mechanism, deactivation or isolation of prodegradants from the polymer could result. This sequestering possibility by added polymers would seem especially promising for dealing with organic contaminants or intermediates.

Any chemicals that are present, by design or inadvertently, will tend to partition between the molten polymer phases that are present during intensive mixing. Physical transfer and diffusion equilibrium of stabilizing chemicals will occur between phases very much more rapidly than inter-dissolution of the polymers in each other.

Partitioning will be according to relative solubility. Therefore, the mere presence of a second polymer phase could profoundly affect the concentration of an additive in PK, and thereby change its chemical stability. An added phase could act as a replacement reservoir for a chemical which is in the process of being consumed or depleted from the surrounding phase.

Partitioning is difficult to foresee or deliberately manipulate because of the difficulty of predicting or determining partition coefficients. This will be particularly true with a thermally unstable polymer. The concept is an important consideration in KRATON® rubber technology, where separated polymer phases arising from the block structure always must be present.

Clearly then, any results obtained on stability from polymer blending should not be interpreted solely on the basis of simple, straightforward polymer-additive interaction.

Indirect benefits on melt stability during processing might arise from the presence of incompatible, lubricating phases that improve processability by a purely physical mechanism. A reduction of 10°C in process temperature might be equivalent to doubling acceptable residence time in the barrel of a processing machine by intervening kinetically in the course of degradation, rather than chemically.

There are at least three purely physical mechanisms by which added materials can result in reduced operating temperature, residence time and power consumption:

1. viscosity reduction by dilution with low molecular weight soluble additives (requires relatively high concentration of the additive to be effective),
2. the "shear-plane lubrication" effect,[5] or "internal lubrication" (can be dramatic with minor amounts of certain lower viscosity, incompatible melts), or
3. reduced adhesion of the melt to steel (might require no more than traces of material).

PHYSICAL PROPERTY MODIFICATION

The blending of CARILON polymers with added materials is expected to constitute the principle route to physical property modification. At the same time, modification of certain non-degradation chemical properties, such as combustion characteristics, also should be possible.

Unfortunately, the only polyketone available in sufficient quantity for this study at the time of its inception was of relatively low molecular weight, one characterized by erratic physical property failure characteristics. For this reason no attempt was made to evaluate the ultimate mechanical properties of its blends, such as strength and elongation to break or toughness. Instead, the study focused more on secondary physical effects and on various chemical effects, including those usually associated with degradation.

A wide range of opportunities for blending a new polymer such as PK with other materials is apparent. A description of some of the expectations from the present study are discussed in the next section under Approach.

The most interesting class of property modifiers will be other polymers. As noted earlier, such combinations can be completely non-miscible, partially phase separated or thermodynamically compatible. The response of physical properties to be expected from a polymer blend can be entirely different depending on compatibility. Blending with other polymers would seem to have potential not only for the controlled modification of mechanical properties, but for most other physical and chemical properties as well.

WRC has extensive experience with incompatible polymer blending as a result of thermoplastic elastomer and interpenetrating network (IPN) research.[6] A large body of technology exists on the relationship of component rheology and degree of physical interaction on melt interdispersion, blend morphology and the resulting properties. Hybridization of component properties through adhering, incompatible, continuous morphology polymer components in the form of IPN structures offer a highly versatile mechanism for controlling property sets, well beyond simple dispersed particle toughening.

Thermodynamically compatible additives offer the only hope for directly modifying barrier character, the β–transition and water absorption of PK. Since barrier characteristics and the β–transition depend intrinsically on the cohesive energy density and free volume of the amorphous phase, these properties may respond to certain, compatible components. Likewise, water absorption depends on polarity and hydrogen bonding capability. Although the consequences of these phenomena might be minimized by various means other than direct, thermodynamic intervention, such means usually would apply to competitive polymers as well as to PK.

Any processing or additive experiment that results in increased crystallinity would provide a higher modulus version and supply a candidate for somewhat improved barrier quality. Nucleation or increased chain mobility of sufficient magnitude to accomplish this, however, seems unlikely.

Compatible additives at concentrations greater than about 15% would tend increasingly to reduce the crystallinity and melting temperature of PK. While being of utmost interest from the viewpoint of improving stability, this type of component also runs the risk of excessively degrading the physical performance quality of PK as an engineering thermoplastic. Stiffness and service temperature might be significantly reduced, counteracting to some extent any desirable properties being sought.

Because of the foregoing considerations one is interested in both compatible and incompatible blends.

SCOPE OF THE BLENDS SCREENING STUDY

Foremost among the goals of this present work was the possibility of improving stability against degradation through blending. The second goal of the blending screening project was to examine the effects of blending various materials on a wide range of properties. It was appropriate and convenient at the same time to include some work on processing variables.

Because the class of PK polymers is so new, little information was at hand at the beginning of this study on how to stabilize it. Presumably new chemistry would be necessary, in addition to that of free-radical interception by hindered phenol, although these approaches certainly were not specifically predictable. This implies that an intensive, broad empirical approach to stabilization should be carried out, far beyond the limited scope of this blending study. Indeed, that has been the historical approach with most other new polymers.

Likewise, the lack of precedent with PK means that the proposed methods for modification of properties were mostly speculative, based on experience with conventional polymer systems.

The project was structured with the expectation of finding both enhancing and degrading effects. Such knowledge would serve as a basis for tailoring performance property sets for end-use applications while at the same time allowing avoidance of poisons and prodegradants. Clear contributions to the understanding of reaction mechanisms were not necessarily expected.

Custom built, small scale intensive mixing equipment has been accumulated at WRC, along with advanced techniques for small scale sample evaluation.[7] These allow convenient blending and testing of small amounts of research material, essential to the envisioned PK blending program.

Recognizing that the blends screening project was empirical in nature and that any one blending approach might become a major project in itself, the goal here was only to obtain some preliminary information on the effects of adding a wide variety of materials to PK. The intent was not to be distracted from the broad screen, no matter how attractive certain blends might look along the way. Therefore, follow-up on interesting leads could not be part of this program.

APPROACH

The overall plan covered the following general classes of experiment:

Process Variables

Additives
- Particulates
- Chemicals
- Solvents and Oligomers
- Polymers

The effects of fillers and fibers on polymer physical properties are reasonably predictable and no attempt was made here to evaluate them.

In the following sections, the names of WRC colleagues are indicated parenthetically where they suggested, or had run experiments with certain additives or if they were otherwise instrumental in the selection of the experiment. All of the additives are described in detail in the Appendix—Materials.

Processing

Blending was carried out on a 15mm Baker Perkins twin screw intensive mixer.[7,9] This extruder is an exact scale-down of the 80mm machine formerly used at WRC.[8a] The extruder screw configuration and the residence time characteristics have been described elsewhere.[9] A standard set of operating parameters needed to be selected for the bulk of the blending experiments to serve as the reference conditions. The conditions for the project were chosen arbitrarily based on common sense and common practice. A number of process variables normally are more or less conveniently under the control of the experimenter and a series of such variables was studied on the base PK polymer at the onset of the present blending project.

The blending method used in these studies consists of feeding fine, PK reactor powder mixed with other fine powders, cryogenically ground if necessary, to the small twin screw extruder. Some of the available operating parameters might become important processing techniques that readily can be controlled in commercial practice, in the event that a need should be demonstrated.

The effects on PK of process variables, such as time-temperature, oxygen, moisture, and shear, need to be understood. These parameters not only will affect melt processability but also susceptibility to subsequent chemical stress from extended exposure to various agents at lower temperatures. All melt processing of PK could be affected by the choice of conditions. A portion of the present study was devoted to exploring the effects of such variables. Unfortunately, results were not available in time to apply them to the remainder of the blending studies, and in fact many questions in this area still remain.

Crosslinking had been identified early as the principle problem associated with melt processing of PK. Time-temperature in the barrel and the presence of oxygen or water could have a profound effect on crosslinking and on subsequent solid state properties such as oven life, UV stability and color. The catalytic degradation effects on PK melts of a variety of substrates, including many different types of virgin steel (as opposed to equilibrium melt conditioned), had been studied but those results were marred by flawed DSC evaluations and are of questionable value.

The process parameters studied were:

Oxygen
- Air blanket vs nitrogen
- Strand quenched vs cooled in air

Temperature
- 240-280°C

Water
Dry vs undried or wet feed

Residence time/shear rate

The presence of oxygen during melt processing could have serious consequences. It would tend to pre-oxidize the polymer, consume antioxidant, form peroxides and commence a number of radical reaction pathways. The higher the temperature and the longer the residence time, the more severe could be degradation from this source during processing.

Also, however, in retrospect, it is unlikely but still conceivable that some amount of air with the extruder feed could have a beneficial effect by oxidatively "titrating" out certain anaerobic melt degradation precursors. Several considerations raise the possibility that such a chemical titration approach might be interesting with other types of reagents as well. Examples of these are the possible presence of degrading precursors in the form of furan structures as postulated by by E. I. Klei, KSLA, the possibility of other intrinsic chemical flaws built into the PK chain termed *genetic defects* by Klingensmith and finally by heterogeneous crosslinking postulated by Gergen and Lutz and demonstrated by Crosby.

The nitrogen blanket employed in these experiments was effective, although not absolutely rigorous. No attempts were made to measure the oxygen levels that were present in the extruder. Many control nitrogen and air blanket experiments were carried out in which other variables were also changed. One run was made in which the strand was allowed to cool slowly in air for comparison to the normal water quenched material.

Temperature measurement on the 15 mm twin screw extruder was by barrel and melt thermocouples supplied with the machine. They were calibrated and working correctly. These devices can at best only reflect average temperature of the melt and, of course, do not indicate local, short time, shear induced hot spots.

The normal operating temperature was 240°C, about 20° above the PK terpolymer melting range. Some experiments also were run at 280°, necessary with the higher melting PK copolymer and certain high melting polymer additives.

Since water is normally dissolved in PK and also is evolved from condensation reactions in the melt, a significant solution activity of water would be expected in the melt during processing. This conceivably might shift chemical condensation equilibrium favorably, reducing the rate of crosslinking in the melt. In addition, there could be effects from enhanced hydration reactions, with unknown consequences.

Results from running with carefully dried feeds were obtained for comparison with undried feeds, which nominally contain up to about 1.5% moisture. Also, a run was made with 3% added water.

Residence time will be a function of the operating speed and feed rate. Unfortunately, throughout the present study the feed rates, and therefore residence times, were not held constant. Only one residence time experiment was run. In it, the shear rate was lowered simultaneously as the residence time was increased.

Particulate Additives

A few common, powdered solids were examined for their effects on PK. These were selected from among materials that sometimes are, or could be used with polymers. The types of solids tested are as follows:

$CaCO_3$

ZnO_2

TiO_2

Basic alumina
(Lutz and G. B. Klingensmith)

Acidic alumina
(Lutz and G. B. Klingensmith)

Talc

Clay

Carbon black
(A. P. Filippov)

Graphite
(E. J. Smutny)

These materials were run at 2-5% concentration, a compromise between trace

amounts, as stabilizers are normally employed, and the higher levels at which fillers are normally used. It was hoped that any unusually beneficial interaction could be identified for further study.

These particulates have differing surface free energy, adsorption and chemical activity characteristics. They included basic, acidic and highly absorptive surfaces, in addition to several additives of miscellaneous surface character. The twin screw extruder is expected to very thoroughly contact each element of the melt with these finely divided, high surface area additives, so that there is ample opportunity for reaction with, or adsorption of, any prodegradant substances present in PK. However, at the molecular segment level, contacting certainly will be incomplete in a single pass.

There is always a possibility that high energy, solid surfaces might adsorb stabilizer (hindered phenol) from the melt, adversely affecting oven life. In cases where that occurs, added, benign polar compounds might readily reverse the process. For this purpose, for example, it is common practice in KRATON G rubber compounding always to add epoxy compounds along with any fillers. No account was made for the possibility of this type of hindered phenol deactivation in these screening experiments and, indeed the oven life results were very poor for particulate blends, possibly due to this phenomenon.

Chemical Additives

A number of small molecule chemicals were blended with PK. These were chosen mostly from among materials commonly used with polymers, or believed to be of adequate stability and low volatility and toxicity. In addition to their specific stabilizing reactivities and solvation effects, the chemicals were selected to cover an extensive range of weak acidity and basicity. This allows for the possibility of stabilizing activity through a buffering mechanism. The following chemical types were included:

Hindered phenol
Hindered phenol-ester
Hindered phenol-Ca phosphonate
Hindered phenol-triazole
Hindered phenol-thioether-triazole
Hindered phenol-hydrazid
Hindered phenol-hindered amine-ester
Aliphatic hindered secondary amine
Amide
Carboxylic acid
Nickel thiocarbamate *(R.Q.Kluttz)*
Sodium stearate

Hindered phenols conventionally are used at concentrations below 1% for the stabilization of most hydrocarbon polymers against oxidative degradation. Higher concentrations usually are less effective. (At least one exception to this generality is found in elastomeric wire and cable coating materials, where polymer crystallinity is low.) The reasons are antagonism, discussed below, and limited solubility in the amorphous phase of the solidified polymer. For the latter reason, **small amounts of a number of chemicals might offer a significant advantage over higher concentrations of a single component.** This could be true even though the single component had been shown to be superior in performance to each of the others individually. (This thought had not occurred to the American Cyanamid research chemists who were working with WRC Elastomers in the early 1980's.)

In the present work the hindered phenols were run at considerably higher concentrations than would normally be employed, usually 2-4%, to see if any unexpected effects would be observed. The approach assumes good compatibility in the melt and the amorphous phase of the solid. The effects of conventional concentrations of hindered phenols on oven life of PK are being studied by H. J. Syrier at KSLA. The approach used by KSLA is to place the additive by solvent evaporation onto PK powder, compression mold and oven age. Barring some extraordinary adsorption, this method of placement deposits the AO by crystallization from solvent, presumably into microscopically large crystals, and does not take advantage of the high surface area of PK powder.

The oven life results from the foregoing solvent deposition technique may be quite different from those that would have been obtained from extruder mixing. Upon melting, the crystals of AO initially present a high local concentration to the PK melt, whereas other regions would not see any AO until the effects of

quiescent diffusion were realized. If diffusion is not complete during compression molding, local concentration antagonism in one region and starvation in others would result. During extruder mixing, the same initial condition will prevail, but the process of diffusion equilibration may be be completed much faster.

Significant differences in results might be found between stabilization results obtained by KSLA and those obtained by WRC, even when similar materials and comparable average concentrations are employed. This would be because of the foregoing difference in technique for dispersing the antioxidants, quite apart from any differences in specific PK samples.

The commercially available hindered phenol antioxidants and UV agents constituted a safe and convenient way to incorporate a number of different chemical moieties, in addition to the phenol group, that otherwise would require extensive preliminary work. These chemicals are stable, of low volatility and have been thoroughly tested for toxicity effects.

Among these chemicals are weak to strong, hindered organic bases. The one small molecule, organic, free acid (supposedly) that was employed, ethylene diamine tetra-acetic acid, later was found to contain largely the sodium salt, making it a crosslinking catalyst. Pure stearic acid would have been a perfectly suitable analogue for carboxylic acid polymers.

The nickel thiocarbamate is a chemical commonly used in conventional rubber as an accelerator, antioxidant and antiozonant. It had been found to help stabilize a PK chemical analogue in the model compound work of R. Q. Kluttz.[10]

Sodium had long been suspected of being a strong catalytic crosslinking agent in PK melts. Beginning with Smith's "glass poison effect", followed by a number of powder blend DSC experiments using stearate salts and by Smutny's more detailed studies, it was proven that sodium at the parts per million level caused extensive crosslinking in PK melts. In the present blending experiments, about 300 ppm Na was added as sodium stearate to follow the effects of deliberate, controlled poisoning of PK on various properties.

Solvent and Oligomer Additives

Polar organic molecules that are not expected to show particular, direct chemical reactivity with PK might be thermodynamically compatible in the melt and possibly the solid, particularly if they are of low molecular weight. Such components could physically modify the melt environment or act as solvents or plasticizers. If so, they might find use as stabilizers, property modifiers, plasticizers or as purge components for processing equipment. The materials tested were:

Pentaerythritol

C^4 sulfone (Sulfolane W)
(E.J.Smutny)

Diphenyl sulfone
(E.J.Smutny)

BPA epoxy

Poly ethylene glycol ether
(Lutz and Smutny)

Asphalt
(Lutz and C. L. Nielsen)

These compounds were tested at 5-20% levels. Unlike the case for polymer blends, equilibrium dissolution is expected to be complete in a single pass, due to the high diffusion rates of the small molecules.

Pentaerythritol, phenyl sulfone and BPA epoxy have been used to some advantage as components of purging mixtures in the small extruder, although the effectiveness was not documented by careful experiments.

Pentaerythritol seemed a likely hydrogen bonding agent for the keto groups of CARILON polymers since it contains no tertiary hydrogen and is thermally stable. Further, it is sufficiently low in melting temperature, volatility and toxicity to melt blend with PK terpolymer. One might expect solubility of pentaerythritol in PK in the molten state, and therefore powerful alteration of the melt environment by such an agent.

The sulfones had previously been shown by E. J. Smutny to be compatible with PK[11] and PK powder had been found by D. L. Handlin to dissolve in hot EPON® 828. Three different types of asphalt were tried because of their mild,

but diverse chemical reactivity. These three representative types of asphaltic materials were obtained from C. L. Nielsen, WRC Fuels and Lubricants.

Polymer Additives

Perhaps the most important part of the blending program consisted of empirical blending of CARILON polymer with the major classes of common commercial and other available research and experimental polymers. These included examples containing the following functionality:

Amide	Carboxylic acid	Fluorine	Nitrile
Amine	Epoxide	Hydrocarbon	Sulfone
Carbonate	Ester	Hydroxyl	Urethane
Chlorine	Ether	Ionomer	

High melting, CARILON E copolymer also was blended with terpolymer, with particular attention being paid to possible nucleation and crystallinity considerations.

These polymers were added at a single, compromise concentration of 10%v. Where the choice was convenient, lower molecular weight grades were selected. Most were blended at 240°C, but where appropriate, as with polycarbonate, polysulfone, polyphenylene oxide and polyethylene terephthalate, 280°C was used.

Polymers having inadequate thermal stability to be run at 240° or requiring process temperatures above 280° were avoided. Examples are polyvinyl alcohol, polyacrylamide and the thermotropic liquid crystal polymers.

Any indications of improvements in processability would be indicative of better economics of fabrication. Such factors also could be important to a polymer that suffers chemically during melt processing, allowing reduced residence time and/or temperatures.

Indications of any degree of compatibility could lead to homogeneous blends of substantially altered properties. If the basic character of the amorphous phase could be altered in this way, then the second order transition or barrier properties might be modulated. However, such changes would certainly be toward reduced melting temperature and crystallinity, which in many instances would be undesirable. This consideration probably limits useful concentrations of additives, or at least of their compatible components, to <20%. On the other hand, more nearly compatible components would be expected to have the greatest interphase adhesion, desirable from the IPN viewpoint, where miscibility is incomplete.

Incompatibility is more likely to prevail in most blends of PK with other polymers. Both interpenetrating polymer network (IPN) formation and rubber toughening are multiphase polymer technologies that are well developed at Westhollow. Their application to PK should allow tailoring of an array of physical properties to meet the demands of various end-uses.

Safety

Prior experience during the course of IPN studies indicated that chemically functional polymers may react with melt blended components in completely unanticipated ways. Unexpectedly, when polycarbonate and nylon 66 were blended together, a chemical reaction between these polymers ensued.[8b] Initially, extrudate from the large twin screw mixer appeared normal. Soon, however, the melt began to discolor, evolve gas and crosslink and the temperatures suddenly rose in a positive feedback loop. Quick reaction by the operators saved the machine from serious damage, but only after a pressure disc blew out and several other emergency devices had activated.

No reference to a reaction between PC and nylon could be found in any of the common reference sources for these polymers or in the manufacturer's literature. When questioned, those producers of the two polymers that were contacted did not indicate knowledge of any such reactivity.

This experience clearly suggests that, since PK is a newly acquired material, blending with it should be carried out with caution for the sake of personnel and equipment safety. It is a highly functional and potentially reactive polymer, known to undergo crosslinking, scission, condensation and furanization with much greater facility than thermoplastics generally. The engineering thermoplastics with which it is to be blended are mostly highly functional and

may have the potential to interact chemically with PK.

The PC/N reaction subsequently was studied in TGA experiments on mixed powder samples of PC and nylon. At equal portions of PC and nylon, the TGA weight loss curve occurred at a much lower temperature than expected from the sum of the curves obtained separately on the two components.[8b]

Based in part on this experience, a test was devised to screen potential PK blending components for reactivity. Fine, cryogenically ground powders of the candidate materials are dry blended with CARILON polymer powder and tested for exothermic chemical activity in a stepwise DSC experiment of increasing severity. In the first DSC cycle the temperature is raised sufficiently to melt all components, plus about 20°C, followed by cooling. In a second cycle the mixture is heated to 280°C and held isothermally for 10 minutes before cooling, to allow extensive opportunity for reaction to take place. In a third cycle the temperature is driven to 320°C.

This test clearly shows the reaction between PC and nylon, Figure 2. The first heating curve was considerably below a baseline that would be predicted by a composite DSC curve of the two components, or by either the second or third heating curves of the powder mixture. Apparently, reaction at the interfaces between the two components begins immediately after the PC glass transition temperature is reached, and continues to the upper range of the first heating cycle. Subsequent heating cycles show little or no further reaction, indicating that reaction was complete at the phase interfaces. Comparison of the first to a a later cycle indicated the extent of the exotherm.

This test was performed on most of the polymers to be blended. In no case was there any unexpected reaction in evidence, and indeed no difficulties were encountered when the extrusions were carried out. This pre-testing protocol was abandoned after this series of blends. Subsequently, in model compound follow-up experiments for R. Q. Kluttz, certain chemicals did undergo reaction in the extruder, although without serious consequence. These probably would have been spotted in advance with the safety test on powder blends.

There is a possibility that one reactive system escaped detection by the DSC safety screen. When a completed poly bisphenol A blend was placed in the DSC for analysis, the pans blew open, precluding the usual melt stability evaluation. No adverse result was seen in the powder screen, and no explanation presently is in hand.

A test of this sort cannot be expected to show the degree of physical interaction between the mixture components that would be present in a well mixed blend because of the relatively small, static area of interfacial contact. It is intended only to detect possible chemical problems.

Choice of Polyketone

The properties of ethylene carbon monoxide copolymer (CARILON E or PK copolymer) appear to make it superior to the propylene terpolymers (CARILON EP or PK terpolymer) as an engineering thermoplastic. It is particularly the higher melting temperature and modulus that make it more attractive. Since the temperatures required for processing of copolymer will have to be about 280°C, and melt stability is known to be a problem, it was decided to utilize the lower melting, EP terpolymer for the blending program.

In order to make the results of screening as consistent as possible, it was desirable to use only one grade of PK throughout. Since at the time this study was initiated, low molecular weight samples had given low or erratic stress-strain results, a PK of LVN100 about 2.0 or higher was sought in order to assure good mechanical properties (see Glossary for definition of various LVN measurements). A small sample of such a polymer, 055/022 with LVN60 of 2.3, had given excellent stress-strain properties. However, no PK's of high enough LVN to assure toughness were available in quantities sufficient for the contemplated study, nor could they be obtained from KSLA at that time.

A compromise material, 056/002A and B (see Appendix—Materials), with LVN60 of around 1.5 and 1.7 respectively, and with remelt temperature of around 223°C was selected from the available materials. Erratic ultimate failure

of compression molded samples of this polymer (the 1.5 LVN sample) could not be overcome by extensive variations of specimen preparation and testing. These included compression molding time, temperature and quench and testing strain rate. No specks or other observable reasons for that behavior were ever found and it was assumed to arise from draw instability, due to too low a molecular weight. In any case, no attempt was made to evaluate the mechanical properties of the blends based on 002.

This polymer is thought to have contained approximately 0.2% or less of Irganox 1076, a hindered phenol stabilizer. Because of the manner in which the AO is added to the powder, the exact concentration is not known. Further, the AO is thought to have been deposited inhomogeneously on the polymer because of "chromatographing" during the solvent evaporation step. The sample was supplied by KSLA as a low bulk density powder, in two batches, A and B. These were originally believed to be essentially the same, although some differences in performance later were observed. These two samples were not mixed together prior to beginning the blend screening study and in the end they were tracked separately. The two batches have since been characterized as follows:

	T_m (°C)	LVN60
056/002A	221	1.48
056/002B	225	1.72

Very significant batch-to-batch variations in the melt stability and other characteristics of PK's from the Moerdijke plant have been observed. It would serve well to use a constant material or preblended batches for any extensive study where such variations could obscure the experimenter's variables.

Blend Characterization

A number of analytical methods for PK were available or under refinement at the time the blends study was begun, while several others had to be devised. Some desired tests, including UV resistance, were not ready in time to be utilized. The same array of tests were not necessarily run on all of the blends, even where appropriate, because of limited resources or sample problems. The measurements employed and the method of sample preparation are described in the Appendix--Analytical Procedures.

The analyses used are summarized below, according to the nature of information being sought:

Chemical Reactivity:

- Gross chemical activity
  - DSC of powder mixtures
- Anaerobic melt stability
  - DSC
  - Rheology
- Oxidative stability
  - Oven life
- Ozone Resistance
  - Chamber test
- Color
  - Yellowness Index
- Combustion character
  - Strip burn
- Crosslinking
  - HFIPA solubility

Physical State:

- Melt lubrication
  - Constant torque feed rate
- Crystallinity
  - DSC
- Melt interaction
  - Polymer phase cell size
- Second order transitions
  - DMTA
- Barrier
  - Oxygen permeability

Responses in these characteristics were evaluated by comparison with results obtained on appropriate controls. All of the samples contained the small background amount of hindered phenol that came in with the CARILON polymers, approximately 0.2% Irganox 1076.

A thermal analysis method, already described in a previous section (Safety), has been designed to check for gross chemical reactivity of PK with additives. It was designed to serve as a safety check for personnel and equipment prior to commencing extrusion.

The level of anaerobic melt stability in moderate and high molecular weight PK has been shown by Gergen to be low, greatly restricting the ease of melt fabrication. Changes in melt stability were judged by a DSC protocol designed for PK, based on early work by Hart.[12] In the absence of oxygen, molten PKs crosslink gradually or rapidly, depending on a number of factors. This crosslinking reduces the ability of the polymer to crystallize in DSC experiments.

Thus, recrystallizability after a 10 min hold at 280°C in the DSC, simulating melt processing of PK copolymer (T_m 260°C), is an inverse measure of crosslinking. This is readily verified by the lack of solubility of DSC sample residues after significant loss in crystallizability, or by parallel plate rheology measurements.

Oxidative stability, the most significant end-use shortcoming of PK, was judged by time-temperature oven aging of 10 mil thick compression molded samples. Since the ultimate properties of the base PK were erratic to begin with, superficial brittleness, formalized for PK by Syrier, KSLA, had to be used as the failure criterion, rather than the more usual 50% loss in ultimate properties. This type of failure occurs at an equivalent tensile elongation of about 15–20%, based on the studies of D. L. Handlin.[13] Ironically, the brittleness criterion is thought to be more reliable in these screening studies than it might have been, because of the marginal properties of the low LVN PK base polymer. The toughness of higher LVN PK might more readily reverse during aging through crosslinking, prior to failure in the brittleness test and escaping detection, thereby confounding the purpose of the test. This seems unlikely with marginally low LVN PK.

D. L. Handlin had shown that PK powder suspended in chloroform is rapidly destroyed by ozone. Therefore, its possible effect on consolidated, molded PK specimens was of concern. One appropriate test was carried out without adverse findings.

Color was conveniently measured on the compression molded samples as Yellowness Index from a tristimulus colorimeter, in a non-standard test. The initial color shows effects resulting from passage through the extruder and compression molding. Color also was measured at the 100°C oven time of failure to indicate the degree to which color developed with oxidative embrittlement.

Any additives, including other polymers, that cause charring at oxidative pyrolysis conditions during combustion, might lead to a flame retardant system for PK's. Combustion character was superficially judged by burning of small compression molded strips, in a rough, non-standard test, using a Limiting Oxygen Index apparatus, at 19.5% oxygen.

Crosslinking of polymers usually can be judged by their solubility and swelling character. Indeed, the extent of crosslinking that occurs in quiescent PK melts readily can be qualitatively observed by HFIPA solution behavior. Observations were made on the HFIPA solution behavior of PK blends and of the appropriate neat polymer components. However, extruded melts that undergo crosslinking are "dynamically vulcanized" (see Glossary) and hence would be broken down into microscopic gel particles, making interpretation less than straightforward. Interpretation of the solubility of the PK-polymer blends is further confounded by the possibility of two-component physical interactions in solution.

No particular effect of additives on the power consumption or on maximum throughput rate during blending had been anticipated. However, there are at least three purely physical mechanisms by which power consumption at constant throughput rate might be reduced. Such effects indeed were observed during the course of the blending studies. These are grouped together as melt lubrication. The effects

were manifested by unaccounted for differences in the feeder settings used to achieve 85% torque, under standard operating conditions.

Crystallinity and melting temperature are both expected to be reduced by the presence of compatible components. Nucleation, on the other hand, would tend to increase the melting temperature. Such changes should be reflected in DSC measurements during the first, rapid heating and cooling cycles of the DSC protocol. Crosslinking, of course, reduces crystallizability.

Interaction between polymer phases in the melt is an important factor in mixing and in the resultant solid phase properties as well. Although rheology plays a critical role in melt interdispersion, melt interaction that results in low interfacial tension is required for achievement of the smallest, most desirable dispersion cell size. This interaction usually can be thought of as purely physical. However, it must be recognized that minute amounts of grafting or certain other chemical changes can be decisive in this regard, *e.g.*, through a "soap" effect. Electron microscopy of polymer blends has been well developed at WRC and was used on the PK polymer blends to determine the morphology and approximate average size of the added polymer dispersion.

PK polymers have two second order transitions, one referred to as the β-transition near ambient temperature and the other called the γ-transition at about -60°C.[14] If the basic character of the amorphous phase is altered by the presence of compatible components, then the second order transitions might be modulated. These transitions were determined for many of the blends by the DMTA dynamic mechanical spectrometer.

Barrier characteristics of any polymer, including PK, can be manipulated to some extent through crystallinity, orientation or diffusion path tortuosity additives, (possibly including high melting PK copolymer). Since such methods apply universally, they would not necessarily give a competitive advantage to PK. However, changes can be induced in the basic permeability characteristics of the transporting, amorphous phase of a polymer by changing the cohesive energy density, free volume or Henry's Law solubility. In PK this might be accomplished through compatible additives. To get an indication of any such possible leads, a few gas permeability measurements were carried out on selected samples of the polymer blends.

RESULTS

EXPLANATION OF THE TABLE OF RESULTS

The detailed results of the blends screening study are summarized in Tables 1-A1 through 1-E3. A brief explanation for each of the data columns, referred to by the bracketed reference numbers {____}, can be found in the first page of the table, Table 1. Reference for the Data Table.

Table 1 is subdivided into 15 pages with consistent format maintained throughout. The experiment group designation is as follows:

Table 1-A **Control** Runs and Process Variables
1-B **Particulate** Additives
1-C **Chemical** Additives
1-D **Solvent** and Oligomer Additives
1-E **Polymer** Additives

followed by a number for the field of results:

1 Detailed run description and **Feed Rate**
2 **DSC, Rheology, Oven Life, Color**
3 **Burn, Solubility, Cell Size, DMTA**

Thus, for example, to find raw data about the effect of particulate additives on burning character, look at Table 1-B3.

The actual test methods that were employed are described in more detail in the Appendix—Analytical Procedures. For various reasons, the accuracy and repeatability of the methods employed in the present study for the most part are not known with certainty. Generally, because of the screening intent of the study, precision was not expected to present any problem, since significant trends only were being sought. Conclusions based on small differences, less than say 10-20%, probably cannot be relied upon and if important, should be confirmed.

Sample Code. The prefix code, PKB (polyketone blend) and the numbers following, constitute the notebook referenced code name for each extruder run that is reported. The suffix

letters usually run in sequence for a series of related and sequential experiments.

Control Code {1}. It was not possible to maintain precisely the same materials and operating conditions for the entire study. Much of the data from the blending experiments only has meaning when juxtaposed against an appropriate control experiment. For this reason special attention has been paid to controls throughout the reporting of this work.

The particular control extruder runs that correspond to the various other experimental runs are identified by a "Control Code", shown in [ ] brackets in the tables. The code then appears without brackets next to each corresponding experimental run.

Careful examination of the Blending Variable Code for each control and each experimental run should reveal even minor differences between these various runs. For convenience in placing results in context, the Control Codes and their data are repeated at the beginning of each table.

Nickname. This column was constructed to assist in the quick identification of each run by the unique variable(s) present, *e.g.*, different atmosphere, temperature, additive or other parameter.

Blending Variable Code {2}. The shorthand Variable Code was devised to compress all of the most important features of a run into a single descriptor. Its form is as follows:

PK grade / principal variable / run conditions
(D, U—dry or undried feed)
(temperature)
(A, N—air or nitrogen blanket)
(RPM)
(residence time in seconds)

Example: 002A/280C A /U-280-A-300-30

Base polymer – PK 056/002A

Principal variable – 280°C (not 240), air (not nitrogen)
Undried feed, 280°C, air atmosphere, 300 RPM, 30 sec residence time.

A discussion of the polyketone grades will be found in the Appendix—Materials.

Additive {3}. Details about the materials that were blended into polyketone also can be found in the Appendix—Materials.

Feed Rate {4}. The runs were usually made at about 85% of the allowable torque on the extruder. Those runs that had higher maximum torque feed rates than their controls may indicate potential processing aids. We now believe that a better experimental procedure would have been to hold the feed rate constant and carefully monitor the torque. This still would have given a measure of processability, while at the same time maintaining constant residence time and degree of mixing throughout.

The feed rates listed in the tables are the feeder setting at maximum torque, a linear function of volume rate for nearly all of the runs, since the same low bulk density PK was used throughout. Relative feed rate is the ratio of the feed rate for that run to that of a suitable control.

DSC {5}. Unfortunately, many of the original DSC results obtained were flawed to varying extents, by poor analytical procedures. A description of the DSC test as it was intended will be found in the Appendix—Analytical Procedures, along with a discussion of the problems experienced with this technique. Since all of the original work was suspect, many of the results reported are from repeat measurements, with the originals having been discarded. Any low melt stability results that seem questionable or particularly significant should be re-examined.

The DSC technique was supposed to have included rigorous exclusion of water and oxygen from the sealed pans and heating and cooling at a rate of 20°/min. The first heating/cooling cycle reflects the crystallinity of the sample in the condition that resulted from cooling of the strand, followed by the recrystallization character after quick melting. The second cycle involved holding the melt isothermally at 285°C for 10 minutes, to simulate processing of the higher melting PK copolymer (although in the absence of conditioned steel), during which time considerable melt instability can be manifested.

Th_1 – melting temperature peak in C, first heat.

Tc_1 – crystallization temperature peak, first cool.

Th_2 – melting temperature, second heat.

Tc_2 – crystallization temperature, second cool.

H_1 – heat of fusion in cal/g, first heat.

C_1 – heat of crystallization, first cool.

H_2 – heat of fusion, second heat.

C_2 – heat of cryst., second cool.

Relative C_2 – ratio of sample C_2 to that of the appropriate control.

This is most likely to reflect changes in melt stability. Values less than 1 show degradation, greater than 1 improvements.

Rheometrics {6}. These results report the slope of the complex, parallel plate viscosity curves, dn/dt in Pascal-sec/minute, measured during the period of time between 5 and 10 minutes from the start of the test, at either 240 or 275°C. All of the measurements reported here were made early in the rheology studies of W. P. Gergen and D. G. Waters.

Oven Aging {7}. Oven aging results reported here are the number of days at temperature in the oven to reach failure by the brittleness bend test, minus one day (that is, the last time at which the specimen passed the check). Although most were tested at 100, 120 and 140°C, the results reported are for 100°C in days prior to failure and oven life relative to an appropriate control.

Yellowness {8}. The data reported are first, the initial yellowness index of compression molded samples prior to aging and second, at the last time prior to brittleness failure in the oven test at 100°C. A general correlation between property loss and color development during the course of time-temperature oven aging of a single material had been noted earlier, but was not found among these various blends.

Oxygen Burn {9}. Strips of 30 mil compression molded sheet were cut to about 0.5 cm wide and burned in a limiting oxygen concentration combustion device. The samples were mounted vertically and lighted at the top in a 19.5% oxygen atmosphere. This is not a standard LOI geometry or procedure and the results cannot be compared with other materials not tested in this way. Charring and slow burning blends would be of the most interest.

Time – time of burn before extinguishment, in seconds. *(cons – consumed entire sample)*

Rate – linear burn rate along strip in inches/minute.

Comments – observations.

The comments are self explanatory, many probably have no particular significance.

Solubility {10}. The blends with other polymers were placed in contact with HFIPA in an effort to determine if the PK phase was still soluble. (Films of control PK were readily soluble.) Listed under blend are observations on a thin, compression molded film of the blend; under add (added polymer) observations on the neat, added polymers without having been blended. The following comment abbreviations are used:

Clear – appears soluble

Sol – soluble

Tlucnt – translucent

S – slight

V – very

Cldy – cloudy

Insol – insoluble

Fibers – insoluble, fibrous

Electron Microscopic Cell Size {11}. No evidence of phase continuity was seen with the 10% added polymers, since these all were droplet-like in appearance. The reported cell size in microns, is a subjective estimate taken from the largest size that was present in significant population.

DMTA β-transition {12}. Dynamic mechanical analyses were run on selected samples, primarily solvent and polymer blends. The

position of the PK second order, β-transition peak, or β-peak, is shown, followed by that of the gamma, or γ-peak. This is followed by the temperature position of transitions attributable to the added material, under added poly, where observed. The peaks were often shifted when the samples were measured wet (results in parentheses) compared to when measured dry (no parentheses).

DISCUSSION OF RESULTS

In the comparisons made here, an attempt has been made to use valid matching of experiments unless otherwise noted; that is, the parameters of the extruder runs are exactly matched, as far as is known. Otherwise, most of the direct comparisons involve only a single variable. The one exception to this is the variation of residence time which results from differences in feed rate, for which no correction could be made.

In retrospect, since one of the primary concerns is with chemistry during processing and subsequently, it is clear that blending at constant torque constitutes one of the weak points in the design tactics of the present study. In the future one should consider holding feed rate constant in such experiments, in order to hold **residence time in the shear field** constant throughout the study. Careful observation of the torque for each run would then still be used to accurately assess processability.

Ozone Resistance

A generalized ozone test was carried out on stressed, 10 mil compression molded control PK specimens in a standard ozone cabinet. **No detrimental effects** on properties or appearance were seen in several months of exposure, and further experiments seemed unlikely to be worthwhile. However, no comment can be made from this experiment on the possible effects of the presence of atmospheric ozone during high temperature oven testing.

In the following discussions, data often have been broken out of the Table 1 series for clarity. Where reference back to Table 1 is desired, use the Nickname and Sample Code to locate exact extruder runs.

Process Variables

Process studies were carried out on PK's without extra additives. The feeds to the extruder were reactor powders containing approximately 0.2% of Irganox 1076, although the exact amount is not known with certainty.

As a result of these and other related preliminary results, a careful study has been designed with W. P. Gergen to further explore the interrelationships during processing between oxygen, water, hindered phenol, temperature, residence time and PK molecular weight.

No particular effects of air or changing temperature upon the feed rate at maximum torque were evident, nor would they be expected. This fact tends to validate the additive blend cases to be discussed later, where large differences in constant torque feed rate indeed were found. Also, no clear effects on color due to the presence of air during processing can be identified in these data.

LVN in HFIPA was found to be about the same for all of the samples in the process variable study. However, some of the filtration rates through microporous filters, part of the LVN procedure, were much slower than others even though no measurable amount of gel was removed in the process. This observation could not be explained satisfactorily by conventional polymer solution theory, and was one of the principal pieces of indirect evidence for heterogeneous crosslinking, which is now thought to be well documented.[4]

Air vs Nitrogen. The comparison between anaerobic processing with nitrogen and exposure of polyketone melts to oxygen during processing are summarized in Table 2. There is one comparison of terpolymer strand cooled in air vs water-quenched and three comparisons of nitrogen vs air blanket during extrusion for terpolymer and one for copolymer.

Using an air atmosphere over the extruder feed probably acts as a brief **oxygen "pulse"**. Oxygen is entrained in the polymer feed and is present early in the melting phase of the process. Subsequently, it will tend to be displaced and purged by evolving gas, water vapor and other volatiles traveling counter-current to the melt, out through the feed hopper. Finally, traces that

remain dissolved in the melt may be consumed by chemical reactions.

The last two experiments described in Table 2, 16B and C, involved injecting a small stream of air into the center of the extruder barrel during runs with a higher LVN terpolymer. Run 16C was at 95 rpm rather than the usual 300. The actual effectiveness of injection was not experimentally verified.

In all six cases where terpolymer was used, extrusion with exposure of the incoming feed to air gave higher C_2. Conversely, anaerobic processing was harmful to recrystallizability. The single, higher melting PK copolymer example did not appear to follow that pattern, although this single result may be in error.

Examination of the remaining data from the rest of the DSC cycles, [Table 1-A2], indicates that the initial melting temperatures and heats of fusion on material directly from the extruder are slightly better in air than in nitrogen. However, the most pronounced effect is seen on the subsequent anaerobic melt stability, during the 10-minute hold at 285°C, where the melt previously exposed to air had higher heat of crystallization than the controls.

Higher C_2 (higher degree of crystallinity) probably results from greater segment mobility in the melt, as a result of lower effective molecular weight. This effect initially was attributed to oxidative radical chain scission, induced by the presence of oxygen, offsetting (or inhibiting) the crosslinking pathway that normally lowers C_2 with time-temperature. This is now thought to be an oversimplification. Another possibility is "reverse crosslinking"; the attack of oxygen on preexisting crosslink bridging moieties.

There does seem to be a possibility that an irreversible "titration" of some bridging moieties or prodegradant component can occur by oxidation. Some evidence of this was seen first by Kluttz with Cahn balance experiments at 150°C.[15] The first, brief pulse of air set off a large weight loss event but a second such pulse did not.

To further develop this train of thought, a technique called Oxygen Pulsed Rheometry (OPR) was conceived and currently is under continued development. In this method the parallel plates of the rheometer are separated during a rheology experiment and the melt is exposed briefly to air. This unusual procedure does not otherwise upset the routine of the run, as proven in control experiments where the plates were similarly separated under nitrogen, without the air pulse, and finding that the viscosity rise curve exactly traces that expected from normal control runs.

A typical response of PK melt viscosity with time is shown in Figure 3. The nitrogen or air pulse was introduced at 5 minutes after start of the test. When a N_2 pulse was used, the slope remained unchanged at a low level, out to the end of the experiment at 30 minutes, exactly as would have been the case if no plate separation had been imposed. When an air pulse was used, however, the viscosity abruptly dropped, followed by a much steeper rise. Oxidative radical scission or de-crosslinking is assumed to account for the initial drop, and indeed at this stage probably would give rise to higher C_2. Thereafter, crosslinking apparently is much more rapid than it would have been otherwise.

An example of further results using the OPR technique is shown in Figure 4. The rate of viscosity rise in the melt at 275°C is shown as a function of the length of time the melt was exposed to air during the pulse; that is, the pulse duration. This rate of rise actually appears to have been reduced when the pulse duration was only a few seconds. If valid, this may indicate better melt stability after the brief oxidative stress, consistent with the DSC conclusions on air processed PK and the prodegradant titration concept.

It should be pointed out that the rheology experiments are run with fluorophosphate coated aluminum plates,[16] possibly not without influence on the melt chemistry.

Exposure of the melt to oxygen would have been expected to reduce oven life, if only by virtue of antioxidant consumption. On the contrary, oven life seems to have been improved in those examples processed at 260-280°C **under air**. The samples processed with air injection (different polymer and AO) were improved by factor 2 to 3. Since no explanation is apparent, this finding may constitute an

important clue to stabilization, if the results are valid.

Commercial extruders are normally run under air atmosphere for most common polymers. As a practical matter, one can now say that processing with an inert blanket that excludes oxygen may not be desirable in practice, even if convenient. Since this conclusion seems contrary to normal expectation, it suggests verification in a simulated commercial processing situation.

Temperature. Results from changing extrusion temperature are shown in Table 3. Included as other variables are dry and undried feed and air instead of the customary nitrogen blanket.

The first cycle DSC results obtained on the products from these extrusions do not indicate a difference in the condition of the polyketone as it cleared the extrusion process due to high processing temperature.

Generally, **higher processing temperature** seemed to reduce somewhat the subsequent melt stability as measured by C_2. The effect may have been more pronounced under nitrogen blanket than with oxygen present, consistent with the preceding findings with air/N_2.

Oven life was harmed significantly by **high temperature processing under nitrogen blanket.** However, consistent with findings already reported, high temperature was **not harmful if air was present** during the extrusion.

There may have been a slight degradation of color at the higher temperatures.

Water. During the early PKB series many different runs were made with dry and undry feed (up to approximately 1.5% water) but only one direct, single variable comparison was carried out. Later, another comparison was made, using a different base polymer, with 3% added water. The results of these, both under nitrogen, are shown in Table 4. No related wet and dry extrusions under air were made.

There is some indication in the second comparison that 3% **water** may have acted as a processing aid, since the feed rate was twice as high as it was with carefully dried feed. (No heat was used in the drying process, 3 days under vacuum.) Water is known to be a solvent for PK under temperature and pressure,[17] although how this could translate to process efficiency at such a low level is not clear. Possibly the effective melt volume was increased by the presence of water vapor, forming a reduced viscosity froth and lowering the residence time.

As with temperature, the first cycle DSC results from these experiments do not indicate a difference in the condition of the polyketone, as it cleared the extrusion process, that might be attributed to the presence of water in the feed.

The effect of water on the subsequent high temperature melt stability under nitrogen is less clear from these results. In the first example of Table 4, C_2 may have been slightly better for the wet processed sample, apparently indicating that drying the feed was detrimental. (Drying had been postulated as a possible source of subsequent, accelerated condensation reactions through a mass effect on the condensation equilibrium.) Also, the Rheometrics viscosity slope with time was lower for the wet sample than for the dry. However, the second comparison of Table 4 found a lower C_2 for the wet processed material.

No effect of **water** on oven life during processing can be seen in the first example of Table 4. However, in the second case, at high hindered phenol level, oven life was reduced to 0.4 and 0.8 by 1.5% and 3.0% water. These changes are statistically significant, too large to be ignored. The difference seems to involve the hindered phenol, 0.2 in the first case and 1.0% in the second. Hints of this phenomenon also have been seen by correlation of C_2 with AO and water content in a large body of other, unrelated data (see Chemicals, DSC, Irganox 1076, Figure 5, later in this section).

Residence Time/Shear Rate. Two comparisons are possible with the present data, in which residence time in the extruder barrel was increased simultaneously as shear rate was reduced. These are shown in Table 5. All runs were nitrogen blanketed.

In the first case, a run was made at 100 instead of the usual 300 rpm. This is estimated to have reduced shear rate from around 1300 to about 420 sec^{-1} and increased residence time from 30 to 45 sec. Subsequent melt stability, C_2,

was 30% higher in the 100 rpm run than in the 300 rpm run. Since Gergen's careful experiments with polyketone on the Rheometrics rheometer have not indicated a particular sensitivity to shear in that device, the meaning of this result is not clear.

In the second comparison of Table 5, Following a suggestion by D. R. Paul,[18] a normal, nitrogen blanketed run at 280°C was halted and the melt was held **quiescent in the barrel** for 10 minutes and then extruded out. This was an extruder simulation of the DSC protocol. Both melt stability and oven life were reduced by the extended holding time. C_1 was only 40% of the corresponding C_2 from the control run, where a similar 10-minute quiescent hold took place in the DSC. Oven life in the sample held in the extruder for 10 minutes was down by 3 days compared to the equivalent DSC treatment, well beyond the precision limit of that test.

In a DSC experiment, the melt is exposed to virgin aluminum (oxide). One can conclude that the DSC protocol in this example was much less severe than the actual practice that it purports to simulate. Holding the melt in the extruder exposes it to possible **catalytic and poisoning effects** from the ripened steel inner surfaces of the barrel and screw and other contamination present in the extruder, and this indeed seems to be the explanation for the discrepancy between the DSC and extruder ten minute soak results.

In related experiments bearing on the catalytic effects of processing machinery on PK melts, an attempt was made to develop char, or "black specks" of the type found in MDU product in a sample of 87/002 terpolymer. A small sample of the polymer was held anaerobically at 250°C for 7 hours, quiescent on a clean chrome plate, in a specially constructed device. The polymer turned amber in color but did not form any carbonacous material visible to the eye. This history was the thermal equivalent to shutting down the Berstoff at 240°C for 14 hours. Like the preceding result, this finding indicates that charring of PK melts in the absence of prodegradant catalysts, at the current process temperatures, **is not an intrinsic characteristic of PK.**

Particulate Additives

Among the nine particulate materials run, three appeared to show 20–30% higher feed rate than expected based on the control runs, Table 1-B1 (relative feed rate). These were **carbon black, bentonite clay and titanium dioxide**. Although the mechanism certainly is not clear, one could postulate reduced melt strength by local melt fracture around poorly adhering particles at high shear stress. Reduced adhesion to the metal surfaces inside the barrel might also occur.

Three of the particulate blends showed evidence of nucleation of the PK in the water quenched strand, Table A2 (Cont'd-1), (DSC Th_1). **Acidic alumina, graphite** and **carbon black** had higher first melting temperatures than their controls by 10, 10 and 5°C, respectively. The effect can still be seen in the first cool, after brief exposure to 285°C, and for graphite, may have survived through the second DSC cycle. Nucleation of polymers by graphitic surfaces is not uncommon. However, the findings discussed later under Polymer Additives, where higher Th_1 data are the rule for a large number of blends which would not be expected to be nucleated, place the significance of these results in doubt.

Graphite and **TiO_2** both appeared to improve melt stability somewhat after the second DSC cycle, giving 1.2 relative C_2.

The **calcium carbonate** blend survived extrusion with little damage and the first DSC cycle with only moderate loss in recrystallizability. In the rheometer, the $CaCO_3$ blend had a lower rate of viscosity rise at 240°C than any of the other blends on which that test was run. This finding is contrary to the slightly low H_1, which is thought to be at the fringe of significance for that measurement.

On the other hand, the $CaCO_3$ blend would not recrystallize at all after the second DSC cycle, indicating very poor high temperature melt stability.

Zinc oxide also showed no evidence of a degrading effect at 240°C in the first DSC cycle. It too badly degraded the melt stability after exposure to 285°C, lowering the relative value to 0.4. This indicates that ZnO_2, like $CaCO_3$, probably could be used with terpolymer, where

processing temperatures are below 250°C, but not with copolymer at temperatures of 280°C and higher.

The **carbon black** blend survived extrusion and the first DSC cycle but would not recrystallize after the second cycle. It too appears to be satisfactory in PK at modest temperatures but would give trouble at high processing temperatures.

Oven aging was severely harmed by most of these particulate additives. The relative values for the particulates are:

Additive	Relative Oven Life
Carbon black	1.1
ZnO_2	1.0
$CaCO_3$	0.8
TiO_2	0.7
Talc	0.4
Basic alumina	0.3
Graphite	0.2
Bentonite clay	0.1
Acidic alumina	0.1

Oven aging of polymers containing particulates can be reduced by **adsorption of antioxidant** onto the particulate surfaces, rendering it ineffective as a radical scavenger. This problem often can be offset by the addition of lower cost polar molecules, such as BPA epoxy, that compete successfully with hindered phenol for the adsorbing sites. This is common practice in KRATON G elastomers, where solid epoxy always is added with fillers. No account was taken of this phenomenon in the present work.

Yellowness Index measurements on these materials are not thought to be meaningful because of selective light absorption by the particles and the opaque, reflective nature of the dispersions.

The burn experiments clearly revealed a potential flame retardant in **calcium carbonate**, Table 1-B3. The thin strip of the 5% $CaCO_3$ blend charred and would not support combustion in the 19.5% oxygen atmosphere used in these tests. Acidic alumina, ZnO_2 and clay seemed to show evidence of more charring than the control but burned nonetheless.

Chemical Additives

The samples of chemicals used for this study were not chemically pure. Since PK melts are very sensitive to traces of certain agents, such as alkali metals, it should be kept in mind that the added chemicals may have affected properties through harmful impurities, introduced inadvertently, that remain unidentified.

Feed Rate. Six chemicals at 1-2% concentration increased the feed rate at constant torque by 40-100%, Table 1-C1 (relative feed rate). These were: **AO 330, Tinuvins 144, 327 and 770, NBC and Zn stearate**. This effect was not seen with Irganox 1076, even at the 4% level. The fact that no increase in feed was seen with Ionol 330, supposedly the same chemical as Ethanox 330, seems to indicate that one of the two observations is in error. No follow-up on any of the feed rate observations has been undertaken.

Anomalous throughput efficiency observations apparently did not arise from chemical effects of the additives on the rate of net crosslinking during the extrusion process. LVN, DSC and other experiments showed no evidence of significantly changed throughput rate with changes in viscosity, crystallizability or crosslinking that occur during the brief trip through the 15 mm twin screw extruder, even when run at 280°C.

DSC. Three chemicals may have nucleated *PK* in the strand, giving higher first melting temperatures, Table 1-C2 (DSC Th_1). These were **EDTAA** (Na salt), **NBC** and **Zn stearate**. Metal salts of organic acids, of course, are among the most commonly used nucleating agents for polymers.

Only one of these chemicals may have benefited melt stability, **Irganox 1076** at 4% concentration, run with dry feed. There is some evidence that poor C_2 may result from an **interaction of water with hindered phenol** during processing. One example of a rough correlation that seems to support this relation, from a diverse source of data, is shown in Figure 5.

The 4% **1076** sample had the highest C_2 observed in any of the blends of this study. This may be indicative of some kind of error although generally it is difficult to get an erroneous, high heat of crystallization. The DSC values have not been corrected for the heat of fusion of the AO, possibly accounting for this result.

Four chemicals destroyed C_2, Table 1-C2, not allowing recrystallization of the PK at the end of the second DSC cycle; **Na stearate, Zn stearate, EDTAA-Na salt** and **Tinuvin 327**. The Na stearate sample was the worst, surviving extrusion with only half the expected crystallinity. The Zn stearate sample also was especially bad, being amorphous already after the first brief heat to 285°C during the first cycle. Zinc *per se* may not be a crosslinking agent for PK since a Zn ionomer blend had high C_2 (discussed under Polymer Additives). The T 327 sample had an exceptionally high rate of viscosity rise in the rheometer, consistent with the poor DSC recrystallizability. (Either or both the 327 and the Zn stearate may have contained an impurity poison.)

The 0.4% **sodium stearate** blend (300 ppm Na) was designed to gain experience with crosslinking in the extruder and to obtain samples for testing of PK having various degrees of crosslinking. The choice of concentration and extrusion time-temperature had been based on results from static DSC powder blend experiments, shown in Figure 6.

The first attempts to extrude this blend were made at 280°C with a residence time of 30 sec. Crosslinking and discoloration were highly evident and the run had to be aborted. Thereafter, the temperature was gradually lowered to 230°C, about the lowest feasible processing temperature with this polymer, where the extrusion was reasonably controlled and samples could be collected.

This 230°C processed, sodium crosslinked PK had lost 60% of its crystallinity already during its brief passage through the extruder, Th_1. No recrystallization was observed after the first excursion to 285°.

In TGA experiments, weight loss of the Na stearate blend began already at 250°C. DSC runs above 300°C resulted in a large endotherm from the boiling out of volatile pyrolysis fragments. After reaching 330°C, the remaining residue appeared to be completely carbonized.

As judged by HFIPA dissolution and swelling, the Na poisoned PK was crosslinked slightly by brief processing at 230°C and progressively by further processing such as mild compression molding. The subsequent sequence of severe crosslinking and carbonaceous char formation with extended time-temperature suggests that a carbon fiber process might be developed with PK. A somewhat higher temperature of activation would be preferable, possibly using zinc as the crosslinking catalyst.

Although the EDTAA sample (Na salt) did process satisfactorily at 240°C, it was degraded after the first DSC cycle and would not recrystallize at all after the second. Presumably this is because of the sodium ion present. This chemical (like Na stearate or Na ionomer) could be used as a controlled crosslinker during dynamic vulcanization (see Glossary) to enhance the formation of IPNs without Kraton G 1651 block copolymer as a rheological control agent.

NBC may have been somewhat detrimental to melt stability of this particular PK, giving only 80% of the expected heat of crystallization after the second cycle. More recent work by R. Q. Kluttz indicates that some batches of PK are far more sensitive to this type of degradation by NBC than others.

Oven Life. Hindered phenol antioxidants are normally added to polymers at concentrations well below 1%. This is done not only for diminishing return cost reasons but because, at higher levels, reversion to oxidative antagonism usually results from additional increments of AO. The result is decreasing oven life with incremental AO additions. A hindered phenol that could be added to PK in high concentrations without causing reversion would be of special interest.

In an earlier, separate study of hindered phenol concentration, using **Irganox 1010** and a higher molecular weight PK, reversion indeed was observed beyond about 1%, Figure 7. (These runs were made with undried feed.) Also indicated in Figure 7 is the fact that the conventional thioester, peroxide decomposer, DLTDP, is detrimental to the oven life at a wide range of concentrations.

Reversion also can be seen in oven life in 2E and 2F, Table 1–C2, where the concentration of **Irganox 1076** of 1 and 4% are used.

Fourteen of the added chemicals in the present study are hindered phenol antioxidants, added at relatively high concentration, usually 2%. At these high levels, reversion from increasing to reduced oven life with added AO increments would be expected to have begun.

The hindered phenols increased oven life over that of the relatively unstabilized control, as expected. The 40-day level reached by the best of these, **Ethanox** (or Ionol) **330**, **Irganox 1024** and **1010**, was equivalent to around 76°C UL service temperature. One would have hoped to see oven life much greater than this level since each doubling of time-to-fail adds only about 7°C to UL rating.

The **remaining hindered phenols** in the study were only about half as effective in oven life, no more than about 20 days at 100°C, less than UL equivalent 70°C. **Tinuvin 770**, the hindered amine UV agent, and **EDTAA (Na)** and both **Zn and Na stearate**, the crosslinking additives, were antagonistic; poorer in oven life than the controls.

The best additive for oven life in these experiments was NBC, giving an 80-day life at 100°C, probably equivalent to a UL rating of greater than 80°C. It would be of great interest to know whether or not the stabilizing effects of this additive can be made to add to those imparted by hindered phenols.

The response of PK to stabilization with NBC is compared to that resulting from a hindered phenol in Figure 8. Here, oven life goes through a maximum as the concentration of hindered phenol increases. However, no sign of reversion is in evidence with NBC at concentrations up to 2%, indicating that higher concentrations may continue to improve oven life. (These two experiments are not well matched. The hindered phenol was run through a single screw extruder using a high molecular weight PK and 50% retention of elongation to break as failure criterion. The NBC samples were run with a twin screw extruder, in the low LVN PK and judged by the brittleness test.)

NBC has the disadvantage of being highly colored. Also, high concentrations of any chemical additive in a crystalline polymer may undergo solid state phase separation resulting in blooming of the additive to the surface of a molded part. This would not be surprising at 3 or 4% NBC in PK.

One UV agent, **Tinuvin 144**, a multifunctional hindered amine, was not harmful in melt stability or oven life, making it a possible candidate for UV stabilization.

The crosslinking agents, **Na** and **Zn stearate**, gave reduced oven life. This activity may not be associated directly with crosslinking *per se*, but rather with some other, purely oxidative pathway.

Color. Two additives resulted in better color in the as-extruded blend than was found in the controls, **Irganox 565** and **stearamide**. Neither of these had as good color as the controls after oven aging to failure at 100°C, but of course they did last twice as long in that test.

After oxidative failure in the oven test, five additive blends were reasonably close in color to the controls, Tinuvin 327, Ethanox 330, Tinuvin 770 (poor initial), Irganox 1425 and 4% Irganox 1076. Of these, the E 330 had the longest oven life, 42 days.

Color had been found in an earlier study to correlate with property loss as a result of oven aging of a single composition of PK. There, time and temperature were the variables, but not blend composition. However, color did not correlate with oven life among the assorted chemical additives used here and clearly cannot ever be used as a surrogate for oven life. This should not be surprising, since the formation of traces of chromophore need not be related, even indirectly, to physical property loss.

Burn. The burn experiments, Table 1–C3, showed charring activity only with those chemicals which appear to be crosslinkers—**Zn** and **Na stearates**. It seems likely that lower reactivity variants can be found in which the onset of crosslinking is shifted to temperatures well above 300°C. Then, charring at pyrolysis temperatures might not be affected significantly, and melt stability arising from premature reactions would not be a problem. A comfortable processing window for flame retarded versions thus would still remain.

Solubility. The **Na stearate** blend was crosslinked enough so that the extruded strand would only swell in HFIPA, but would not dissolve. Its crystallinity had been reduced to 0.6 of the control. Compression molding to prepare the DMTA specimen (next section) must have crosslinked the material still further.

DMTA. The dynamic mechanical spectrum of the base PK used in the blend screening studies was measured by DMTA on a compression molded powder film and on a similar processed control, Figures 9A and 9B. The β-transition peak, resulting from long range motions in the amorphous phase, is found at about 31°C for a completely dry film. A shift in modulus is also apparent at this transition.

If the film is then **saturated with water** and the spectrum remeasured, lower half of Figure 9B, the β-peak becomes larger and shifts down by 15° and the modulus shift becomes greater. (See Appendix—Specimen Preparation for sample equilibration time model.) From a practical viewpoint, it is unfortunate that this transition and modulus shift occur right at ambient conditions.

The γ-transition results from much shorter segment motion than the β-transition and corresponds to a true glass transition. It was at around -60° for dry PK and -66° wet. This is low enough not to be a practical problem for most applications. This peak was disperse and not precisely resolved for many of the blend samples.

It was desired to see what effect crosslinking would have on the mechanical spectrum by examining the low temperature processed Na stearate blend. Although there was some difficulty compression molding this material, an acceptable film for testing by DMTA could be prepared. The dynamic mechanical spectrum of this blend is shown in Figure 9C.

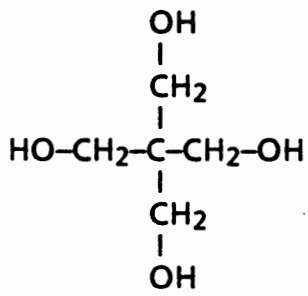
Here, the the β-transition in the low crystallinity, lightly **crosslinked sample** can be seen to have been increased five-fold in magnitude from its normal level. A corresponding, very large change in modulus is associated with this dispersion peak. Further, the peak temperature increased from around 30°C to about 45°C. When the crosslinked sample was run saturated with water, the peak fell about 24°, to around 21°C, about a 10° greater drop than occurs in the control.

This form of polyketone, possibly plasticized with a small molecule sulfone, might be a strong, leathery material resembling plasticized vinyl.

Solvent and Oligomer Additives

Feed Rate. These possible solvents for PK were incorporated at 5-20% and could be expected to increase constant torque feed rate by dilution and/or lubrication. Indeed, Table 1-D1 shows this clearly for nearly all of these additives. Even though present at only 5%, most effective torque reduction was found with the **flux** and **sour asphalts**. The blown asphalt had no effect.

The **pentaerythritol**



was more effective in torque reduction at 10% in PK 002A than it was at 20% in the higher molecular weight PK 002B. This may have been because of partial melt incompatibility in the latter case, where it could act as a shear-plane lubricant in addition to a dilution effect.

DSC. The DSC results are shown in Table 1-D2. Good solvents for the melt would tend to increase heat of fusion, due to greater segment mobility during crystallization, and melting temperature would be lowered by interaction with the solvent. However, interpretation will not be straightforward. One should expect that Tm will be reduced by solvent interaction, not necessarily from that of the control, which was crystallized from the melt, but rather from some higher, notional point corresponding to the melting temperature of a solvent-free, recrystallized sample of the polymer.

Another complication is the possibility of miscibility at high temperatures, but with liquid phase separation occurring prior to crystallization as temperature is lowered, a result of an upper critical solution temperature. Such conditions are less conducive to the development of high degrees of crystal perfection in the phase separated polymer concentrate.

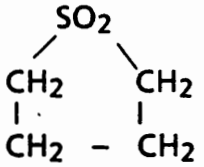
The foregoing implies that the normal way of judging melt stability, by C_2 relative to that of a control, will not be valid in cases where solvency for the PK is present. In these blends it must be judged by loss of crystallinity from H_1 to H_2 and from C_1 to C_2.

R. C. Allen has shown that both water and ethylene glycol are solvents or "plasticizers" (T_m is reduced rather than T_g) for PK.[17] Those experiments were carried out in a DSC using high pressure pans. Similar results would be expected from various hydroxyl, ester and ketone and containing solvents.

On the first melting, Table 1-D2, Th_1, the **pentaerythritol** samples had greatly depressed melting temperatures yet high heats of fusion, probably indicative of even greater PK interaction than was the case with C4 sulfone. (Missing data here results from unresolvable peak overlap of the PK and the crystalline pentaerythritol.) Electron microscopy of the 20% pentaerythritol blend clearly showed separated, dendritic, crystalline pentaerythritol, probably a result of delayed crystallization after the melt had been cooled. Like the C_4 sulfone blend, these mixtures were very poor in melt stability at 285°C by DSC, supported by the high Rheometrics viscosity slope at 275°C.

In any case, melt stability of the pentaerythritol blend was poor, since crystallinity fell off sharply with DSC cycling.

By the foregoing criteria, **C_4 sulfone** (Sulfolane W),



would appear to be a good solvent for PK. Its blend has about the same Th1 as the control and much higher heat of fusion. Melting temperature probably is depressed from some higher, solvent-free value, fortuitously to about the same temperature as that of the unadulterated control. C_4 sulfone had previously been found by Smutny to be a good PK solvent.[11] This is illustrated in Figure 10, where the depression of melting temperature of both co- and terpolymer with increasing solvent is shown.

A relative C_2 value of 1.2 in this case gives a false impression of stability because it is compared to a melt crystallized control. This blend lost about 10 cal/g between H_1 and C_1, already during the first brief melting at 285°. By C_2, it had lost nearly half of its original crystallinity, a C_2 relative to its own H_1 of only 0.5.

Diphenyl sulfone,

$$C_6H_6\text{–}SO_2\text{–}C_6H_6,$$

also low viscosity, showed evidence of slight solid phase incompatibility in the DSC (its T_m was visible), yet surprisingly it did not improve processability much either by dilution or by shear-plane lubrication. No evidence of crosslinking was seen. Lack of improved processability may mean that compatibility was complete at mixing conditions, with phenylsulfone crystallizing out after solidification and showing up in the DSC and DMTA.

Melt stability of the phenyl sulfone appears to have been good for the first brief heat to 285°C and probably also for the 10 min hold.

Epoxy, polyethylene glycol and the three grades of **asphalt**, at the 5–10% level, all increased Th_1 by nearly 10° yet did not increase the degree of crystallinity, H_1. This also might have resulted from solvency at high temperature followed by liquid phase separation prior to complete crystallization. D. L. Handlin had previously found PK powder to be soluble in hot EPON 828. Melt stability of these five blends is judged to have been poor.

The DSC data through Th_2 (prior to the 10-minute hold at 280°), indicate that the **sour and blown asphalts** and the **epoxy** gave the highest PK melting temperatures while those of **PEG** and the **flux asphalt** were much lower,

probably due to melt degradation already after the short heat to 285°C. Indeed, both the PEG and flux asphalt blends had low C_2, confirming poor melt stability. The epoxy blend melt stability appears to have been reasonably good.

Oven Life. Oven life was badly affected by most of the solvents and oligomers tried in this series. Least damaging were the blown and flux asphalts. Many such asphaltic materials exhibit "natural" antioxidant activity from the substituted condensed aromatics.

Color. Three of these additives improved the color of the extrudate, **pentaerythritol**, **C_4 sulfone**, **phenyl sulfone**. (The asphalts, of course, are black.) The short oven life accounts for the low color of the oven aged samples.

Burn. The burn results, Table 1-D3, showed nothing of interest regarding possible flame retardants.

Solubility. Only four of the blends were tested for HFIPA solution character. The **PEG** blend was clear, indicating that the PK may not have been crosslinked appreciably.

The **C_4 sulfone**, **phenyl sulfone** and **epoxy** blends, on the other hand, gave cloudy suspensions, possibly indicative of crosslinking, or at least marginal solubility for some reason. However, the C_2 crystallinities of these blends, after 10 minutes at 285°C, were around 1.0. This seems to indicate that crosslinking in the original extrudate was unlikely to have been present. Another possible explanation, interaction between the two solutes (PK and the added solvent), seems unlikely to have caused precipitation in HFIPA. The meaning of these solution/suspension results remains clouded.

DMTA. Dynamic mechanical spectroscopy was carried out on six of the solvent blends, Table 1-D3 (and Table 7), in the form of dry compression molded films. The β-transitions of the PK in both the **pentaerythritol** and the PEG blends (Figures 9D, E and I) were close to that of the control sample. The **epoxy** sample (Figure 9H) also appeared little changed, although the wet β-peak was at about 19°C, slightly higher than expected from the control. The T_g of the epoxy is visible at 99°C.

The **PEG** sample showed a small peak at 57°C, presumably due to melting of free PEG. If so, its melting temperature appears to have been depressed by about 12°, from 69°C, possibly a sign of a degree of compatibility.

The β-transitions of both the **C4 sulfone** and the **diphenyl sulfone** blends were depressed by about 29 and 15°, respectively, Figures 9F and 9G. The liquid C_4 sulfone seems likely to have been completely swelled (dissolved) in the PK amorphous phase. However, some of the normally solid phenyl sulfone apparently was phase separated, possibly by delayed crystallization, evidenced by the transition visible at 119°C. Pure phenyl sulfone melts at 125°C. These findings appear to be consistent with the DSC interpretations. (The apparent rise in modulus shown in Figure 9F at 60–70° is an artifact.) When run wet, lower half of Figure 9G, the phenyl sulfone blend β-peak was shifted down by about 15°, to around 0°C.

These dynamic mechanical results indicate that liquid sulfone derivatives might be found that could be used as practical plasticizers for PK and that certain polysulfones might be compatible.

The γ-transition temperatures appeared to be reduced 15–20° by the sulfones. (This peak often is not well resolved and any clamping problems with the cold, stiff samples obscures the precise shape of the curves.)

The solvent/oligomer blend DMTA results are compared with those of the polymer blends in the next section.

Polymer Additives

This series of blends, Table 1-E, was prepared by intensively mixing added polymers at 10%v. The table lists the polymers more or less in order of decreasing hydrogen bonding capability or polarity, from high to low.

Feed Rate. Many of these blends had higher relative feed rates than their controls, Table 1-E1. If real, the effect probably is due to shear-plane lubrication resulting from the incompatible, added polymers.[5] The power of this mechanism may be in evidence with the Na ionomer blend, which clearly underwent crosslinking during processing, yet still had a 1.3 relative feed rate. (The 0.4% Na stearate blend was 1.0.) This effect may make nearly all PK/polymer blends more processable than an

unblended base PK. The relative feed rates apparently do not track polarity (decreasing in Table A5) or viscosity (not shown) of the added polymer.

DSC. The DSC results are shown in Table 1-E2. The DSC technique and some of the associated problems are discussed in the Appendix—Analytical Procedures, DSC. Some of the results reported here may be suspect where the recrystallizability is low, since the DSC time protocol was not always followed. The following treatment generally assumes they are valid.

The PK heat of fusion data have been corrected for the added polymer, based on control measurements on the pure polymers and assuming the same degree of crystallization in the blends. One exception was found in the results from the blends of terpolymer with PK copolymer. Where this correction was not feasible because of peak overlap, results are not reported at all.

In all blends of PK with other **crystalline polymers**, the fusion characteristics of the added polymers did not appear to be changed significantly. Where these first order transitions could be resolved, no particular depression of T_m or change in crystallinity from interaction with the PK was in evidence. On subsequent DSC cycles, designed to accentuate PK degradation, these polymers did not degrade.

The DSC data for these blends are difficult to compare directly from Table 1 since there is a large number of materials and because there are four different control samples involved. Therefore, the results have been converted to simpler terms, Table 6, as follows:

1. Differential peak temperature—difference between peak temperature and that of the corresponding control
2. Relative Heat of Fusion—enthalpy of fusion divided by that of the control.

The validity of the melting and freezing peak temperature differences from their controls might be estimated by looking at the differences between sequential cooling and heating cycles, Tc_1 and Th_2, where differences should not be present. This has been done for the polymer blends, Table 6. Here, the total number of degrees up or down cancels and the standard deviation is 5°. From this one can estimate that differences of 10° or more between the various individual samples and their controls probably are significant.

Similarly, the standard deviation for the relative heats of fusion and crystallization of polymer blends and their controls, rel C_1 and rel H_2, was about 0.1. Differences in individual relative heats of 0.2 or greater probably are significant.

Table 6 shows that among the blends where the PK was not degraded during extrusion (judged by subsequent DSC results), nearly all had first melting temperatures higher than those of their controls (Th_1), more than two thirds by 7 to 12°. Increased differential T_m does indeed appear to be the rule in these blends. (The standard deviation of 5° is for individual measurements.) This result was unexpected and is not readily explained.

High T_m does not appear likely to have resulted from increased chain mobility through a solvency effect with these diverse polymers, one of which is a hydrocarbon (PMP) and most certainly would not be expected to have any miscibility whatsoever.

Examination of the relative H_1 results in Table 6 shows that the first heats of fusion generally are within about ± 0.1, which is roughly the significance range. Although the melting temperatures are high, the crystallinity of the PK phase in these blends apparently was affected little, or not at all, by blending.

One phenomenon consistent with the high T_m's and nearly unchanged heats of fusion would be nucleation. For example, high melting PK, possibly copolymer, has been suspected of being present from synthesis in at least some samples of PK terpolymer. D. L. Handlin found that birefringence did not disappear on the microscope hot stage from a KSLA sample of terpolymer until about 260°C. G. B. Klingensmith similarly found material melting at least up to 250°C in a Moerdijk sample of terpolymer.

Blending might disperse any copolymer or other high melting PK material in a way that could nucleate bulk crystallization or increase T_m by epitaxy or as a result of miscible solution

formation. Here, however, nucleation by high melting PK components can be eliminated as an explanation. Such an effect would have been manifested in the processed control samples as well as the blends, and would not appear as a differential between blend and control.

Nucleation seems anomalous as the explanation for elevated T_m in the PK polymer blends since no rationale is apparent. It is true, however, that knowledge about the additives actually present in these blending components, which might transfer to the PK, is very limited. Such transfer seems unlikely to be the explanation because of the diverse types of polymers that were added, most of which showed the effect.

An alternative to nucleation would be that, during the blending process, some crystallization inhibitor present in the raw PK is being removed by partitioning or sequestering into the added polymer phase. This too conceivably might occur with one or two polymers, but not with such a high proportion of the present blends.

Several deliberate blends of **PK copolymer** were made with terpolymer to observe interactions. Runs were made at 10 and 50%w concentration, both above and below the melting temperature of the copolymer. (In this case no correction has been made to the DSC heats of fusion.)

The effect of blending higher melting copolymer into terpolymer on the crystallization peak temperature of the melts as a function of copolymer concentration is shown in Figure 11, along with the the values of nucleation temperature. When the combinations of co- and terpolymer are blended at 280°, the crystallization peak temperatures are linear additive. Blending at 240°, however, below the T_m of copolymer, did result in higher peak temperatures for the blends.

Nucleation was taken as the first measurable deviation from the baseline upon cooling in the first DSC cycle. The nucleation temperatures of the blends are higher than linear additive, whether or not the copolymer was melted during extrusion. In this blend, higher nucleation temperature did not necessarily result in higher bulk crystallization temperature. (Nucleation in polymers can be greatly affected by the time-temperature heat soak of the melt prior to cooling.)

The enthalpies of crystallization for the same two blends are shown in Figure 12, along with those of the unmodified starting polymers. Both of the blends have lower crystallinity than the sum of the unmodified contributions would predict. This lower crystallinity suggests that blending these two grades to achieve intermediate melting temperature would not be as effective for modulus and barrier as using pure terpolymer of that same melting temperature.

The **polyvinyl phenol** mixture clearly might be an exception to the nucleation explanation for increased T_m. Its higher T_m easily could arise from a "solvent" effect, since the PVPhenol molecular weight is only 4,000, practically an oligomer. It will be shown in a later section that this is a miscible blend. Its melt stability by the standard developed under solvents was reasonably good during the first DSC cycle but marginally poor during the 10-minute hold at 285°C.

Returning to Table 6, several blends had very poor melt stability. The polyvinyl pyridine mixture barely made it through the extruder at 240°, having a relative H_1 of only 0.3; that is, only 30% of the heat of fusion found in the processed control was found in this blend after extrusion. Further, the melting peak temperature was depressed by 56°. The first DSC heating cycle to 285° then destroyed that little remaining crystallizability.

Similarly, the as-extruded **sodium ionomer** blend had only 0.6 of the expected heat of fusion and it too would not recrystallize after the first heating cycle. In this case the result is known to be due to alkali metal induced crosslinking.

For seven of the blends, the heats of fusion in Table 6 indicate some degradation in the melt after brief exposure, and after 10 minutes exposure to 285°. The results on these blends with downgraded melt stability are summarized below:

Poor DSC Melt Stability

Added Poly	Relative Enthalpy		
	H_1	C_1	C_2
PVPyridine	0.3	0	
Na Ionomer	0.6	0	
SAN	0.9	0.8	0.2
PEtOxazoline	1.0	1.1	0.4
ANS	1.1	0.9	0.6
P Acetal	0.8	0.9	0.7
P Sulfone	0.9	1.0	0.8

The SAN blend was peculiar in that it showed only 20% second cycle recrystallizability heat, yet its crystallization temperature was actually slightly higher than its control. (The DSC time protocol may not have been adhered to for SAN, see discussion of DSC vs rheology, below.) **PSulfone** similarly showed no depression of the PK T_{c2}.

Results from the PBPA blend are not available because the DSC pans blew open from internal gas pressure during the first heating cycle. Apparently there is some hitherto unsuspected reaction taking place that did not show up in the powder mixture safety screen. Although it seems unlikely that appreciable residual solvent from the original EPONOL resin solution could remain after processing, that also could be responsible for pressure in the DSC pan. Safety precautions perhaps should be taken with this combination.

The **nylon 6/6** blend appears to have greatly *stabilized the PK melt*, resulting in a 1.6 relative C_2. Six of the other blends also appear to show increased melt stability by 20% or more. These are:

Improved Melt Stability

Added Poly	Relative Enthalpy		
	H_1	C_1	C_2
Nylon 6/6	1.0	1.5	1.6
PET	0.9	1.4	1.3
PPO	1.0	1.3	1.3
PC	1.1	1.2	1.2
PBT	1.0	1.2	1.2
Zn ionomer	1.1	1.2	1.2
PVDF	0.9	1.0	1.2

The most outstanding of these clearly is the nylon 6/6 blend, which retained its relative recrystallizability at a level 60% higher than the control after the full DSC treatment. It also had 40° higher crystallization temperature, T_{c2}. (The N/6 blend, processed at 240°C rather than at 280, had a C_2 of 1.0)

The **PET** blend seemed especially good after the first, short cycle to 285°. Anomalous among this group is **the PBT** blend, which had a second freezing temperature 14° lower than its control.

The remainder of the blends showed no clear effects one way or the other on PK melt stability from having been blended with the added polymers.

Rheology. The rate of viscosity rise at 275° was very low indeed for **N6**, indicating possible melt stabilization by this added polymer. However, since the C_2 was 1.0, indicating no improvement, these two methods do not seem to agree. N6/6 might have been even better in rheology slope, judging from the DSC measurements, but that sample was not run.

Comparison of the rheology results at 275° with the DSC relative C_2 (285°) data, both of which purport to measure high temperature melt stability, does not show a good correlation in some cases. The blends of PK with **TPU**, **polyvinyl-phenol** and **PBT** all had reasonably good C_2's, 1.0–1.2, yet their viscosity slopes seemed higher than expected. The PVPhenol blend slope, on the other hand, is more than an order higher than the controls, clearly in conflict with a relative C_2 of 1.0. In the case of the N6 blend the reverse was true.

Unfortunately, rheology on control 2, 10E, which is the PK used in the foregoing blends, is not available and no more of the sample exists. According to Gergen's model, based on molecular weight, control 1 should have had a slope of 120, one half the observed 260. Perhaps then, control 2 would have been the calculated 260 or twice that, 520.

Comparisons between C_2 and rheology slope cannot be rigorous for a number of reasons. Differences between these two tests include in the DSC a 10° higher temperature and probably more rigorous temperature and atmosphere

control. Shear is present in the rheometer but not in the DSC experiments. Fluorophosphated aluminum surfaces are present in the rheometer and in most, but not all, of the DSC analyses.

Some chemical effect from the foregoing may cause crosslinking in the rheometer in certain cases. The result could be a high rheometer slope even though the DSC recrystallizability appears normal on the same material.

In cases where the DSC indicates poor recrystallizability but the rheology slope is low, the DSC results may be in error because of lack of adherence to the intended time-soak protocol. Alternatively, a quite different mechanism may be in operation. **Dynamic vulcanization** and **shear-plane lubrication** of the crosslinking PK phase could combine to give both a low rate of rise in apparent viscosity and at the same time a rapidly decreasing C_2 recrystallizability.

These postulated explanations suggest that whenever there is a lack of agreement between DSC C_2 and rheology slope, one should seek an explanation.

Rheology measurements, Table 1-E2, indicate very poor melt stability for the following two blends at 275°C, indicating they could not be blended with the higher melting PK copolymer:

Poor Melt Stability by Rheometry

PBPA (poly BPA hydroxy ether)

Polyvinyl-phenol

Further testing at 240°C might indicate possible usefulness of these two particularly interesting additives with PK terpolymer. Switching to stainless steel rheometer plates would eliminate the possibility that the fluorophosphated aluminum caused the high rate of viscosity increase. The PBPA blend blew open the DSC pans on the first heating, a result not obtained with any of the other blends.

Oven Aging. One great hope for the polymer blending program was improved oven life of PK through contacting with immiscible materials of a wide variety, as outlined in the Introduction—Stabilization.

Oven aging results shown in Table 1-E2 were disappointing. Only the TPU and nylon 6/6 blends gave longer oven life than their controls. Each of these additives appeared to double the time to failure over their respective controls. Several possibilities to explain this finding are apparent, other than the sequestering and related theories, on which high expectations had been based.

In the case of TPU, the improvement may be illusory, arising from the fact that the low modulus TPU is a toughener, allowing the blend to pass the flex test even though the PK component has failed. Alternatively, some component, possibly a stabilizer chemical, in the added TPU (or the nylon) might be transferring to, and thereby stabilizing, the PK.

In the case of N6/6, oven life of the high temperature processed control sample was poorer than would be expected if it had been processed at 240°C. However, the blend indeed was processed at 280°C rather than the more usual 240°C, and the process study had indicated reduced oven life for controls processed at higher temperatures. The improvement in oven life may legitimately have arisen from the presence of N6/6.

Color. Initial yellowness of the extruded blends was not improved or affected much by many of the added polymers. Those that harmed the initial, unaged color were:

Harmed Initial Color

Added Poly	Yellowness
ANS	127
Na ionomer	78
PBPA	75
PPO	44
PET	25
Control	18

Yellowness after oven aging to failure was improved in many cases. However, these observations are confounded by the shorter oven-time to failure for those blends. Only in the case of **poly ethyl oxazoline** was there a possible real improvement in oven-aged color.

Oven-aged color was clearly worse than a correspondingly aged control in the blends with **PBPA, SAN and Na ionomer.**

Burn. Burn results on the polymer blends, Table 1-E3, indicate that the **Na ionomer** blend would not support combustion (as indeed the Na stearate blends would not, even at the low level of 300 ppm Na).

The progressive chemical effect of alkali metal as temperature increases toward pyrolysis probably is: crosslinking → condensation → charring. This sequence is based on a number of observations not only in DSC and TGA experiments, but by E. R. George in process machines with and without glass present. In retrospect, the outright flame inhibiting effect of Na ionomer is not surprising.

Examination of the remainder of the burn results shows three samples that charred in excess of that seen in the controls:

Charred During Burn
- Added Polymer
  - PPO
  - Polyvinyl phenol
  - FEP

The likelihood of these materials being useful in flame retarded PK will depend on other factors. A flame retarded version of PC would be interesting to try in this context, possibly in combination with $CaCO_3$. Alternatively, the flame retardant chemicals that are used in PC could be tried in PK.

Solubility. PK is normally completely soluble in HFIPA at room temperature. However, when crosslinked, it swells but does not dissolve. This characteristic often is used qualitatively to confirm crosslinking. With blends of PK and other components that are also soluble in HFIPA, attempted dissolution sometimes can be used to estimate the state of crosslinking of the PK component. As a more rigorous control, co-solubility of the neat materials with PK in HFIPA easily could have been determined, but was not.

Listed in Table 1-E3 are the results from HFIPA solution tests. The appearance of HFIPA solutions or suspensions of the PK/polymer blends after extrusion is tabulated, along with the solubility of the neat, added polymers determined in separate experiments.

Examination of these results identifies four blends that might have been expected to give clear solutions since both components are soluble, but did not. These were:

Cloudy HFIPA Solution (crosslinked?)
- Added Polymer
  - PBPA
  - PC
  - Polyethyl oxazoline
  - SAN

The explanation for these cloudy solutions most likely is that crosslinking of the PK phase took place during extrusion, resulting in HFIPA gel suspensions. Indeed, all of these polymer blends except PC have previously been shown to be melt unstable by rheometry or by thermal analysis, consistent with crosslinking of the PK. However, if neat PC and PK are co-soluble, the result for that blend is anomalous, since no prior evidence of crosslinking was found.

An alternative that could cause cloudy PK solutions is that some other chemical changes have altered the solubility characteristics of the PK phase without crosslinking, making it less soluble in HFIPA. This seems to have been observed by others in *m*-cresol solutions of processed or degraded PK but it was not expected in HFIPA.

The insoluble PMP residue consisted of extremely fine, uniform fibers. This finding is a reminder of the possibility of forming *in situ* oriented fibers in immiscible thermoplastic blends by rheology and shear management. This would be a particularly interesting case because interfacial adhesion between the matrix and fibers might be better than in earlier attempts, where hydrocarbon-hydrocarbon pairs were used. (The surface energy of drawn crystalline hydrocarbon surfaces may be high because of the high crystalline density.)

Phase Size. Most polymer blends are incompatible, in many cases completely so. It must be recognized, however, that many blends in which there is a sufficient degree of interaction will be "partially" miscible. For example, if the chosen blending temperature places a mixture above its lower critical solution

temperature, phase separation will result in partial dissolution of each polymer into the other. For polydisperse components, fractionation also can occur, with lower molecular weight components of one phase preferentially migrating to the other. As a result, phase volume of the added polymer might appear to remain the same or it might change.

Observing phase size and projected area by EM tells little if anything about phase composition, *per se*. To some extent, one might detect the presence of one phase in another by staining or other decoration or by special microscopic techniques. These require further evaluation than was feasible in the present screening study and were not undertaken.

Small phase size, especially sub-micron, is highly desirable in an incompatible polymer blend because it tends to imply low interfacial tension in the melt. This is a sign of phase interaction that should result in good interphase adhesion in the solid.

Phase size in a blend will be a function of the viscosity ratio of the components (at temperature and shear rate) and their relative volumes, in addition to their interfacial tension.[6] In the present study, the rheology of the components is not known for at least two reasons—interphase partitioning (partial miscibility) and the changing degree of PK crosslinking during the course of mixing. "Dynamic vulcanization" of the PK also may be occurring in some cases. Generally, the condensation polymers used are much lower in viscosity than the PK and, in the present experiments, are at low volume fraction. Such conditions favor interdispersion by a purely physical, shear stress transfer process, even where high interfacial tension is present.

Experience with IPN's over the years suggests that sub-micron phase size cannot be achieved by ordinary mechanical mixing without low interfacial tension. This can result from very close solubility parameter (*e.g.*, PP/PB) or the presence of bridging molecules such as *in situ* block graft polymers (*e.g.*, in KG-MA/nylon).

Scanning transmission electron microscopy (STEM) was carried out on all of the PK/polymer blends of this study. Ruthenium staining was found to darken PK, greatly enhancing contrast for many of the blends. In all except two cases, the morphology and phase size of the added polymers were clearly revealed. Some comments on these results will be found in the Appendix—Analytical Procedures, Electron Microscopy. The approximate phase sizes for the blends are tabulated in Table 1-E3 and compared with the dynamic mechanical results in Table 7.

The structures appear to be dispersed in all cases. The formation of IPNs at such low volume fraction and in the absence of a rheology control agent was not expected and indeed did not occur. The phase sizes do not go through a minimum with increasing polarity, down the list in Table A5 (Cont'd-2), but rather show a scatter throughout the entire range. This suggests that the sequence selected was incorrect and/or that grafting or other soap effects are present in some of the blends.

In the case of the FEP blend, sufficient contrast for accurate phase size determination was not inherent, nor could it be developed either in untreated samples or with ruthenium or osmium staining, before or after electron beam damage. Apparently the PK and FEP stain approximately equally. FEP is believed to be incompatible with PK based on faint images that were sometimes observable and on other considerations.

Like FEP, **polyvinyl phenol** was not detected in its PK blend by the STEM technique on the extruded strand. In this case, extensive efforts to develop contrast were not made. Since the characteristic PVPhenol Tg was not found at all by DMTA in a compression molded sample of this blend, and the highly water sensitive PK β-transition was raised nearly 40° (to be discussed later), the added PVPhenol is assumed to have dissolved completely in the PK. Because of its relatively low concentration, the degree of crystallinity of the PK was not changed from that of the control. (T_m was not depressed from that of the melt crystallized control, although it may have been from that of a hypothetical, solvent recrystallized PK.)

The cell sizes for the remainder of the polymer blends are depicted schematically in Figure 13. With the exception of those blends that are thought not to have been adequately mixed, this size scale might be taken as a very

rough indicator of degree of interaction in the melt between PK and the added polymers, especially where sub-micron structures were formed. Grafting or related chemical changes may have occurred. As they stand in this screening study, those dispersions having a size below about 1 μ would seem to be of the most interest. Others suspected of inadequate processing, of course, would have to be studied further to make such a determination.

Nylon 6/6, PBPA and **poly-ethylene/vinyl alcohol** (PEt/Valc, Eval F) had very small phase size, 0.2–0.3 μ. Such a small phase size could indicate that these polymer melts have very low interfacial tension or are in the process of dissolution. If they are partially miscible with PK, variations in temperature, volume fraction and/or molecular weight of the components might result in more complete miscibility.

In any case, very small phase size probably is indicative of excellent interphase adhesion. Blends of a wide range of composition, IPN's with good properties and coextrusions without adhesive tie layers should be possible with these combinations.

The **PEt/VAlc** blend was particularly interesting. The dark boundary region of the tiny PEt/Valc inclusions had a peculiar appearance. They appeared to be surrounded by irregular, diffuse tendrils, forming a halo. This might indicate some incomplete kinetic process, such as phase dissolution or separation, frozen-in by solidification. On the other hand, it seems just as likely to be an artifact from the section preparation. (Some efforts were made to microtome the blend under completely dry conditions but the results were not conclusive.) None of the other blends had obvious signs of such interlayers. (See also the discussion under Oxygen Barrier, end of this section.)

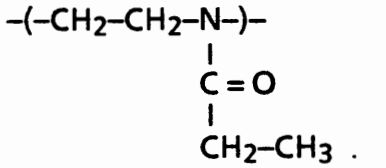
Nylon 6 formed relatively large inclusions, unlike the ultra-fine dispersion of N66. However, these particles clearly had PK dispersed inside. Their appearance resembles the phase inverted rubber inclusions in a typical HIPS, where the effective rubber phase volume is extended by included polystyrene. The inner "cell" size of the nylon was estimated to be about the same as that of N6/6 processed at 280°C, although of course the internal morphology is skeletal rather than matrix.[8c]

It is easy to speculate that, in their interaction with PK at any given temperature, nylon 6 and 6/6 might well be physically undistinguished from each other in the melt. This would follow from the fact that their composition and amide group molarity are equivalent in the melt, although the crystalline versions are quite different. If the two blends had been processed at the same temperature, this would leave unexplained the difference in morphology that was observed. However, the N6 blend was mixed at 240°C whereas the N6/6 blend was mixed at 280°C. Proof that mixing temperature was critical to morphology would be, after processing a N6 blend at 280°C, finding the structure typical for N/66.

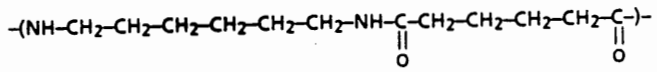
Similarly, the **polyacetal** blend appeared to have small inclusions inside larger structures. Like N6, this blend also was processed at 240°. However, in this case 280°C would be too high a processing temperature for the polyacetal.

Such morphology suggests that compositions of minor amounts of PK in PAcetal or nylon processed at 240°C would be extremely fine and uniform. Fine, well adhering dispersions of PK, crosslinked to prevent crystallization, might make excellent toughened versions of these polymers.

Polyethyl oxazoline formed cells in PK nearly an order larger than did N6/6 (and perhaps N6 at 280°). The structure of PEtOxazoline is



It contains one amide group for each 4 aliphatic carbons. This is contrasted to N6/6 (and essentially N6 in the melt),



which contains one amide group for each 5 aliphatic carbons. The difference in melt interaction may be merely an effect of higher amide functionality. There are electronic and steric differences as well, although no chemistry was shown to occur between either of these and PK using the powder blend, thermal analysis safety check.

Aromatic polyester (**PBT**, **PET**), aromatic nitrile (**SAN**, **ANS**), aliphatic ether (**polyacetal**) and aromatic succinic anhydride (SMA) all appeared to interact reasonably well with PK in the melt, forming dispersions of 1 μ or less. The next group (TPU, PVDF, PC, PVPyridine) formed cells slightly over 1 μ. Some degree of interaction, possibly indicative of adequate interphase adhesion for good mechanical properties, seems to be present with this group of added polymers.

Polycarbonate, a viscous melt normally processed above 300°, may be insufficiently mixed in the brief residence at 280° to indicate the true level of interaction. Further, the dynamic mechanical results to be discussed below seem to indicate a degree of intermiscibility with PK. For these reasons interfacial adhesion may be much better than indicated by the 1.4 μ size found in these experiments.

Polyvinyl pyridine was dispersed predominantly as >1 μ cells. However, there also were large numbers of extremely small particles present, about 0.05 μ in diameter.

Most of the remaining polymers—**ionomers** (**Zn and Na**), poly aromatic ether (PPO), aliphatic ester (**polycaprolactone**) and hydrocarbon (PMP)—seem to be the least interactive of all, forming cells of around 2 μ or greater, moving out of the range generally considered of greatest interest for incompatible blends.

Sulfone containing polymers are of particular interest because of the solvency effects noted earlier, under Solvents and Oligomers. **Polysulfone** gave a bimodal distribution in the PK blend. Most of the PSulfone resides in a few, very large inclusions. In that case, poor mixing seems certainly to have resulted from the processing temperature being too low, even at 280°C. The recommended process temperature for PSulfone is even higher than for PC, >320°C, a temperature range not considered feasible for PK at its present state of melt stability.

Clearly the **PMP** blend had the highest melt interfacial tension, the largest cell size (fiber cross-section), and presumably the poorest interfacial adhesion. Similar results would be expected with **PE**, **PP**, **PB**, and probably **PS**, and with any other non-functional, hydrocarbon polymers in the absence of grafts or other "soap".

Image analyses were run by P. B. Himelfarb and R. B. Lewis on five of the blends where the STEM photomicrographs had particularly good contrast. The size distributions of these are shown in Figure 14. The first four showed a precipitous drop in phase size on the small particle end of the distribution, whereas the last, the PEt/VAlc blend, appeared quite different, having a pronounced tail on the small size end.

The subjectively estimated phase sizes listed earlier are compared to the image analysis sizes at the distribution peak, along with the relative projection areas (phase volume), as follows:

Added Poly	STEM Phase Size (μ) Subj.	Image Anal.	Total Projected Area, %
PVDF	1.4	1.0	9.4
PC	1.4	1.0	8.7
Epoxy	1.0	0.6	5.1
SAN	0.8	0.4	21.3
PEt/VAlc	0.3	0.4	17.0

Here it can be seen that subjective estimates of phase size are higher than, but more or less track the image analysis peak results. An exception is seen in the last blend, where the distribution shape changes. Phase volumes are lower than the 10% added volume for the blends having the larger dispersion sizes and higher volume for the smallest dispersions.

These image analysis results are intriguing. It seems possible that new insight into the mechanisms involved in mixing of incompletely miscible blends might be developed using this

technique for analysis. At the very least, examination of subsequent passes through the mixer would allow monitoring the approach to pseudo-equilibrium morphologies and phase volumes as the degree of mechanical intermixing increased.

DMTA. Since not many dynamic mechanical loss spectra for PK have been published, DMTA curves for all of the blends on which this measurement was made are included in Figures 9A through 9AE. Many of these were run both dry and saturated with water (lower half of each figure, where available). No experiments were carried out to demonstrate the degree of reversibility of the water effect.

Unresolved specimen clamping problems in the DMTA apparatus sometimes caused erratic behavior in the dispersion curves. This could affect the accuracy of individual results reported here. The absolute level of modulus shown in the curves are known to be invalid for this reason. The shapes of the modulus-temperature traces, however, are believed to be precise and valid where there was no transient clamp slippage during the course of a run. Obvious error is involved where the modulus appears to rise with temperature.

Results from dynamic mechanical analysis of the polymer blends are tabulated in Table 1-E3. These data also are listed in Table 7, along with that from the solvent and oligomer blends for which DMTA data is available, and for one chemical (crosslinked) blend. They are listed in order of descending β-transition temperature. Also tabulated for comparison are the dispersed phase cell size data.

The large majority of blends in Table 7 have dry β-peaks that cluster around that of the control sample, from about 28 to 35°. It is presumed that relatively small differences between these, $\pm 3°$, are not significant. Generally, the β-transitions of the PK phase in the blends are shifted down by about 15° after the specimen has been equilibrated in water. (Appendix—Specimen Preparation shows a predictive model for approximating the water or oxygen equilibration time for samples of any geometry at various temperatures.)

In some of the blends, evidence of the components that had been compounded into the PK could be seen in the DMTA spectrum. These transitions occurred at temperatures appropriate to the known characteristics of the additives. In many cases the runs were not carried to sufficiently high temperatures to resolve the additive transition, in which case any depression that might have occurred would escape detection.

The γ-transitions of many of the blends are poorly resolved and the accuracy of their peak temperatures is correspondingly low. For the most part they seem unaffected by blending. There apparently is a slight trend toward lower γ-transition in the **wet samples**. These results are reported in Table 7 without further comment.

The highest β-peak temperature of all was found with the low molecular weight **polyvinyl phenol**, shown in Figure 9N. In this sample the β-peak of the PK (31°) and the glass transition of the PVPhenol (150°) appear to be merged into a single peak at 68°, indicating complete compatibility of the two polymers. The molecular weight of the PVPhenol is only 4,000, making it practically an oligomer. (Unfortunately, the DMTA scan was not run well beyond the 150° transition region of the unmodified PVPhenol, to prove unequivocally that no remnant of that transition was present.) This is the only compatible blend that was found of PK with another polymer.

The merged peaks of PK and PVPhenol were shifted more by water saturation than that of the neat PK, down 33°, from 68 to 35°C. (The sharp maximum at around 60°C is an artifact.)

The next group of three blends in Table 7 had very large β-transitions at around 45°C. Two of these, the **Na stearate** and **Na ionomer** blends, had been crosslinked by passage through the extruder, as judged by DSC and by solubility in HFIPA. The DMTA curves are very similar, as shown in Figures 9C and 9AC. When the β-transitions of these two crosslinked blends were determined wet, the peak temperatures were found to have dropped by about 24°, to around 21°C, more than normal for unmodified PK.

The PBPA blend has a PK β-transition in the same region that was found for the two crosslinked blends, Figure 9O, 47°C. One would be tempted to conclude that dissolution of the high T_g PBPA in the PK amorphous phase

raised the β-transition. However, this blend had been judged to be melt unstable by its rapid viscosity increase at 275° and its formation of a cloudy HFIPA solution. (DSC data is not available because the pans blew open on the first heat.) Therefore, one must tentatively conclude that the large, elevated β-peak may have arisen from crosslinking, and indeed, the curve strongly resembles the two crosslinked PK's (Figures 9C and 9AC). The magnitude of the modulus change also resembles that of the Na crosslinked blend. A water insensitive peak arising from the PBPA is visible at around 93°.

The remarkably small cell size of the PBPA dispersion would seem to indicate extremely low interfacial tension during mixing, possibly arising from a degree of cross-polymer reaction. Evidence of some reaction was seen in that the DSC pans blew open during the first heating cycle. Conceivably the blend was at first compatible in the melt but phase separated as the PK underwent crosslinking and/or as the sample was cooled. This would be consistent with the small phase size. The possibility that the high PK β-peak temperature arose at least to some extent from some of the PBPA remaining dissolved in the amorphous phase of the solid cannot be ruled out.

Union Carbide markets several grades of the poly-bisphenol A type polymer in solid form, trade named "Phenoxy" resin. These would be interesting PK blending components for further study, although some caution may be warranted due to the DSC pan blow-out problem using Eponol resin.

Apparently, **crosslinking** at a level high enough to prevent dissolution, but insufficient to completely inhibit crystallization, greatly increases the size of the β-transition of PK and raises its temperature by around 25°. (Since DSC and solubility measurements were not made on the compression molded DMTA specimen, a degree of uncertainty about the details remain.) Because the crosslinking density is presumed to be low, its influence must be on very long chain segments. This would indicate that an increase in β-transition should be possible from a relatively minor amount of high T_g material dissolved in the amorphous phase, encouraging from a practical standpoint. This apparently was the case with PVPhenol.

As expected, the γ-transition, reflecting much shorter segment length motions, did not appear to be affected at all by crosslinking.

It is tempting to speculate that the size of the β-peak will be a more sensitive, earlier detector for the onset of crosslinking in blends than will loss of crystallizability. This peak can be analyzed in the presence of most other components. Presumably rheology might be more sensitive than either DMTA or DSC, but it measures the net effect of all phases and might be confounded in this context by such factors as shear-plane lubrication.

It appears that the more the β-transition temperature is increased in modified PK's, either by dissolution of high T_g materials or by crosslinking, the more will be its sensitivity to lowering by water saturation. From a practical viewpoint, this probably is not a particularly encouraging result.

The next group of 23 blends shown in Table 7 had β-transitions close to that of unmodified PK. Many show evidence of the added polymer phase, notably PPO (9-Z), PEOx (9-J), PSulfone (9-T), PBT (9-W), PEG (9-I), epoxy (9-H), PET (9-V), PAcetal (9-Y), SAN (9-R) and ANS (9-Q). Control DMTA's were not run on the pure materials for comparison to the blends.

The PC blend gave peculiar results, as shown in Figure 9U. The β-peak is found at 32 and 15°C, normal for dry and wet PK. However, no peak is present in the region of the PC T_g, 150°C. Instead a large, water insensitive transition can be seen at 85°C. One explanation would be that enough of the PK has dissolved into the minor PC phase to depress its T_g. Its lack of sensitivity to water would would arise from a predominance of PC in the mixed phase.

The ANS blend, Figure 9Q, had a large loss peak, like those of the crosslinked specimens. However, unlike those, the transition temperature was near that of the control, not elevated to over 40°C.

The two remaining, low β-transition temperature blends in the bottom group of Table 7, contain the solvents **phenyl sulfone** and **C_4 sulfone**, already discussed in an earlier section, Figures 9G and F. These blends have transitions depressed by about 15 and 30°. The phenyl sulfone exhibits a peak in the region of its

melting temperature, indicating some separation of crystalline phase phenyl sulfone in the compression molded DMTA specimen.

The sulfone solvents also appear to have lowered the γ-transition temperatures by 15–20°. Therefore, phenyl sulfone or a similar non-crystalline compound might be useful as an impact improving additive for PK's under conditions of temperature and strain rate close to their ductile-brittle transition.

Barrier Characteristics

The permeability of all polymers follow certain patterns. Surprisingly, the ratio of permeability coefficient for any two non-interacting, permanent gases is approximately the same through all polymers. This is always true, providing only that diffusion is Fickian (dissolution, diffusion and evaporation); that is, providing there are no short-cutting mechanisms such as microvoids or holes. Fickian diffusion is the transport mechanism that will give the lowest possible permeability through a semipermeable material.

The foregoing allows comparison of PK against all other polymers, as shown in Figure 15, where CO_2 permeability is plotted against O_2 permeability. These data are collected from widely diverse, open literature sources and are subject to a number of variables. However, the overall pattern spans seven orders of magnitude, and is unmistakable. The PK point is a very rough composite of data obtained by L. E. Gerlowski, WRC, on various compression molded films, and was not carefully reviewed (it appears to be somewhat high in CO_2 permeability).

As a generality, the oxygen barrier quality of polyketones is good, but not exceptional, falling near PET, nylon and cured epoxies.

On a much smaller scale, polymers in general do show some differences in selectivity to permanent gases. These are due to specific interactions between the penetrant gas and the amorphous phase of the polymer (through which permeation takes place). Polymer crystallites are essentially impermeable, occupying space and making the diffusion paths tortuous. The details of CO_2/O_2 selectivity are roughly illustrated in Figure 16. Here, less than one order of selectivity separates the common polymers, shown as a function of overall barrier effectiveness as represented in this case by the oxygen permeability. In this chart it can be seen clearly that permanent gas selectivity is not a function of overall barrier quality.

PK appears to have a higher carbon dioxide/oxygen selectivity (if it is about 8) than most of the other common polymers, and may be unique in its region of barrier quality. However, it is far too good a barrier to be useful in its present form as a CO_2 separation membrane, where high flux is essential, unless its strength and high temperature character could be exploited somehow in an extremely thin film device. Compared to PK, for example, silicone rubber has slightly poorer selectivity but 10,000 times higher permeability.

D. R. Paul[18] measured the CO_2/CH_4 equilibrium Henry's Law solubility ratio for a PK film (<1.0 LVN60), finding it to be 8.2 (0.475/0.058). This is higher than found in hydrocarbons (around 3) but lower than for some ester containing polymers (up to >11).

If flaws or pinholes are present in a barrier film, transport through them will occur by a Graham Effusion mechanism, which has a selectivity determined only by the geometry of the pores, not by the composition of the polymer. As more flaws are present, this component of transport will progressively add to the Fickian component (which still continues to operate) until it dominates. For CO_2 and O_2, the permeation selectivity will thus approach 0.8 (inverse ratio of gas molecular weights squared).

Once the Fickian ratio is known for a particular polymer, it should remain approximately constant unless there is some change in amorphous phase state or composition. For PK the CO_2/O_2 ratio probably should be about 5 to 6 (based on blends data series to be discussed later). This fact can serve as a practical check on the validity of results obtained on any particular specimen. If the ratio comes out significantly lower, say less than about 3, one has to consider the possibility that Graham flaws may be present and that the barrier quality of the material of that specimen actually may be better than indicated by the measurement. When this is understood, the Fickian component—the actual permeability of the material—often can

be estimated for a specimen, even in the presence of pinholes.

Water vapor selectivity is also of particular interest. In the case of water, the interaction with polymers is profoundly more powerful than that of simple gases and the range of differences is much greater. This is shown in Figure 17, where selectivity covers six orders. Unlike CO_2, the selectivity of water can be seen to follow a definite pattern—the better the gas barrier character of a dry film, the higher its water selectivity. This is because polar, hydrogen bonding, high cohesive energy density amorphous phases are the least permeable (but only when dry) and at the same time the most susceptible to interaction with water.

For wet films, the selectivity favoring water (and other polar penetrants) becomes even more pronounced. In the limit, the best barrier polymers like polyvinyl alcohol become highly plasticized in high humidity, and are even water soluble. When wet, such films present hardly any obstacle at all to any type penetrant, even though when dry they are the best barriers of all against permanent gases. At the other extreme, polyolefins have the lowest selectivity to water and are all about the same in barrier quality, wet or dry. PK falls in the moderately high region of water selectivity, with PVDC, PVF and polyether sulfone. It will be a poorer barrier against oxygen in a humid atmosphere.

A few of the blends from this screening study were selected for test as oxygen barriers. Permeability testing is time consuming and was not a routine analytical procedure at WRC. The measurements were made by L. E. Gerlowski, and are shown below:

Permeability Results

Added Polymer	PO_2[a]	PCO_2[a]	PCO_2/PO_2	WVTR[b]
Control	4.4	22.0	5.0	13.5
PEt/VAlc	0.7	–	–	–
PVDF	5.3	32.2	6.1	14.1
PBT	5.1	27.2	5.3	21.2

[a]cc-mil/100in^2-day-atm at 30°C.
[b]g-mil/100 in.^{2}-0.9 RH diff. at 100°C.

Several other films, the PBPA, PVPhenol and carbon black blends, were too poor quality to measure.

The **polyethylene-vinyl alcohol** blend gave preliminary indications of having a six-fold lower oxygen permeability than the control, a very exciting result. The only morphological model that could account for this level of improvement for incompatible mixtures would be perfect layers of the two pure components in series; that is, the weighted harmonic average of the component permeabilities. The closest practical approach to such a structure would be du Pont's "Selmar" type morphology, and it would not be likely to form in these experiments, nor indeed is it apparent in the electron micrographs of the PEt/VAlc blend.

On the other hand, if the permeability improvement resulting from blending PEt/VAlc is real, and is not morphological in nature, both of which appeared to be the case, then the probable explanation is that most of the PEt/VAlc dissolved into the PK during mixing. Upon crystallization of the PK, the dissolved portion of the PEt/VAlc would concentrate in the amorphous phase, through which penetrants must pass. There, the cohesive energy density would be increased by hydrogen bonding between the PK carbonyl and PEt/VAlc hydroxyl groups.

In this scenario, the remaining incompatible portion of PEt/VAlc, visible by STEM as 70% greater in projected area than the amount added, would be highly swollen with PK, accounting for its substantial volume fraction. This suggests that a grade of PK might be a useful, compatible additive for PEt/VAlc, or for higher alcohol content variants which otherwise would not be processable.

In view of the interest in exploiting PK as a barrier material, further work with PK and compositional and molecular weight variants of polyethylene-vinyl alcohol seem justified. Greater mixing time-intensity at a lower temperature might have further dispersed or completely dissolved the PEt/VAlc. Perhaps a solution blended mix of polyvinyl alcohol and low melting PK could be processed without undue degradation of either phase. PVAlc

analogues would also be of interest as blending components.

Another avenue for possible smaller barrier improvements would be with blends showing an increased degree of crystallinity, for whatever reason. These would include blends having a high relative H_1 or H_2. Included by this reasoning might be: C_4 sulfone, TPU, PEt/VAlc, ANS, PBT and Zn ionomer.

SUMMARY

About 100 blending runs were made in which process conditions and many additives were screened for various possible effects. Variables included air, water, temperature, residence time/shear rate, particulates, chemicals, solvent/ oligomers and polymers. A summary of many of the results is shown schematically in Figure 8. The following is a brief description of the more interesting findings.

Physical Effects. More than half of the additives, including all types examined, increased the feed rate at constant torque over that of a corresponding control. None decreased it, even when severe crosslinking was occurring.

One polymer, low molecular weight polyvinyl phenol, was compatible with polyketone, markedly increasing its β-transition temperature. Polycarbonate showed some signs of compatibility.

Extremely fine dispersion cell size, 0.2-0.3 μ, was found with nylon/66, poly bisphenol A hydroxy ether and poly ethylene/vinyl alcohol. Nylon/6 and polyacetal also appeared to be on the verge of forming very fine dispersions. Many of the remaining polymers formed dispersions of about 1 μ. The least polar added polymer formed a very large dispersion.

Several sulfone additives were found that are plasticizers for polyketone, reducing melting temperature and both the β- and the γ-transition temperatures. Saturation with water lowers the β-transition of all blends.

One polymeric additive, poly ethylene/vinyl alcohol, appears to have reduced the permeability of polyketone to oxygen.

Chemical Effects. No unexpected reactions of PK with added materials were encountered.

Molded polyketone, relaxed or stressed, does not appear to have a noticeable susceptibility to ozone.

Melt stability and oven life were either harmed or helped by many of the additives. Anaerobic melt stability at 285°C was improved by exposure to air during processing, and by the addition of TiO_2, graphite and nylon/66. Oven life was improved by exposure to air, stearamide, nylon/66 and perhaps by thermoplastic polyurethane.

Melt stability and oven life were both harmed by the crosslinking agents.

Charring of polyketone terpolymer at current process temperatures apparently is not intrinsic to the polymer. Possible catalytic degradation of the melt from contact with the steel extruder barrel was seen.

Sodium containing polymers and chemicals can be used for controlled crosslinking and charring of polyketone, suggesting a carbon fiber process.

$CaCO_3$ was found to be a potentially useful flame retardant.

Hindered phenol may harm melt stability in the presence of water.

Oven-aged color was improved by polyethyl oxazoline.

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Table 1. Reference for the Data Table

Table 1 is subdivided into 15 pages with consistent format maintained throughout. The experiment group designation is as follows:

Table 1-A Control Runs and Process Variables
1-B Particulate Additives
1-C Chemical Additives
1-D Solvent and Oligomer Additives
1-E Polymer Additives

followed by a number for the field of results:

1 Detailed run description and Feed Rate
2 DSC, Rheology, Oven Life, Color
3 Burn, Solubility, Cell Size, DMTA

Thus, for example, to find raw data about the effect of particulate additives on oven life, look at Table 1-B2.

Sample Code. PKB code name for each extruder run. sequence for a series.

Control Code {1}. Control experiment identification.

Nickname. Shorthand to assist in the quick identification runs.

Blending Variable Code {2}. Codes the most important features of runs.

PK grade / principal variable / run conditions
(D, U - dry or undried feed)
(temperature)
(A, N - air or nitrogen blanket)
(rpm)
(residence time in seconds)

Additive {3}. Specific identification of materials that were blended.

Reed Rate {4}. Feeder setting at 85% of allowable torque on the extruder and rate relative to appropriate control.

DSC {5}. Dry, sealed under nitrogen, 20°C/minute, cycled to 285°, back to 23°, up to 285°, held for 10 minutes, back to 23°C.

Except for blends of terpolymer with copolymer, the heats of fusion have the contribution from added component backed out, assuming it to be unchanged from its neat form.

Th_1 - melting temperature peak in C, first heat.
Tc_1 - crystallization temperature peak, first cool.
Th_2 - melting temperature, second heat.
Tc_2 - crystallization temperature, second cool.
H_1 - heat of fusion in cal/g, first heat.
C_1 - heat of crystallization, first cool.
H_2 - heat of fusion, second heat.
C_2 - heat of cryst., second cool.
Relative C_2 - ratio of C_2 sample to C_2 control.

(continued)

Table 1 (Cont'd). Reference for the Data Table

Rheometrics {6}. Rate of parallel plate viscosity rise.

Oven Ageing {7}. Time to embrittlement minus one day.

Yellowness {8}. Color by tristimulus analysis.

Oxygen Burn {9}. Time and rate of burn in constant atmosphere.

Solubility {10}. Behavior of blend and neat added component in HFIPA.

Electron Microscopic Cell Size {11}. From STEM on microtomed strand.

DMTA β-transition {12}. Dynamic mechanical analyses dry and soaked in water to equilibrium.

Table I-A1. Control Runs and Process Variables

SAMP CODE No	CONTR CODE {1}	NICK-NAME	BLENDING VARIABLE CODE {2} (PK /variable / conditions)	ADDITIVE {3}	FEED {4} Set	FEED {4} Rel
2A		250°C A	002A/250°C A /D-250-A-300-30	(dry btch A 116/002 terpoly, 250°C,air,300rpm,30s)	60	
2C	[3]	ctrl	002A/Control /D-240-N-300-30	(dry, 240°C, nitrogen blanket, 300rpm, 30sec)	60	
2B	[3]	strand air	002A/Strnd Air/D-240-N-300-30	(strand taken in air instead of water)	60	
2D		air	002A/Air /D-240-A-300-30	(air blanket)	55	
2G		260°C N	002A/260°C N /D-260-N-300-30	(260°C, nitrogen)	50	
2H		260C° A	002A/260°C A /D-260-A-300-30	(260°C, air)	60	
3A	[1]	ctrl	002A/Control /U-240-N-300-30	(STD CONDITIONS-undried, 240°C, nitr, 300rpm, 30s)	60	
3B		N	002A/Slow /U-240-N-100-45	(100rpm)	40	
3D	[4]	ctrl	002A/Control /U-280-N-300-30	(std cond for high temp additives, 280°C, nitrogen	65	
3C		280°C A	002A/280°C A /U-280-A-300-30	(280°C air)	65	
3E		copoly N	001 /Copoly N /U-280-N-170-30	(PK copoly 056/001 at 280°C in nitrogen)	35	
3F		copoly A	001 /Copoly A /U-280-A-170-30	(PK copoly in air)	37	
6D		no Ox poly	003 /Anaerobic/U-240-N-300-30	(anaerobic grade of terpolymer 056/003)	53	
10E	[2]	ctrl	002B/Control /U-240-N-300-30	(batch B of 056/002 terpolymer)	40	
15A	[5]	1%AO ctrl	87-2/1%AO ctrl/U-240-N-300-30	(high feed rate control)	75	
16B		air inject	87-2/AirInject/U-240-A-300-30	(air injected into barrel)	95	
16C		A inj slo	87-2/AirInjSlo/U-240-A-095-45	(air inject, 95rpm)	100	
16F		bone dry	87-2/Bone Dry /D-240-N-300-30	(rigorously dried, maintained feed)	55	
16D		3% water	87-2/3%H_2O /U-240-N-300-30	(3% water added to feed)	110	
16E		10 m hold	87-2/10m Hold /U-280-N-300-600	(280°C, held quiescent in barrel 10 min)	-	

(continued)

Table I-A2. Control Runs and Process Variables

SAMP CODE No	CONTR CODE (1)	NICK-NAME	DSC (5) Temp (°C) Tm_1	Tc_1	Tm_2	Tc_2	Heat (cal/g) H_1	C_1	H_2	C_2	REL C_2	RHEOMETRICS dn/dt (6) 240°C	275°C	100°C OVEN AGEING (7) (da)	Rel	YELLOWNESS Aged (8) -	100°C
2A		250°C A	226	168	218	144	20.2	17.7	17.6	12.3				11		17	62
2C	[3]	ctrl	228	172	217	149	19.0	16.0	17.3	12.1		125		9		13	60
2B		strand air	231	179	223	169	21.2	20.9	23.7	18.0				9		10	56
2D		air	230	175	223	158	20.8	18.4	18.9	14.3		166		9		11	58
2G		260°C N	231	172	217	139	19.5	15.6	16.8	9.4				5		16	54
2H		260°C A	229	176	221	159	22.5	17.7	19.0	13.3				9		13	59
3A	[1]	ctrl	230	176	221	155	21.5	17.5	20.4	13.0		104	259	9		13	58
3B		N	228	179	220	167	22.6	20.2	23.0	17.0				10		13	54
3D	[4]	ctrl	228	158	206	130	18.7	12.5	12.7	10.3				4		17	59
3C		280°C A	230	172	220	157	22.9	17.1	18.7	13.3				5		17	64
3E		copoly N	257	208	249	190	26.6	23.5	22.7	17.2				6		26	87
3F		copoly A	260	208	247	183	24.4	19.1	21.5	14.2				10		35	98
6D		no Ox poly	226	175	214	155	18.0	16.9	17.4	11.7			610	6		22	72
10E	[2]	ctrl	230	184	224	171	22.3	17.2	18.5	13.4				9		18	60
15A	[5]	1%AO ctrl	223	170	213	152	19.7	17.4	18.5	12.1				16			
16B		air inject	222	171	215	159	20.0	18.1	19.0	14.0				47			
16C		A inj slo	223	171	215	156	18.9	17.5	18.1	13.5				47			
16F		bone dry	224	173	218	165	22.6	18.7	21.4	15.9				46			
16D		3% water	223	171	217	160	19.5	18.1	21.2	14.8				35			
16E		10 m hold	221	147	189		16.9	4.6	5.5	0.0				13			

(continued)

Table I-A3. Control Runs and Process Variables

SAMP CODE No	CONTR CODE {1}	NICK-NAME	19.5% OXYGEN BURN {12} Time (sec)	Rate (in/m)	Comments	SOLUBILITY in HFIPA {11} Blend	Add	EM CELL SIZE u{9}	DMTA Transitions (°C) {10} Dry (Wet) PK b-peak	PK g-peak	Added Poly
2A		250°C A	53	2.5	WEAK SAMPL						
2C	[3]	ctrl									
2B		strand air									
2D		air	cons	2.7	TYPICAL						
2G		260°C N	21	1.3	TYPICAL						
2H		260°C A	7	18.7	FLAMNG DRP						
3A	[1]	ctrl	cons	6.5	WEAK SAMPL						
3B		N	61	1.6	TYPICAL						
3D	[4]	ctrl	7	8.6	TYPICAL						
3C		280°C A	cons	5.4	TYPICAL						
3E		copoly N	17	1.7	TYPICAL						
3F		copoly A	75	1.9	TYPICAL						
6D		no Ox poly	15	5.2	SPARKED						
10E	[2]	ctrl	82	1.9	TYPICAL				31(16)	-60(-60)	
15A	[5]	1%AO ctrl									
16B		air inject									
16C		A inj slo									
16F		bone dry									
16D		3% water									
16E		10 m hold									

Table I-B1. Particulate Additives

SAMP CODE No	CONTR CODE {1}	NICK-NAME	BLENDING VARIABLE CODE {2} (PK /variable / conditions)	ADDITIVE {3}	FEED {4} Set	FEED {4} Rel
3A	[1]	ctrl	002A/Control /U-240-N-300-30	(STD CONDITIONS-undried, 240°C, nitr, 300rpm, 30s)	60	
10E	[2]	ctrl	002B/Control /U-240-N-300-30	(batch B of 056/002 terpolymer)	40	
5A	1	CaCO3	002A/5 CaCO3 /U-240-N-300-30	CaCO3 Pfeizer MM	60	1.0
5B	1	bas alumna	002A/5 B Almna/U-240-N-300-30	basic alumina Aldrich 19944-3	55	.9
9G	2	acd alumna	002B/5 A Almna/U-240-N-300-30	acidic alumina Aldrich 19996-6	35	.9
5C	1	ZnO2	002A/5 ZnO2 /U-240-N-300-30	ZnO2	55	.9
5D	1	talc	002A/5 Talc /U-240-N-300-30	talc Cypress Minerals Beaverwhite	55	.9
7A	1	TiO2	002A/5 TiO2 /U-240-N-300-30	TiO2 duPont Tipure R-101	70	1.2
7E	1	C black	002A/2 C Black/U-240-N-300-30	carbon black, neutral Witco Cotinex N-330	75	1.3
11A	2	clay	002B/5 Clay /U-240-N-300-30	bentonite clay Bentone 38	50	1.3
11G	2	graphite	002B/2 Grphite/U-240-N-300-30	graphite Alpha 00641	45	1.1

(Continued)

Table I-B2. Particulate Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	DSC (5) Temp (°C) Tm_1	Tc_1	Tm_2	Tc_2	Heat (cal/g) H_1	C_1	H_2	C_2	REL C_2	RHEOMETRICS dn/dt (6) 240°C	275°C	100°C OVEN AGEING (7) (da)	Rel	YELLOWNESS Aged (8) -	100°C
3A	[1]	ctrl	230	176	221	155	21.5	17.5	20.4	13.0		104	259	9		13	58
10E	[2]	ctrl	230	184	224	171	22.3	17.2	18.5	13.4				9		18	60
5A	1	CaCO3	228	168	206		19.7	14.3	16.8	0.0	0	66		7	.8	37	69
5B	1	bas alumna	232	171	218	149	18.6	17.9	18.2	12.6	1.0	126		3	.3	48	65
9G	2	acd alumna	238	183	223	157	20.5	15.9	15.8	11.2	.8			1	.1	58	71
5C	1	ZnO2	224	174	216	134	21.5	17.8	19.8	4.6	.4			9	1.0	16	48
5D	1	talc	216	175	211	151	21.7	18.6	21.1	13.4	1.0			4	.4	20	48
7A	1	TiO2	232	172	220	161	21.4	17.9	18.3	15.2	1.2			6	.7	9	17
7E	1	C black	235	177	220	158	20.4	13.0	13.0	0.3	0		260	10	1.1	9	4
11A	2	clay												1	.1	47	77
11G	2	graphite	238	188	228	177	20.3	18.0	18.0	16.5	1.2			2	.2	9	9

(continued)

Table I-B3. Particulate Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	19.5% OXYGEN BURN (12) Time (sec)	Rate (in/m)	Comments	SOLUBILITY in HFIPA (11) Blend	Add	EM CELL SIZE u(9)	DMTA Transitions (°C) (10) Dry PK b-peak	(Wet) PK g-peak	Added Poly
3A	[1]	ctrl	cons	6.5	WEAK SAMPL						
10E	[2]	ctrl	82	1.9	TYPICAL				31(16)	-60(-60)	
5A	1	CaCO3	0	-	NO BURN						
5B	1	bas alumna	17	8.4	FLAMNG DRP						
9G	2	acd alumna	79	1.5	CHAR						
5C	1	ZnO2	94	1.6	CHAR-SMOKE						
5D	1	talc	10	15.6	TYPICAL						
7A	1	TiO2	128	1.3	SM FLAME						
7E	1	C black	cons	2.5	TYPICAL						
11A	2	clay	19	6.6	CHAR						
11G	2	graphite	65	1.8	TYPICAL						

Table I-C1. Chemical Additives

SAMP CODE No	CONTR CODE {1}	NICK-NAME	BLENDING VARIABLE CODE {2} (PK /variable / conditions)	ADDITIVE {3}	FEED {4} Set	FEED {4} Rel
3A	[1]	ctrl	002A/Control /U-240-N-300-30	(STD CONDITIONS-undried, 240°C, nitr, 300rpm, 30s)	60	
10E	[2]	ctrl	002B/Control /U-240-N-300-30	(batch B of 056/002 terpolymer)	40	
2C	[3]	ctrl	002A/Control /D-240-N-300-30	(dry, 240°C, nitrogen blanket, 300rpm, 30sec)	60	
2E	3	1% I-1076	002A/1 I 1076 /D-240-N-300-30	hindered phenol-ester Ciba Geigy Irganox 1076	60	1.0
2F	3	4% I-1076	002A/4 I 1076 /D-240-N-300-30	hind phen-ester Ciba Geigy Irganox 1076	60	1.0
4A	1	2% I-1076	002A/2 I 1076 /U-240-N-300-30	hind phen-ester Ciba Geigy Irganox 1076	65	1.1
6E	-	1%1076-PKE	-003 /1 I 1076 /U-240-N-300-30	-hind phen-ester Ciba Geigy Irganox 1076	- 75	-
6F		2%1076-PKE	003 /2 I 1076 /U-240-N-300-30	hind phen-ester Ciba Geigy Irganox 1076	85	
4B	1	2% I-1010	002A/2 I 1010 /U-240-N-300-30	hind phen-ester Ciba Geigy Irganox 1010	65	1.1
4D	1	2% I-1425	002A/2 I 1425 /U-240-N-300-30	hind ph-Ca phosphonate Ciba Geigy Irganox 1425	65	1.1
4E	- 1 -	2% I-565	-002A/2 I 565 /U-240-N-300-30	-hind ph-thioether-triazole C G Irganox 565	- 65	1.1 -
6A	1	2% I-1024	002A/2 I 1024 /U-240-N-300-30	hind phen-hydrazid Ciba Geigy Irganox 1024	65	1.1
10C	2	2% E-330	002A/2 Et 330 /U-240-N-300-30	hind phenol Ethyl AO 330	80	2.0
4C	1	2% Inl-330	002A/2 IONOL /U-240-N-300-30	hind phenol Uniroyal Ionol 330	65	1.1
6B	- 1 -	2% T-770	-002A/2 Tin 770/U-240-N-300-30	-aliphatic-hind sec amine C Geigy Tinuvin 770	- 85	1.4 -
6C	1	2% T-327	002A/2 Tin 327/U-240-N-300-30	hind phen-triazole Ciba Geigy Tinuvin 327	95	1.6
10B	2	2% T-144	002A/2 Tin 144/U-240-N-300-30	hind phen-hind amine-ester C Geigy Tinuvin 144	70	1.8
4F	1	stearamid	002A/2 Stramid/U-240-N-300-30	stearic amide Ashland Chem Adogen 58	65	1.1
10G	- 2 -	EDTAA	-002B/2 SEQ Na /U-240-N-300-30	-Etdiam acetic acid Na salt C Geigy Sequestrene AA	- 45	1.1 -
11B	2	NBC	002B/2 NBC /U-240-N-300-30	Ni bu thiocarbamate duPont Trylex 866752	60	1.5
13B	2	ZnStearate	002B/2 ZnSt /U-240-N-300-30	Zn stearate ICN Biomedicals 20030x	60	1.5
14I	2	NaStearate	002B/0.4 NaSt /U-230-N-300-30	Na stearate ICN Biomedicals 22828x	40	1.0
14J	- 2 -	NaStearate	-002B/0.4 NaSt /U-230-A-300-30	-Na stearate ICN Biomedicals 22828x	- 40	1.0 -

(continued)

Table I-C2. Chemical Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	DSC (5) Temp (C) Tm_1	Tc_1	Tm_2	Tc_2	Heat (cal/g) H_1	C_1	H_2	C_2	REL C_2	RHEOMETRICS dn/dt (6) 240°C	275°C	100°C OVEN AGEING (7) (da)	Rel	YELLOWNESS Aged (8) -	100°C
3A	[1]	ctrl	230	176	221	155	21.5	17.5	20.4	13.0		104	259	9		13	58
10E	[2]	ctrl	230	184	224	171	22.3	17.2	18.5	13.4				9		18	60
2C	[3]	ctrl	228	172	217	149	19.0	16.0	17.3	12.1		125		9		13	60
2E	3	1% I-1076	227	175	216	156	18.9	17.2	18.2	11.1	.9		357	17	1.9	16	73
2F	3	4% I-1076	227	172	217	161	20.3	19.5	22.2	16.5	1.4			11	1.2	13	62
4A	1	2% I-1076	230	161	211	137	20.3	16.6	17.0	11.3	.9						
6E	-	1%1076-PKE	227	175	217	163	18.7	18.0	18.8	14.3			400	17	1.9	18	90
6F		2%1076-PKE	226	170	217	157	20.7	19.8	21.8	16.3				20	2.2	17	95
4B	1	2% I-1010	230	170	218	154	19.4	17.4	17.6	13.2	1.0			38	4.2	15	
4D	1	2% I-1425	228	165	214	137	21.7	17.2	19.0	11.6	.9			11	1.2	13	76
4E	1	2% I-565	228	166	214	140	18.8	16.9	16.9	11.7	.9	116		20	2.2	11	143
6A	1	2% I-1024	231	180	217	169	21.6	16.3	20.3	12.9	1.0		400	35	3.9	21	96
10C	2	2% E-330	233	170	218	156	21.6	17.6	18.2	14.7	1.1			42	4.7	14	76
4C	1	2% Inl-330	229	169	216	152	18.8	17.2	16.5	12.5	1.0			44	4.9	10	
6B	1	2% T-770	233	168	215	152	20.7	18.3	19.3	14.7	1.1		330	3	.3	86	69
6C	1	2% T-327	225	163	211		21.5	17.4	20.5	0.0	0		19,000	11	1.2	19	58
10B	2	2% T-144	230	168	219	149	21.1	19.1	19.4	13.1	1.0			10	1.1	13	136
4F	1	stearamid	230	170	213	150	19.8	16.3	16.5	12.0	.9			17	1.9	11	114
10G	2	EDTAA	238	168	210		21.8	12.3	13.8	0.0	0			4	.4	71	106
11B	2	NBC	237	181	225	152	20.5	16.1	17.5	10.0	.8			80	8.9	85	
13B	2	ZnStearate	238				22.2	0.0			0			4	.4	25	
14I	2	NaStearate	185				9.7	0.0						5	.6		122
14J	2	NaStearate												3	.3		126

(continued)

Table I-C3. Chemical Additives

SAMP CODE No	CONTR CODE {1}	NICK-NAME	19.5% OXYGEN BURN {12} Time (sec)	Rate (in/m)	Comments	SOLUBILITY in HFIPA {11} Blend	Add	EM CELL SIZE u{9}	DMTA Transitions (°C) {10} Dry (Wet) PK b-peak	PK g-peak	Added Poly
3A	[1]	ctrl	cons	6.5	WEAK SAMPL						
10E	[2]	ctrl	82	1.9	TYPICAL				31(16)	-60(-60)	
2C	[3]	ctrl									
2E	3	1% I-1076	cons	8.3	SLOW LIGHT						
2F	3	4% I-1076	cons	5.1	TYPICAL						
4A	1	2% I-1076	cons	4.9	TYPICAL						
6E	-	1%1076-PKE	55	1.8	TYPICAL	-	-	-			-
6F		2%1076-PKE	cons	2.3	TYPICAL						
4B	1	2% I-1010	cons	3.4	TYPICAL						
4D	1	2% I-1425	cons	5.9	TYPICAL						
4E	1	2% I-565	cons	3.7	TYPICAL	-	-	-			-
6A	1	2% I-1024	74	1.8	TYPICAL						
10C	2	2% E-330	cons	3.9	TYPICAL						
4C	1	2% Inl-330	cons	5.6	TYPICAL						
6B	1	2% T-770	cons	4.7	TYPICAL	-	-	-			-
6C	1	2% T-327	47	3.3	FLAMNG DRP						
10B	2	2% T-144	cons	3.7	TYPICAL						
4F	1	stearamid	cons	5.4	TYPICAL						
10G	2	EDTAA	52	2.6	TYPICAL	-	-	-			-
11B	2	NBC	cons	1.5	SM FLAME						
13B	2	ZnStearate	38	0.6	Char						
14I	2	NaStearate	0	-	NO BURN	GEL			46(21,60)	-60(-65)	
14J	2	NaStearate	0	-	NO BURN	GEL	-	-			-

Table I-D1. Solvent and Oligomer Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	BLENDING VARIABLE CODE (2) (PK /variable / conditions)	ADDITIVE (3)			FEED (4) Set	FEED (4) Rel
3A	[1]	ctrl	002A/Control /U-240-N-300-30	(STD CONDITIONS-undried, 240C, nitr, 300rpm, 30s)			60	
10E	[2]	ctrl	002B/Control /U-240-N-300-30	(batch B of 056/002 terpolymer)			40	
7D	1	20°C(OH)4	002A/20 Peryth/U-240-N-300-30	pentaerythritol	Aldrich	P 474-5	80	1.3
12G	2	10°C(OH)4	002B/10 Peryth/U-240-N-300-30	pentaerythritol	Aldrich	P 474-5	80	2.0
9A	2	C4 sulfone	002B/20 Sulfln/U-240-N-300-30	tetramethylene sulfone	Shell Chem	Sulfolane W	85	2.1
7C	1	phensulfon	002A/20 PhSulf/U-240-N-300-30	diphenyl sulfone	Aldrich	P 3535-9	70	1.2
7B	2	epoxy	002B/10 Epon /U-240-N-300-30	epoxy resin	Shell	EPON 1009	70	1.8
10A	2	PEG	002B/10 PEG /U-240-N-300-30	polyethylene glycol ester	Aldrich	PEG 5000	90	2.3
11F	2	asphalt 1	002B/5 Asp W36/U-240-N-300-30	sour asphalt	Shell	W-36	75	1.9
11D	2	ashpalt 2	002B/5 Asp1712/U-240-N-300-30	blown asphalt	Shell	1712	40	1.0
11E	2	asphalt 3	002B/5 AspW370/U-240-N-300-30	flux asphalt	Shell	W-370	90	2.3

(continued)

Table I-D2. Solvent and Oligomer Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	DSC (5) Temp (C) Tm_1	Tc_1	Tm_2	Tc_2	Heat (cal/g) H_1	C_1	H_2	C_2	REL C_2	RHEOMETRICS dn/dt (6) 240°C	275C°	100°C OVEN AGEING (7) (da)	Rel	YELLOWNESS Aged (8) -	100°C
3A	[1]	ctrl	230	176	221	155	21.5	17.5	20.4	13.0		104	259	9		13	58
10E	[2]	ctrl	230	184	224	171	22.3	17.2	18.5	13.4				9		18	60
7D	1	20°C(OH)4	199			124	24.2	21.5		4.0			7,000	0	0	16	20
12G	2	10°C(OH)4	217	112	169	0	23.2	12.0	12.2	0.0				1	.1	11	16
9A	2	C4 sulfone	229	168	217	154	29.9	19.7	21.4	16.0				4	.4	12	41
7C	1	phensulfon-	217	160	201	147	17.8	15.1	17.7	13.3				1	.1	9	27
7B	2	epoxy	238	179	225	151	22.8	17.1	18.6	12.1				2	.2	17	34
10A	2	PEG	239	169	220	127	21.2	18.0	21.1	9.8				2	.2	26	50
11F	2	asphalt 1	240	179	228	160	21.9	18.4	19.5	14.4				4	.4	124	98
11D	2	ashpalt 2	239	187	229	177	22.6	18.6	18.7	14.0				6	.7	151	129
11E	2	asphalt 3	239	167	218	139	21.1	15.7	17.2	10.8				8	.9	120	130

(continued)

Table I-D3. Solvent and Oligomer Additives

SAMP CODE No	CONTR CODE {1}	NICK-NAME	19.5% OXYGEN BURN {12} Time (sec)	Rate (in/m)	Comments	SOLUBILITY in HFIPA {11} Blend	Add	EM CELL SIZE u{9}	DMTA Transitions (°C) {10} Dry (Wet) PK b-peak	PK g-peak	Added Poly
3A	[1]	ctrl	cons	6.5	WEAK SAMPL						
10E	[2]	ctrl	82	1.9	TYPICAL				31(16)	-60(-60)	
7D	1	20°C(OH)4	88	1.6	TYPICAL				34	-51?	
12G	2	10°C(OH)4	117	1.3	TYPICAL				33	-60	
9A	2	C4 sulfone	18	4.9	FLAMNG DRP	S CLDY	SOL		2	-80	
7C	1	phensulfon-	44	2.8	SMOKEY	S CLDY	SOL		16(0)	-75(-78)	119(115)
7B	2	epoxy	25	2.0		S CLDY	SOL	1.0	31(15)	-60(-65)	99(100)
10A	2	PEG	cons	2.9	TYPICAL	CLEAR	SOL	6.0	33	-60	57?
11F	2	asphalt 1	cons	5.1	SPARKED						
11D	2	ashpalt 2	cons	4.1	SPARKED						
11E	2	asphalt 3	cons	2.8	TYPICAL						

Table I-E1. Polymer Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	BLENDING VARIABLE CODE (2) (PK /variable / conditions)	ADDITIVE (3)			FEED (4) Set	FEED (4) Rel
3A	[1]	ctrl	002A/Control /U-240-N-300-30	(STD CONDITIONS-undried, 240°C, nitr, 300rpm, 30s)			60	
10E	[2]	ctrl	002B/Control /U-240-N-300-30	(batch B of 056/002 terpolymer)			40	
2C	[3]	ctrl	002A/Control /D-240-N-300-30	(dry, 240C, nitrogen blanket, 300rpm, 30sec)			60	
3D	[4]	ctrl	002A/Control /U-280-N-300-30	(std cond for high temp additives, 280C, nitrogen			65	
12A	1	PEOxazline	002A/10 PEOxaz/U-240-N-300-30	polyethyl oxazoline	Dow	XAS-10874.01	80	1.3
2J	3	N6	002A/10 N6 /D-240-N-300-30	nylon 6	Allied	Capron 8552	60	1.0
12D	4	N66	002B/10 N66 /U-280-N-300-30	nylon 66	duPont	Zytel 101	60	.9
8A	2	TPU	002B/10 TPU /U-240-N-300-30	thermopl polyurethane	Dow	Pellethane 2103 80AE	75	1.9
8C	2	PVPhenol	002B/10 PVPhen/U-240-N-300-30	polyvinyl phenol	Polyscience	6527	70	1.8
8G	2	PVPyridine	002B/10PVPyrdn/U-240-N-300-30	polyvinyl pyridine	MP-Dajac	8573	-	-
8F	2	Poly BPA	002B/10 Eponol/U-240-N-300-30	Poly bisphen A hydroxy ether	Shell	Eponol 53-L-32	75	1.9
9B	2	Et/VAlchol	002B/10 EtVAlc/U-240-N-300-30	copoly ethylene-vinylalcohol	Kurray	Eval F	65	1.6
8D	2	ANS	002B/10 ANS /U-240-N-300-30	copoly acrylonitrile-styrene	Sohio	Barex 210	75	1.9
7F	2	SAN	002B/10 SAN /U-240-N-300-30	copoly styrene-acrylonitrile	Dow	Tyril 1000-27	70	1.8
9F	2	SMA	002B/10 SMA /U-240-N-300-30	polystyrene maleic anhydride	Arco	Dylark 332	50	1.3
13A	2	PSulfone	002B/10PSulfon/U-280-N-300-30	polysulfone	Carbide	Udel P-1700	40	1.0
12C	4	PC	002B/10 PC /U-280-N-300-30	polycarbonate	Mobay	Merlon M-40	80	1.2
12B	4	PET	002B/10 PET /U-280-N-300-30	poly ethylene terephthalate	Celanese	Celenex 2113	90	1.4
7G	2	PBT	002B/10 PBT /U-240-N-300-30	poly butylene terephthalate	GE	Valox 310	75	1.9
9D	2	C5 PEster	002B/10C5PEstr/U-240-N-300-30	poly caprolactone	Carbide	PCL P-300	55	1.4
12H	2	P Acetal	002B/10PAcetal/U-240-N-300-30	poly acetal copolymer	Celanese	Celcon M-90	50	1.3
13C	4	PPO	002B/10 PPO /U-280-N-300-30	poly phenelene oxide	GE	0.46IV	60	.9
2I	3	PVDF	002A/10 PVDF /D-240-N-300-30	poly vinylidine fluoride	Pennwalt	Kynar 460	60	1.0
9C	2	FEP	002B/10 FEP /U-240-N-300-30	fluorinated poly et-pr	Polysciences	4615	45	1.1
9E	2	Na Ionomer	002B/10NaIonmr/U-240-N-300-30	Na PE ionomer	duPont	Surlyn 8528	50	1.3
8B	2	Zn Ionomer	002B/10ZnIonmr/U-240-N-300-30	Zn PE ionomer	duPont	Surlyn 9730	75	1.9
8E	2	PMP	002B/10 PMP /U-240-N-300-30	poly methylpentene	Mitsui	TPX MX-004	75	1.9

(continued)

Table I-E2. Polymer Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	DSC (5) Temp (°C) Tm_1	Tc_1	Tm_2	Tc_2	Heat (cal/g) H_1	C_1	H_2	C_2	REL C_2	RHEOMETRICS dn/dt (6) 240°C	275°C	100°C OVEN AGEING (7) (da)	Rel	YELLOWNESS Aged (8) -	100°C
3A	[1]	ctrl	230	176	221	155	21.5	17.5	20.4	13.0		104	259	9		13	58
10E	[2]	ctrl	230	184	224	171	22.3	17.2	18.5	13.4				9		18	60
2C	[3]	ctrl	228	172	217	149	19.0	16.0	17.3	12.1		125		9		13	60
3D	[4]	ctrl	228	158	206	130	18.7	12.5	12.7	10.3				4		17	59
12A	1	PEOxazline	229	177	217	94	21.2	19.9	20.7	5.1	.4			9	1.0	13	50
2J	3	N6	229	173	219	154	16.4	17.0	17.7	11.6	1.0		177	2	.2		48
12D	4	N66	239	186	228	170	18.9	18.7	20.1	16.1	1.6			8	2.0		108
8A	2	TPU	237	184	229	165	23.8	18.8	20.3	14.5	1.1		670	20	2.2	20	97
8C	2	PVPhenol	235	184	222	158	22.0	20.6	22.2	13.8	-		4,100	4	.4		86
8G	2	PVPyridine	174				7.0	0.0			0						
8F	2	Poly BPA	-- DSC pan blew open --										10,000	10	1.1	75	149
9B	2	Et/VAlchol	239	179	221	153	23.8	17.4	15.7	12.1	.9		220	5	.6		49
8D	2	ANS	242	180	223	154	24.8	15.8	18.3	7.4	.6					127	
7F	2	SAN	239	180	220	174	19.2	12.9	18.3	2.9	.2		230	0	0	19	98
9F	2	SMA	240	186	228	168	22.5	20.4	20.8	15.0	1.1			3	.3	22	56
13A	2	PSulfone	239	186	223	170	19.1	16.6	15.9	11.3	.8			1	.1	22	
12C	4	PC	237	179	222	166	20.9	14.8	15.4	11.6	1.2			1	.3	19	44
12B	4	PET	239	184	224	157	17.3	16.9	19.5	12.1	1.3			1	.3	25	39
7G	2	PBT	234	182	222	157	22.6	21.4	24.4	16.2	1.2		650	1	.1		40
9D	2	C5 PEster	239	178	228	157	20.0	16.3	16.0	13.4	1.0			4	.4	15	47
12H	2	P Acetal	239	178	221	157	18.6	15.6	15.0	9.8	.7			1	.1	20	39
13C	4	PPO	234	183	224	168	19.1	16.5	16.5	12.3	1.3			1	.3	44	
2I	3	PVDF	227	176	218	159	18.0	15.3	17.5	14.5	1.2		300	1	.1	19	31
9C	2	FEP	240	185	228	159	20.2	16.9	16.8	11.6	.9			3	.3		46
9E	2	Na Ionomer	215				13.0	0.0			0			10	1.1	78	143
8B	2	Zn Ionomer	239	188	232	179	23.7	20.0	22.5	16.5	1.2		280	2	.2	20	44
8E	2	PMP	237	179	224	160	22.9	16.8	16.0	12.9	1.0		210	3	.2	17	73

(continued)

Table I-E3. Polymer Additives

SAMP CODE No	CONTR CODE (1)	NICK-NAME	19.5% OXYGEN BURN (12) Time (sec)	Rate (in/m)	Comments	SOLUBILITY in HFIPA (11) Blend	Add	EM CELL SIZE u(9)	DMTA Transitions (°C) (10) Dry (Wet) PK b-peak	PK g-peak	Added Poly
3A	[1]	ctrl	cons	6.5	WEAK SAMPL						
10E	[2]	ctrl	82	1.9	TYPICAL				31(16)	-60(-60)	
2C	[3]	ctrl									
3D	[4]	ctrl	7	8.6	TYPICAL						
12A	1	PEOxazline	86	1.3	TYPICAL	S CLDY	SOL	1.3	34	-60	81
2J	3	N6	cons	2.8	TYPICAL	V CLDY	SWELD	.8(.2)	30	-60	
12D	4	N66	92	1.6	TYPICAL	CLEAR	SOL	.2	30	-60	
8A	2	TPU	cons	6.9	TYPICAL	CLEAR	SOL	1.3	31	?	
8C	2	PVPhenol	47	1.6	CHAR	TLUCNT	INSOL	0	68(35)	-58(-63)	
8G	2	PVPyridine					SOL	1.4			
8F	2	Poly BPA	cons	2.2	SPARKED	CLOUDY	SOL	.3	47(21)	-60(-64)	93(93)
9B	2	Et/VAlchol	67	2.0	TYPICAL	CLEAR	SOL	.3	29	-60	
8D	2	ANS				CLEAR	SOL	.8	28	?	100
7F	2	SAN	cons	4.4	TYPICAL	S CLDY	SOL	.8	28	-	
9F	2	SMA	cons	2.5	TYPICAL	V CLDY	SWELD	1.0	30	-	
13A	2	PSulfone	cons	3.1	TYPICAL	CLOUDY	GEL	(2.5)11	33	-60	
12C	4	PC	99	1.7	TYPICAL	CLOUDY	SOL	1.4	32(15)	-60(-60)	85(85)
12B	4	PET	48	1.7	TYPICAL	CLEAR	SOL	1.0	30	-	92
7G	2	PBT	8	8.7	WEAK SAMPL	CLEAR	SOL	.7	33(15)	-60(-67)	60(58)
9D	2	C5 PEster	cons	3.3	TYPICAL	CLEAR	SOL	3.5	30	-65	
12H	2	P Acetal	cons	2.2	TYPICAL	CLEAR	SOL	.7(.2)	28	?	
13C	4	PPO	20	1.8	CHAR	OPAQUE	INSOL	3.1	35	-62	
2I	3	PVDF	cons	6.3	FLAMNG DRP	V CLDY	INSOL	1.4	28	?	
9C	2	FEP	149	.9	CHAR	CLEAR	INSOL	(invis)	28	-	
9E	2	Na Ionomer	3		NO BURN	OPAQUE	INSOL	1.8	44(20)	-60(-67)	
8B	2	Zn Ionomer	cons	4.6	TYPICAL	OPAQUE	INSOL	2.0	30	-60	
8E	2	PMP	cons	5.2	TYPICAL	FIBERS	INSOL	11.0	30	-60	

Table 2. Process Variables

Effect of Oxygen

Samp Code	Key Variable		Rel C_2 Air/N	100°C Oven Life days	Rel Air/N	Yellowness 100°C init	aged
2C	Strand H_2O quench			9		13	60
2B	Strand air cooled		1.5	9	1.0	10	56
2C	N_2	D-240		9		13	60
2D	Air		1.2	9	1.0	11	58
2G	N_2	D-260		5		16	54
2H	Air		1.4	9	1.8	13	59
3D	N_2	U-280		4		17	59
3C	Air		1.3	5	1.3	17	64
3E	Copoly N_2	U-280		6		26	87
3F	Copoly Air		.8	10	1.7	35	98
15A*	N2 087/002	U-240		16			
16B*	AirInject		1.2	47	2.9		
16C*	AirInj Slo rpm		1.1	47	2.9		

N_2 - Nitrogen blanket.
Air - Air blanket.
D - Dried feed.
U - Undried feed.
Copoly - Polyketone copolymer instead of terpolymer.
AirInj - Air injected into extruder barrel.
Slo - 95 rpm instead of 300.

Table 3. Process Variables

Effect of Temperature

Samp Code	Key Variables		C_2 (cal/g)	C_2 Rel Hi/240	100°C Oven Life (days)	100°C Oven Life Rel Hi/240	Yellowness (initial)
2C	240°C	D	12.1		9		13
2G	260	D	9.4	.8	5	.6	16
3A	240	U	13.0		9		13
3D	280	U	10.3	.8	4	.4	17
2D	240	D-A	14.3		9		11
2A	250	D-A	12.3	.9	11	1.2	17
2H	260	D-A	13.3	.9	9	1.0	13

D - Dried feed.
U - Undried feed, ~1.5% H_2O.
A - Air blanket instead of nitrogen.

Table 4. Process Variables

Effect of Water

Samp Code	Key Variable		Feeder Set	Feeder Rel Wet/Dry	DSC C_2	DSC Rel C_2 Wet/Dry	Rheom dn/dt 240°C	100°C Oven Life 100°C	100°C Oven Life Rel Wet/Dry
2C	Dry	240-N_2	60		12.1		125	9	
3A	Undry	240-N_2	60	1.0	13.0	1.1	104	9	1.0
16F*	Bone Dry	240-N_2	55		15.9			46	
15A*	1.5% H_2O	240-N_2	75	1.4	12.1	.8		16	.4
16D*	3% H_2O	240-N_2	110	2.0	14.8	.9		35	.8

* These contained 1% AO, all others <0.2%.

Table 5. Process Variables

Effect of Residence Time/Shear Rate

Samp Code	Key Variable		Feed Set	C_2	Rel C_2 Slo/Fst	100°C Oven Life days	Rel Slo/Fst
3A	30sec	300rpm	60	13.0		9	
3B	45sec	100rpm	40	17.0	1.3	10	1.1
15A	30sec	300rpm	75	12.1		16	
16E	600sec	(300rpm)	-	(C_1)4.6	.4	13	.8 0

Table 6. Polymer Blends

DSC Control Comparison

Blend Nick-Name	Peak Temperature Difference ($T-T_{control}$, °C)				Relative Heat ($H/H_{control}$)			
	Th_1	Tc_1	Th_2	Tc_2	H_1	C_1	H_2	C_2
PEOxazoline	-1	1	-4	-61	1.0	1.1	1.0	.4
N6	1	1	2	5	.9	1.1	1.0	1.0
N66	11	28	22	40	1.0	1.5	1.6	1.6
TPU	7	0	5	-6	1.1	1.1	1.1	1.1
PVPhenol	5	0	-2	-13	1.0	1.2	1.2	1.0
PVPyridine	-56				.3	0		0
PBPA		(DSC pans blew.)						
Et/VAlchol	9	-5	-3	-18	1.1	1.0	.8	.9
ANS	12	-4	-1	-17	1.1	.9	1.0	.6
SAN	9	-4	-4	3	.9	.8	1.0	.2
SMA	10	2	4	-3	1.0	1.2	1.1	1.1
PSulfone	9	2	-1	-1	.9	1.0	.9	.8
PC	9	21	16	36	1.1	1.2	1.2	1.2
PET	11	26	18	27	.9	1.4	1.5	1.3
PBT	4	-2	-2	-14	1.0	1.2	1.3	1.2
C5 PEster	9	-6	4	-14	.9	.9	.9	1.0
P Acetal	9	-6	-3	-14	.8	.9	.8	.7
PPO	6	25	18	38	1.0	1.3	1.3	1.3
PVDF	-1	4	1	10	.9	1.0	1.0	1.2
FEP	10	1	4	-12	.9	1.0	.9	.9
Na Ionomer	-15				.6	0		0
Zn Ionomer	9	4	8	8	1.1	1.2	1.2	1.2
PMP	7	-5	0	-11	1.0	1.0	.9	1.0

Table 7. Phase Size and Second Order Transitions

%v	Additive	Cell Size (u)	Transitions, dry (wet) (°C) PK β-trans	Additive	PK γ-trans
	Control		31 (16)		-60 (-60)
10	PVPhenol	0		68 (35)	-58 (-63)
10	PBPA	.25	47 (21)	93 (93)	-60 (-64)
.4	Na Stearate		46 (21)(60)		-60 (-65)
10	Na Ionomer	1.8	44 (20)		-60 (-67)
10	PPO	3.1	35		-62
10	PEOx	1.3	34	81	-60
20	Pentaerythritol		34		-51?
10	PSulfone	2.5	33		-60
10	PBT	.7	33 (15)	~60 (58)	-60 (-67)
10	PEG	6.0	33	57?	-60
10	Pentaerythritol		~33		-60
10	PC	1.4	32 (15)	85 (85)	-60 (-60)
10	Epoxy	1.0	31 (15)	99 (100)	-60 (-65)
10	TPU	1.3	31		?
10	PET	1.0	30	92	-
10	PMP	11.0	30		-60
10	Zn Ionomer	2.0	30		-60
10	SMA	1.0	30		-
10	C5 Ester	3.5	30		-65
10	N 66	.2	30		-60
10	N 6	.8(.2)	30		-60
10	Et/VAlc	.3	29		
10	PAcetal	.7(.2)	28		?
10	PVDF	1.4	28		?
10	FEP	-	28		-
10	SAN	.8	28		-
10	ANS	.8	28	100	?
20	Diphenylsulfone	-	16 (0)	119 (115)	-75 (-78)
20	C4 sulfone	-	2		-80

Table 8. Summary of Results

Cond. or Additive	PHYSICAL				CHEMICAL					
		Cell	β-	O_2	Melt Stab.		Oven		Flame	Cross-
	Feed	Size	Trans	Perm	240°C	280°C	Life	Color	Ret.	link
PROCESS										
Air	0				+	+	+	(-)		
Temperature	0				0	(-)	-	(+)		
Water	+		-			(-)	(0)	-	0	
Time/shear	(-)				0	?	?	0		
PARTICULATE										
$CaCO_3$	0				(+?)	-	(-)		Y	
alumina	0				0	0	-		0	
ZnO_2	0				0	-	0		(?)	
talc	0				0	0	-		0	
TiO_2	(+)				+	+	-		0	
C black	+				+	-	0		0	
clay	+						-		(?)	
graphite	0				+	+	-		0	
CHEMICAL										
hind. phen.	0,+				0	0	+	(0)	0	
UV add.	+				0	0,-	-,+	-,+	0	
stearamide	0				0	0	+	(-)	0	
EDTAA(Na)	0				0	-	-	+	0	Y
NBC	+				0	(-)	+	+	0	
Zn stearate	+				0	-	-	+	Y	Y
Na stearate	0		+		-	-	-	+	Y	Y
SOLVENT										
pentaerythr.	+				-	-	-	0		
C_4 sulfone	+		-		-	-	-	-		
phenyl sulfone	0		-		0	0	-	-		
epoxy	+				-	-	-	-		
PEt glycol	+				0	-	-	0		
asphalt 1	+				0	-	-	+		
asphalt 2	0				-	-	-	+		
asphalt 3	+				-	-	0	+		
POLYMER										
PEOxazine	(+)	0	0		0	-	0	0	0	(Y?)
N/6	0	-	0		0	0	-		0	
N/66	0	-	0		0	+	+		0	
TPU	+	0	0		0	0	+	0	0	

(continued)

Table 8 (Cont'd). Summary of Results

Cond. or Additive	PHYSICAL				CHEMICAL					
		Cell	β-	O_2	Melt Stab.		Oven		Flame	Cross-
	Feed	Size	Trans	Perm	240°C	280°C	Life	Color	Ret.	link
POLYMER (cont'd)										
PVPhenol	+		+		0	(-)	-		(?)	
PVPyridine		-	0		-	-				
PolyBPA	+	-	+				0	+	0	(Y?)
Et/VAlc	+	-	0	-	0	0	-		0	
ANS	+	0	0		(+)	-		+		
SAN	+	0	0		(-)	-?	-	0	0	(Y?)
SMA	(+)	0	0		0	0	-	(+)	0	
PSulfone	0	(+)	0		(-)	(-)	-	(+)	0	
PC	0	(+)	0		0	0	-	0	0	
PET	+	0	0		0	(+)	-	+	0	
PBT	+	-	0	0	0	0	-		0	
C5 PEster	+	+	0		0	0	-	(-)	0	
P Acetal	(+)	-	0		-	-	-	0	0	
PPO	0	+	0		0	(+)	-	+	(Y)	
PVDF	0	+	0	0	0	0	-	(+)	0	
FEP	0		0		0	0	-		(?)	
Na Ionom	(+)	+	+		-	-	0	+	Y	Y
Zn Ionom	+	+	0		0	0	-	0	0	
PMP	+	+	0		0	0	-	0	0	

+ Increased.
0 Close to control.
- Decreased.
Y Yes
( ) Marginal.
? Uncertain.

Table 9. Electron Microscope Results on CARILON® Polymer Blends

Natural and Ruthenium Decorated

PKB No:	Added Polymer	STEM on Strand Size (u)	Added Poly Appearance Natural	RuO_4
2I	PVDF	1.4	black	no contr
2J	N6	.8(.2)		black
7F	SAN	.8	light	black rim
7G	PBT	.7	sl dark	dark*
8A	TPU	1.3	(disbond)	black
8B	Zn Surlyn	2.0	light	v light
8C	PVPhenol	compatible (?)		
8D	ANS	.8	light	white
8E	PMP	11.0	white	white
8F	PBPA	.25	sl light	light
8G	PVPyridine	1.4		uniform grey, drk rim
9B	PEt/Valc	.3	sl light	dark
9C	FEP	?	no contr	no contr
9D	PCaprolactone	3.5	sl drk	no contr
9E	Na Surlyn	1.8		light
9F	SMA	1.0		dark,black rim
12A	PEOx	1.3		(dissolved during cut)
12B	PET	1.0		dark
12C	PC	1.4		v dark
12D	N66	.2		sl dark
12H	PAcetal	.7(.2)		dark
13A	Polysulfone	11-2.5		dark
13C	PPO	3.1		light

* Carbon coated grid. Normal Ru stain gave no contrast.

NOTES:

2I Irregular shape, not smooth oval.
2J N6 phase had inclusions, like HIPS. Max phase width inside was 0.2u.
7F Cryo gave black boundaries on Ru staining. (No RT for comparison.)
8F RT slice gave black boundaries on Ru stain, Cryo did not.
8G Bimodal; 1.4 with some .05u.
9B Boundary staining apparently gave black borders. Halo may indicate thick, mixed interlayer collapse or artifact.
9D Larger cells torn open.
12D Very small, evenly dispersed.
12H Ovals tore out during beam exposure. Appeared to have inclusions like 2J.
13A Bimodal; a few large gobs - 11, many 2.5u.
13C Bimodal; 3 and .4u.

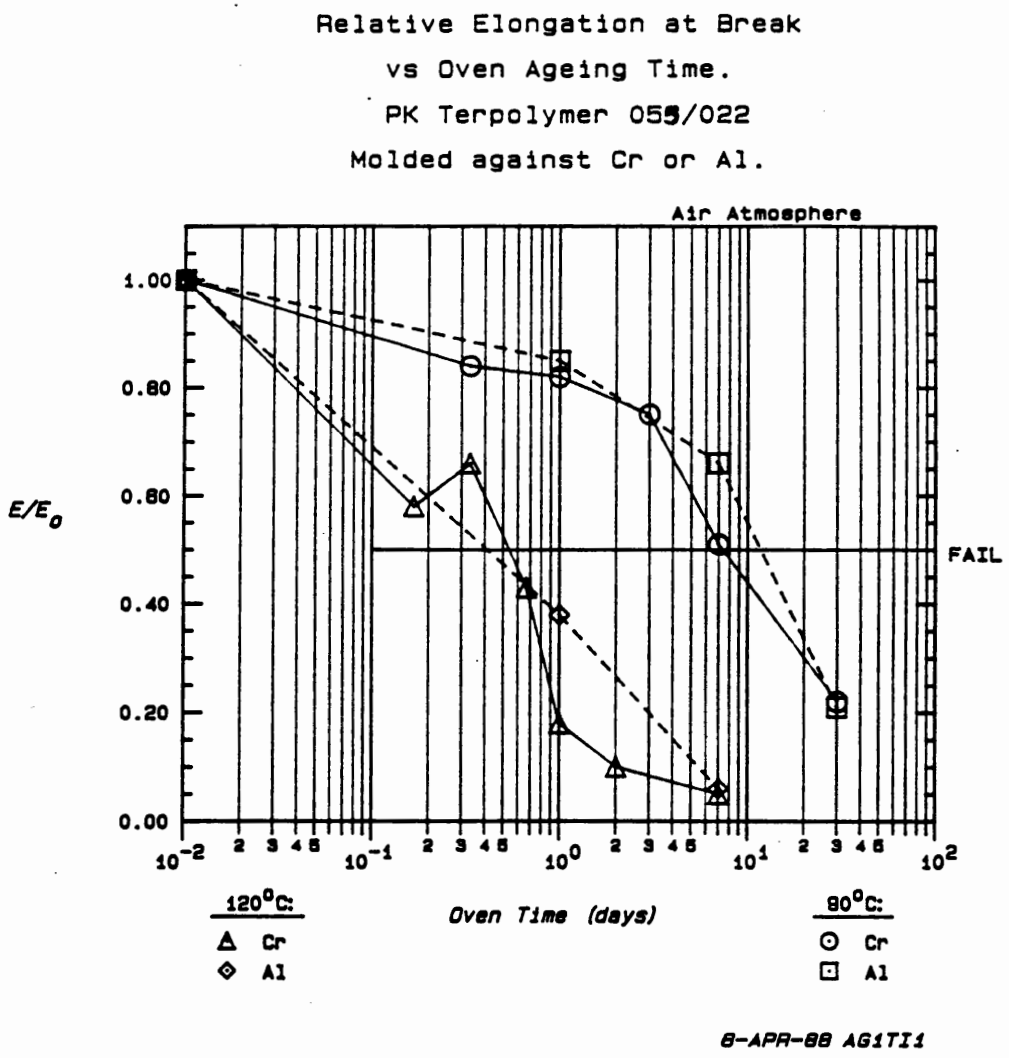

Figure 1. Property Loss in Polyketone with Oven Ageing Time

011882

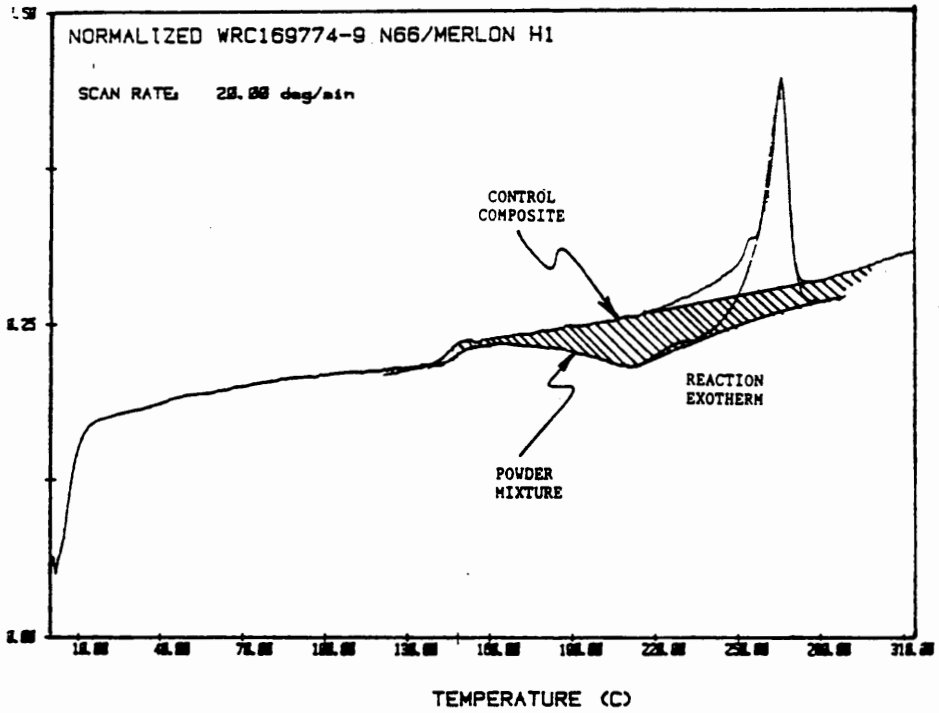

Figure 2. DSC of Mixed Polycarbonate-Nylon 66 Powders Showing Chemical Reaction

011882

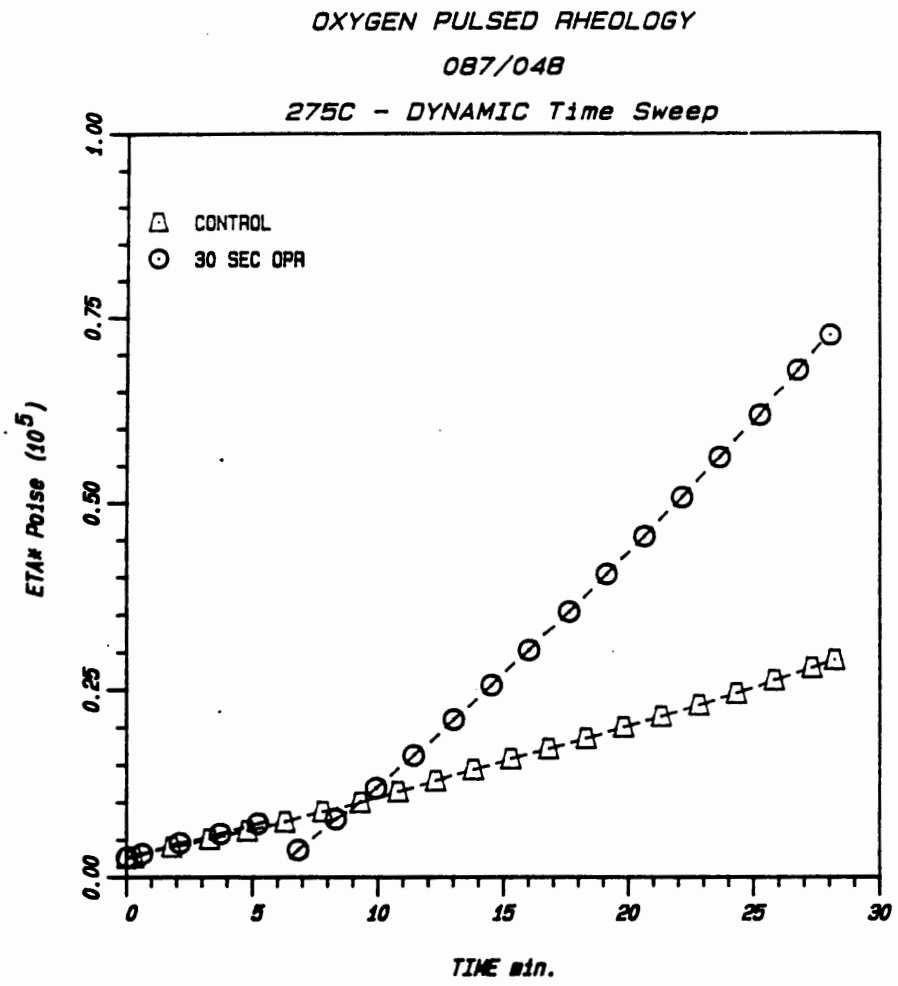

Figure 3. Effect of Oxygen Pulse on Rate of Viscosity Rise in Polyketone Melt

011882

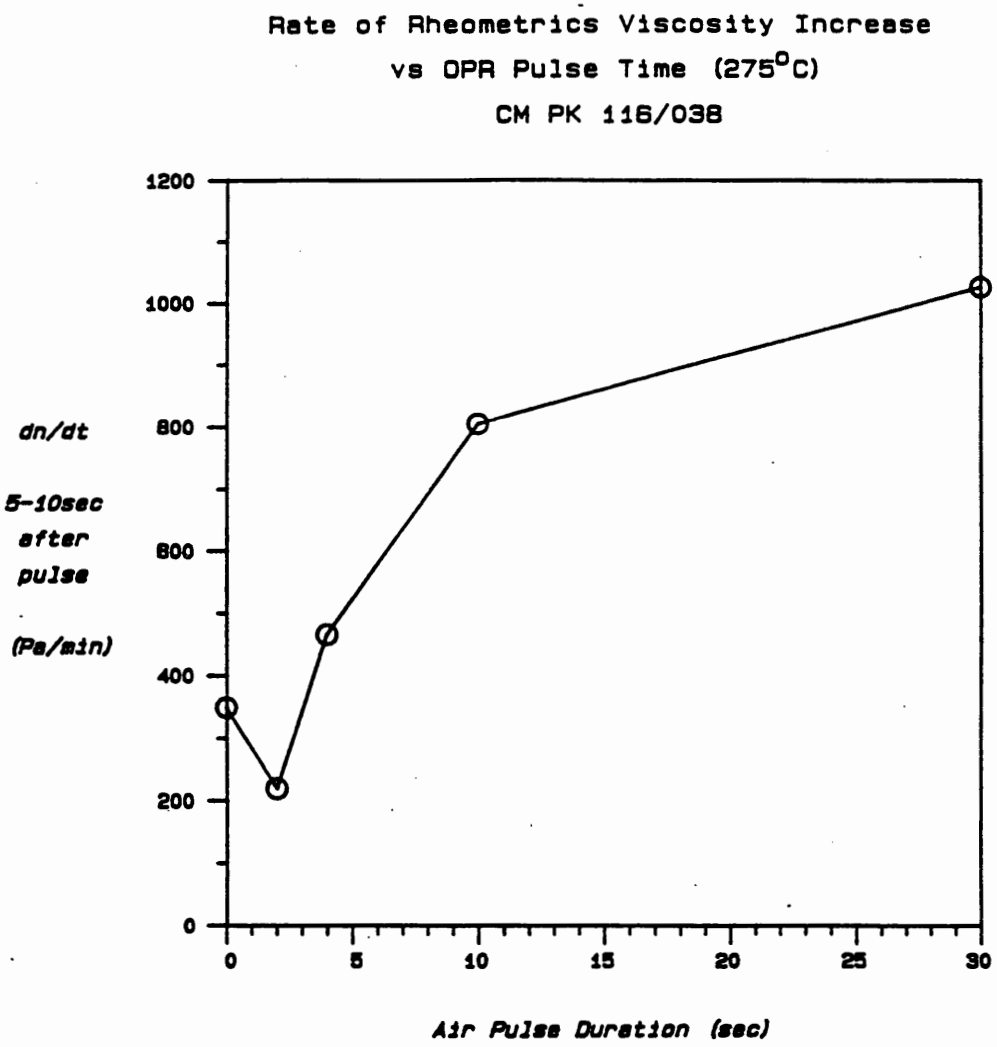

Figure 4. Effect of Air Pulse Duration on Rate of Viscosity Rise of Polyketone Melt

011882

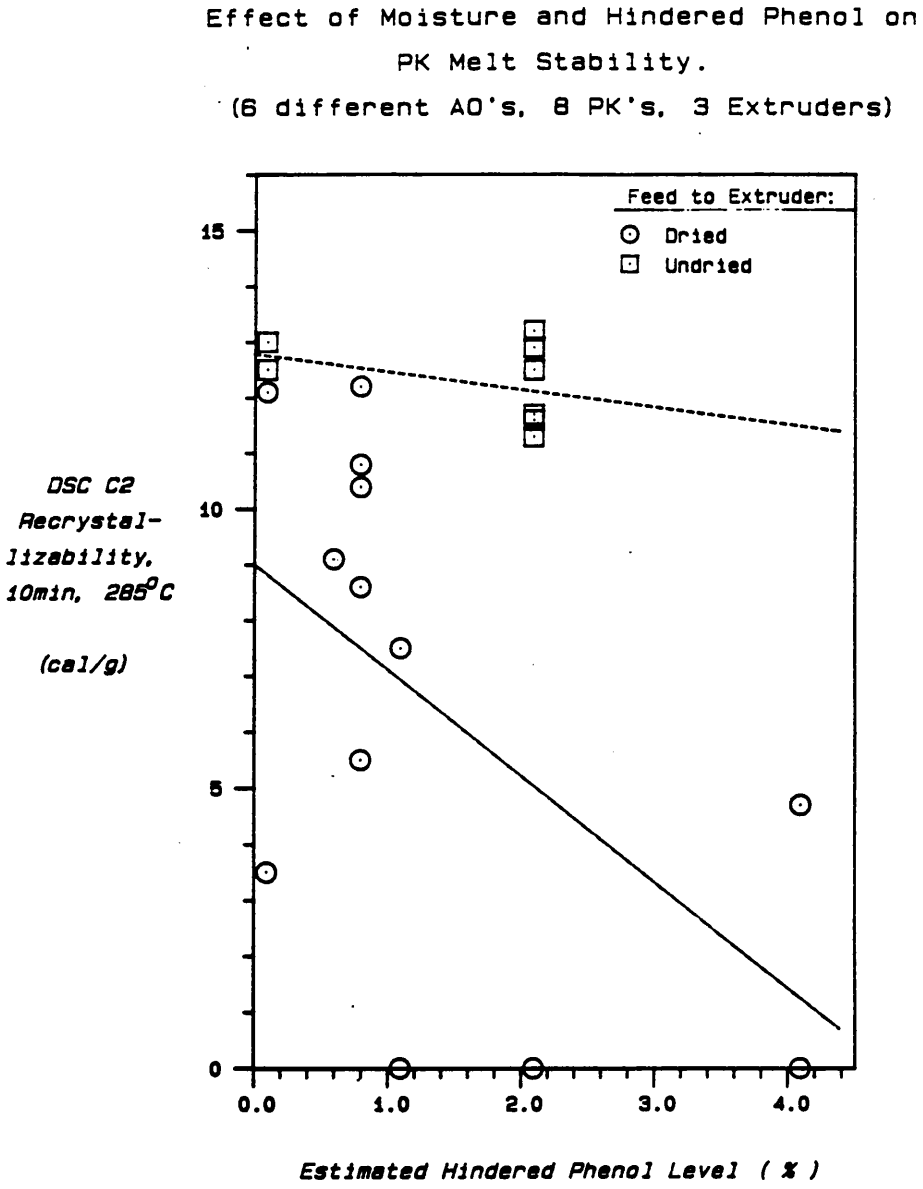

Figure 5. Possible Interaction Between Water and Hindered Phenol in Anaerobic Polyketone Melts

011882

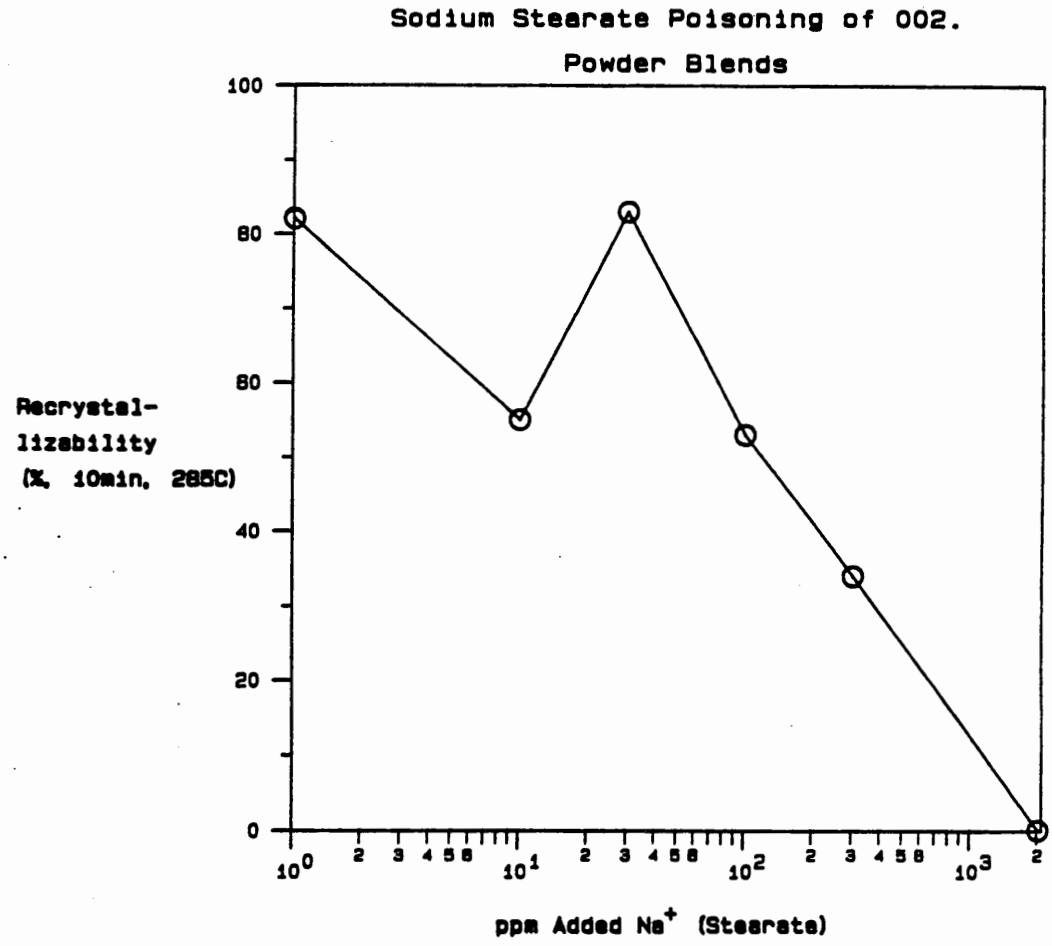

Figure 6. Effect of Sodium on Recrystallizability of a Polyketone Melt

011882

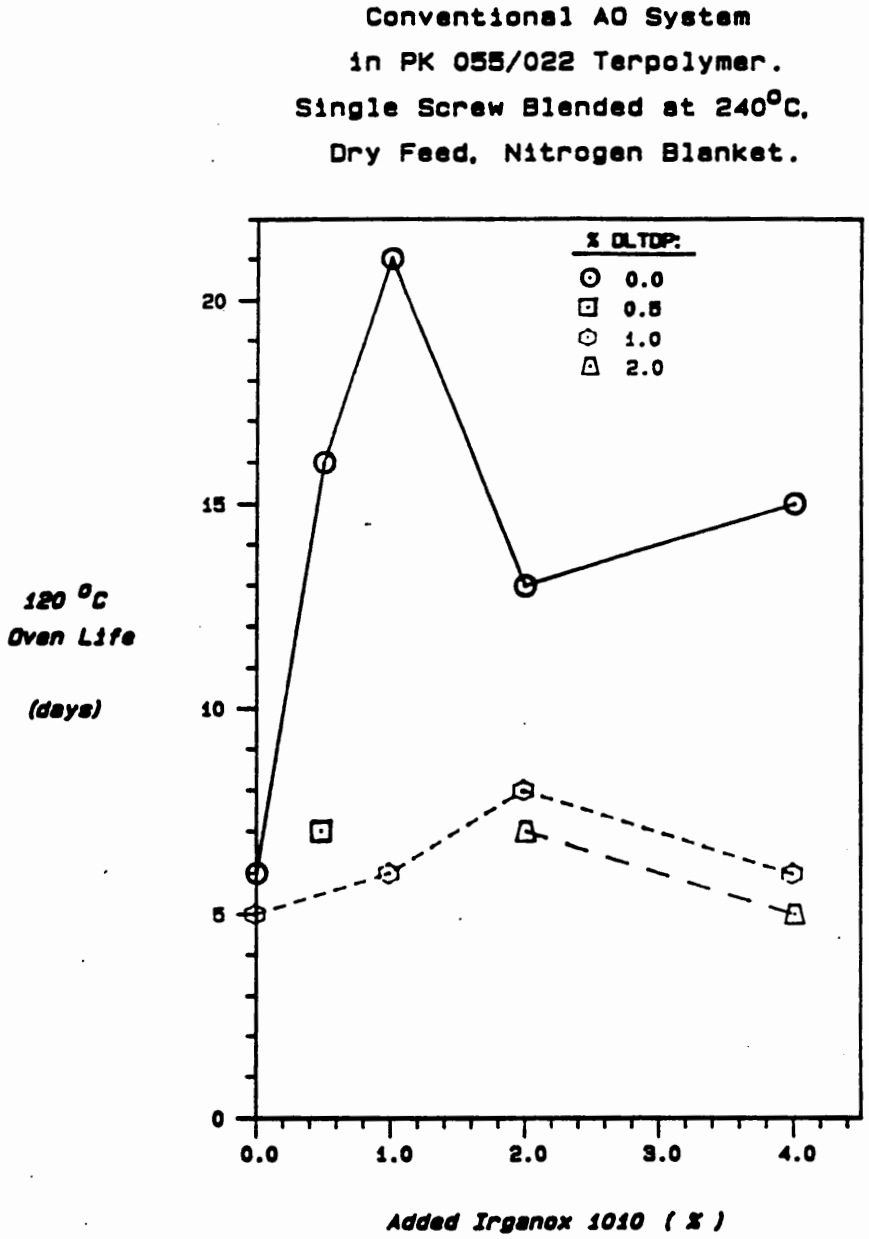

Figure 7. Oven Life Antagonism by High Concentrations of Hindered Phenol

011882

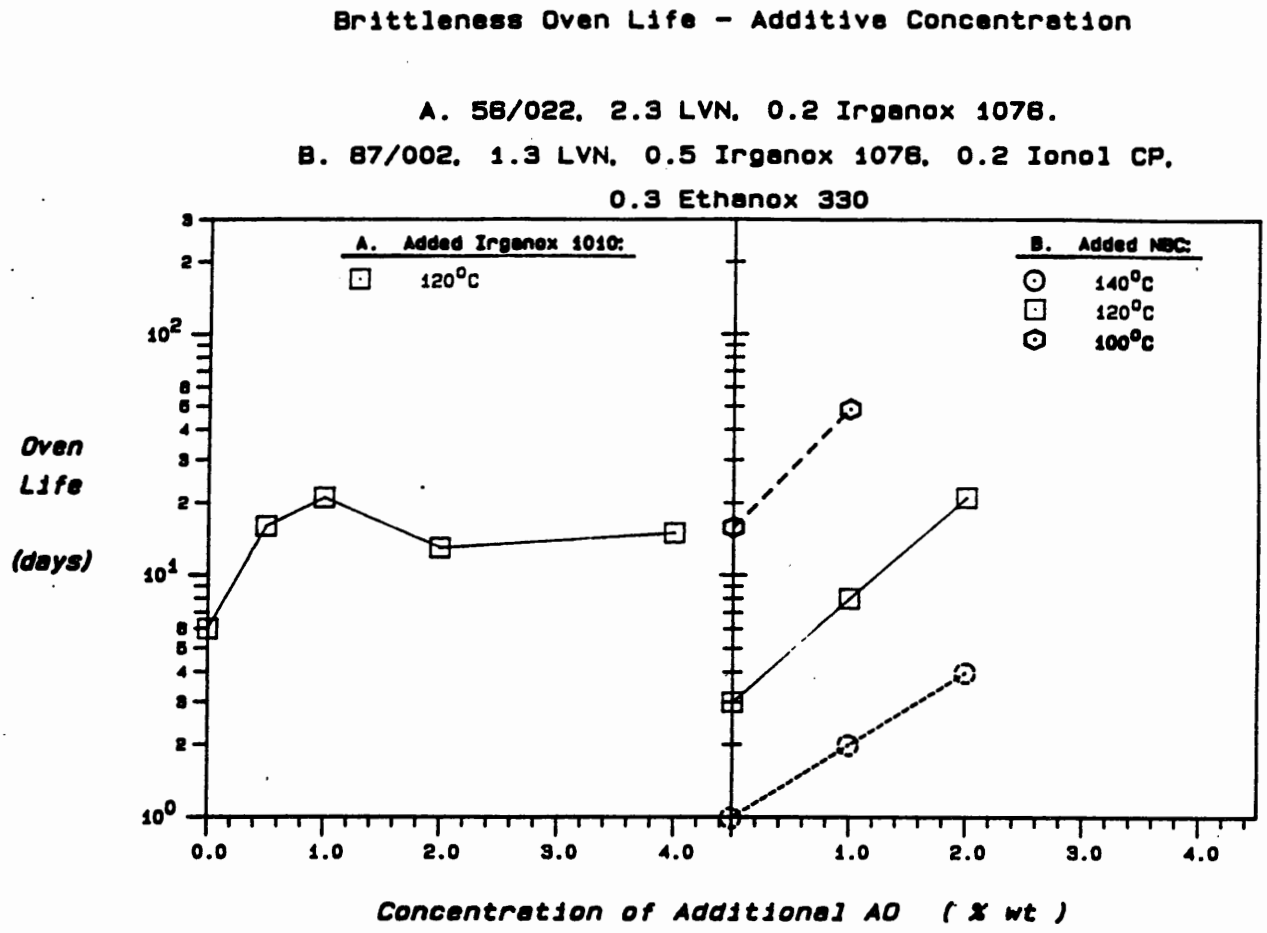

Figure 8. Comparison of Concentration Effects of a Hindered Phenol and Nickel Dibutyl Dithio Carbamate

011882

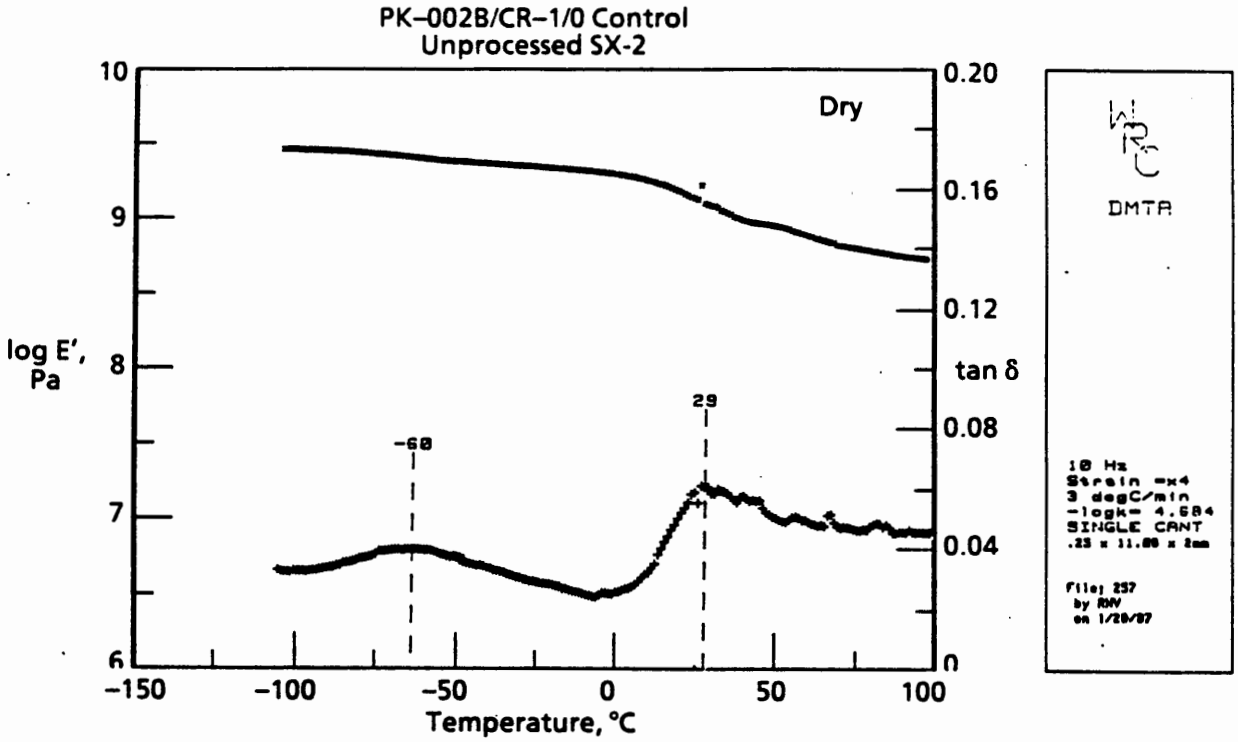

Figure 9-A. DMTA of Compression Molded Powder

011882-1

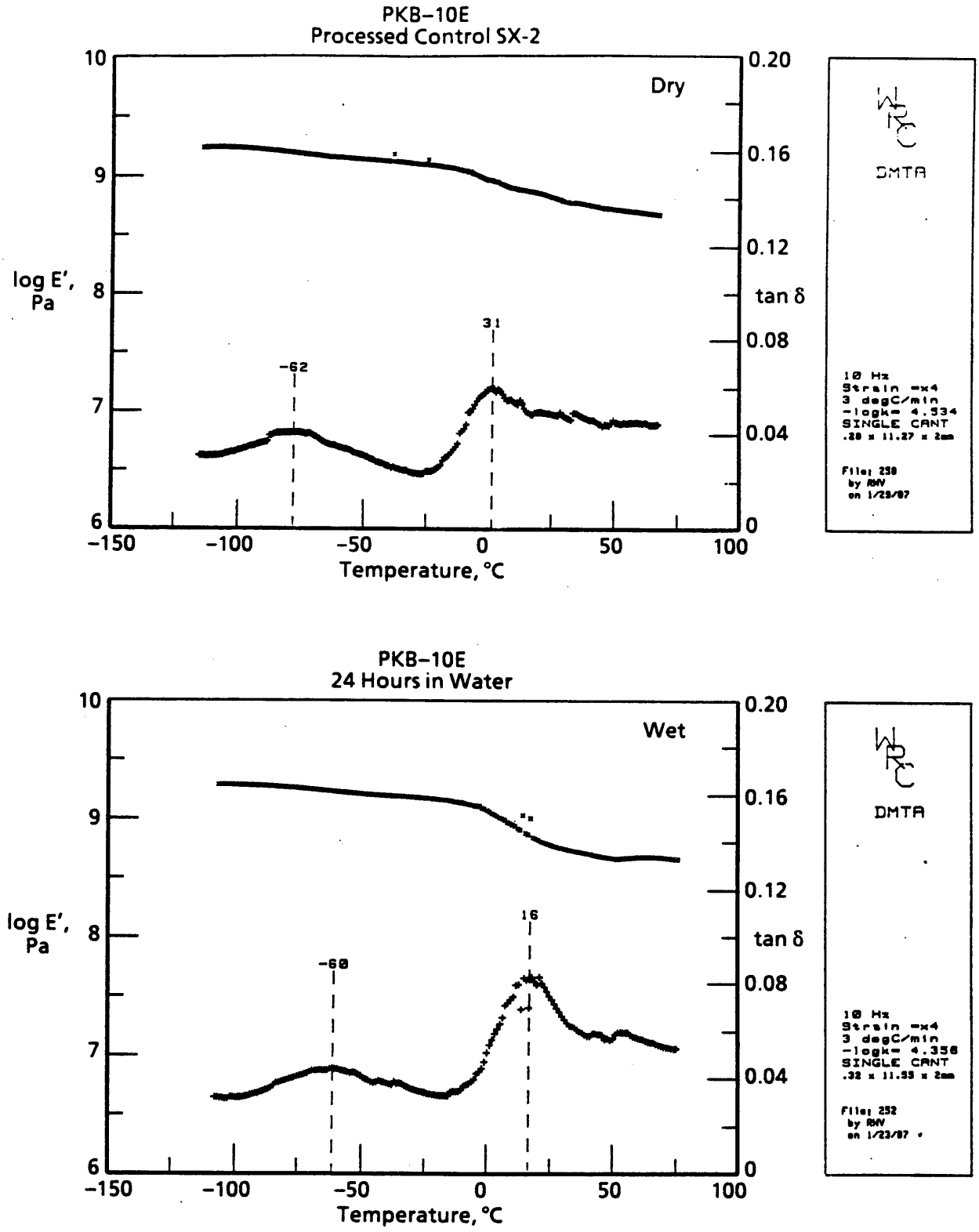

Figure 9-B. DMTA of Processed Control

011882-2

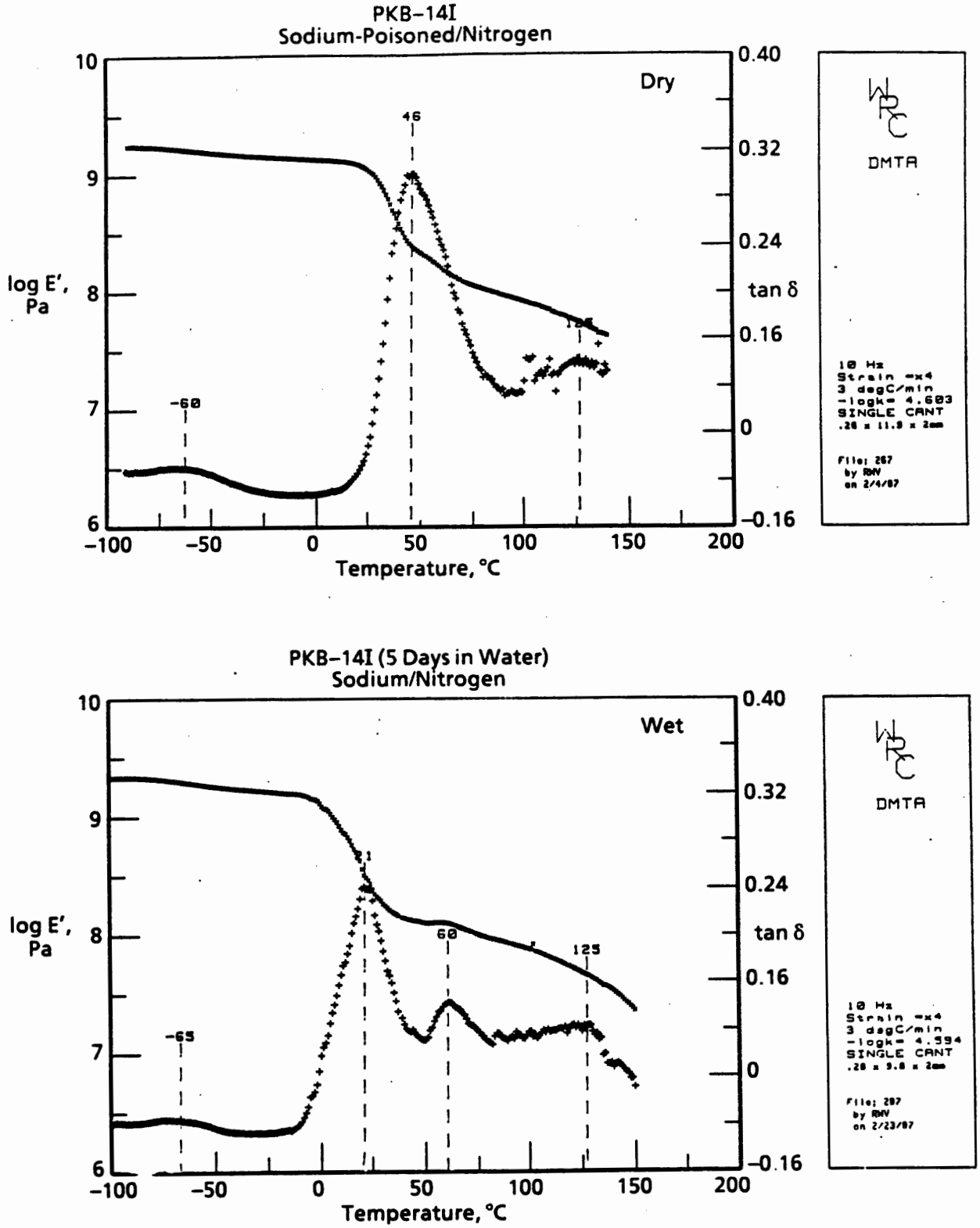

Figure 9-C. DMTA of Sodium Stearate Blend

011882-3

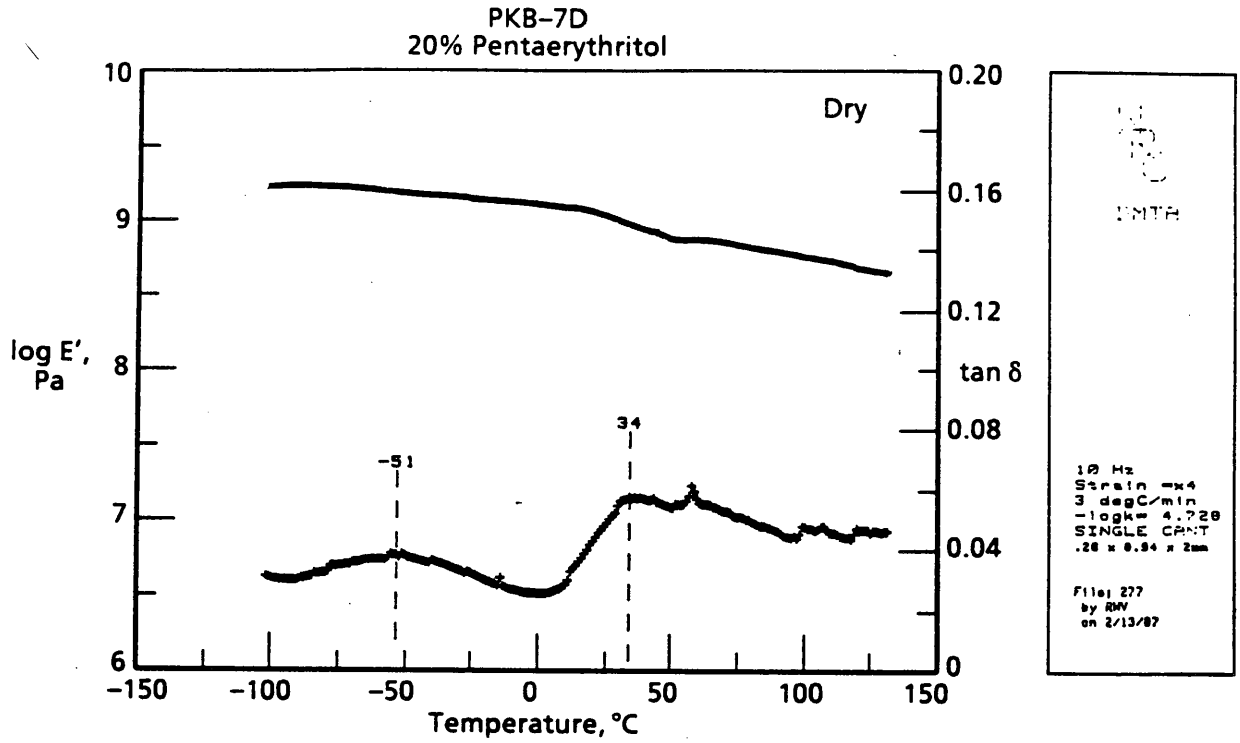

Figure 9-D. DMTA of 20% Pentaerythritol Blend

011882-4

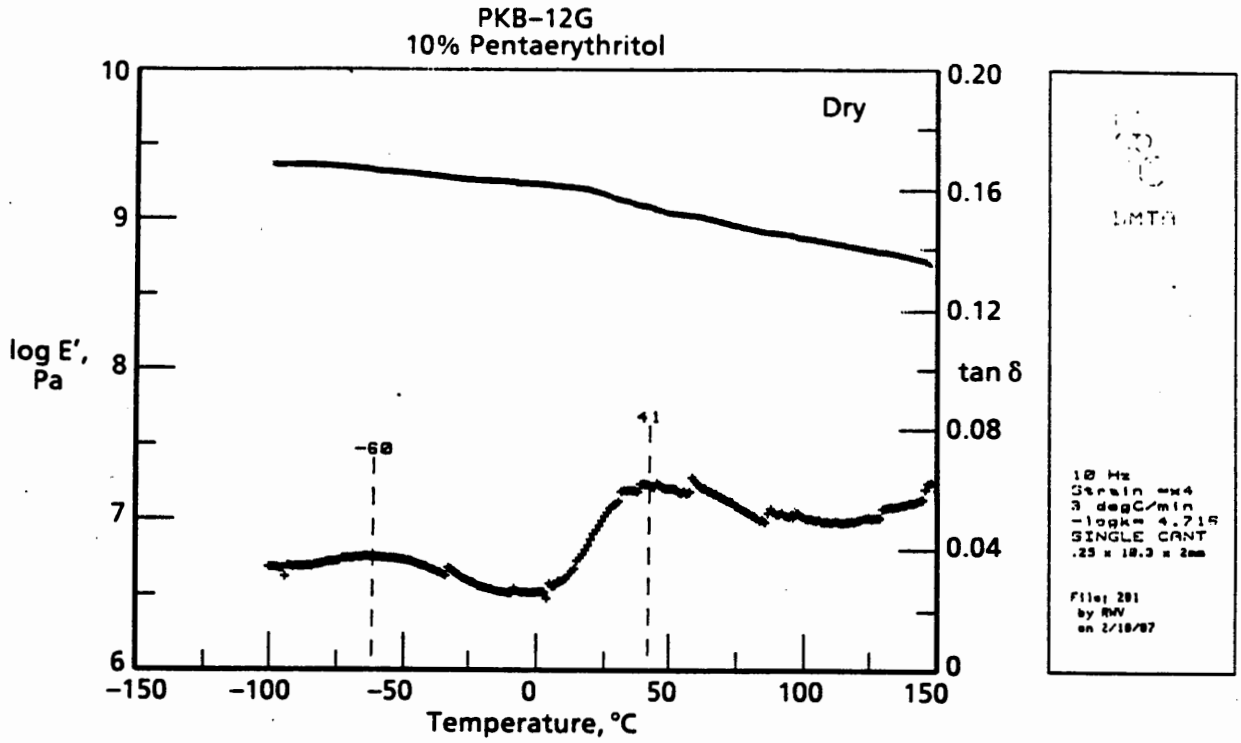

Figure 9-E. DMTA of 10% Pentaerythritol Blend

011882-5

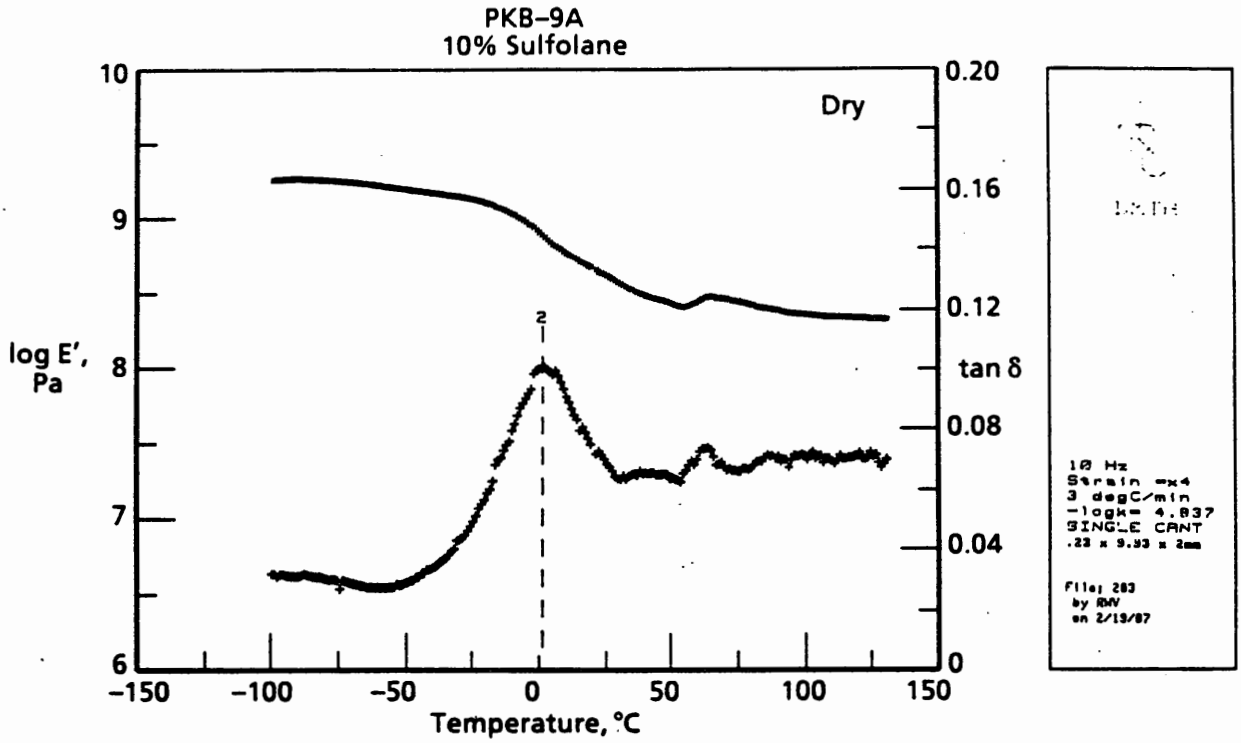

Figure 9-F. DMTA of C_4 Sulfone Blend

011882-6

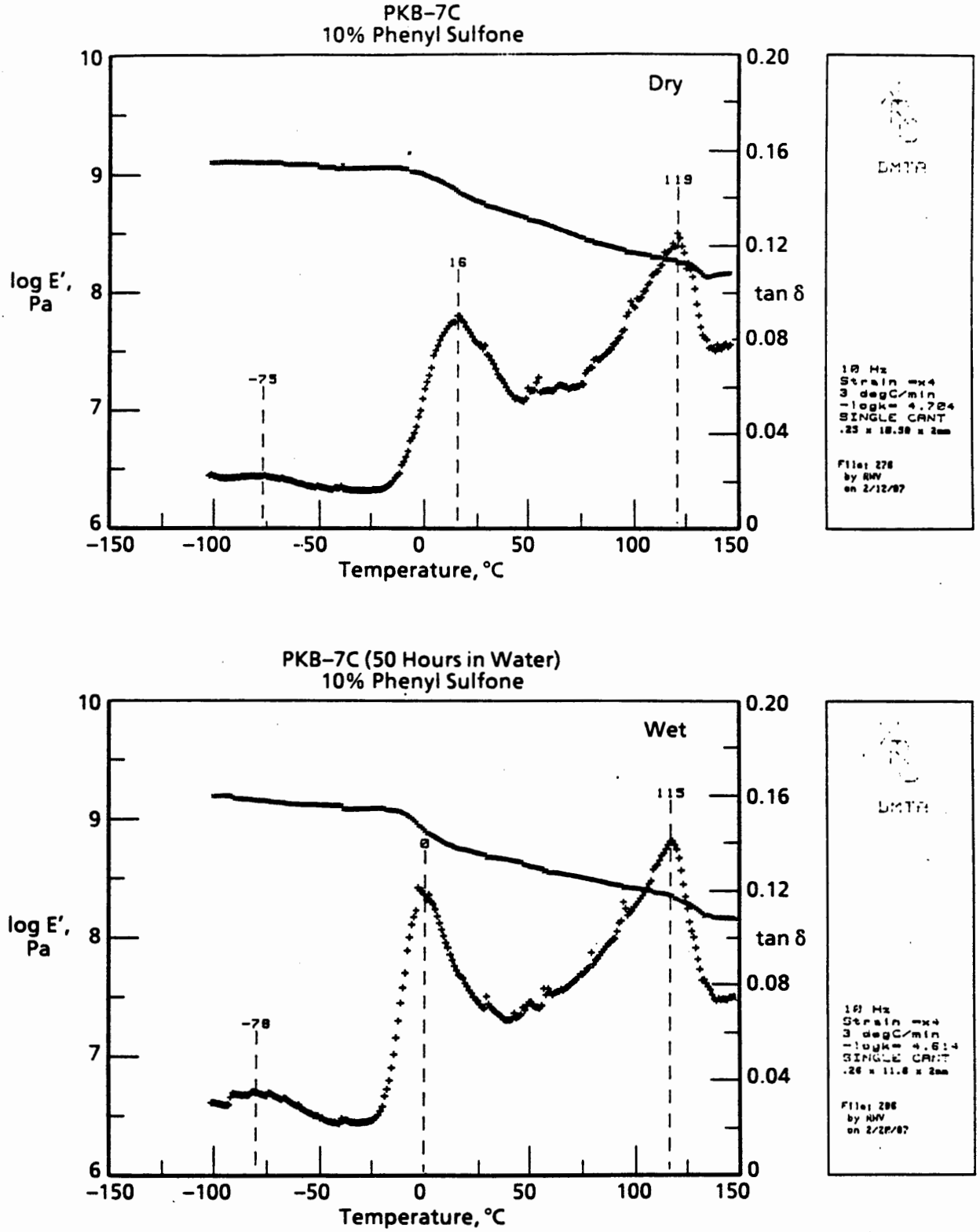

Figure 9-G. DMTA of Diphenyl Sulfone Blend

011882-7

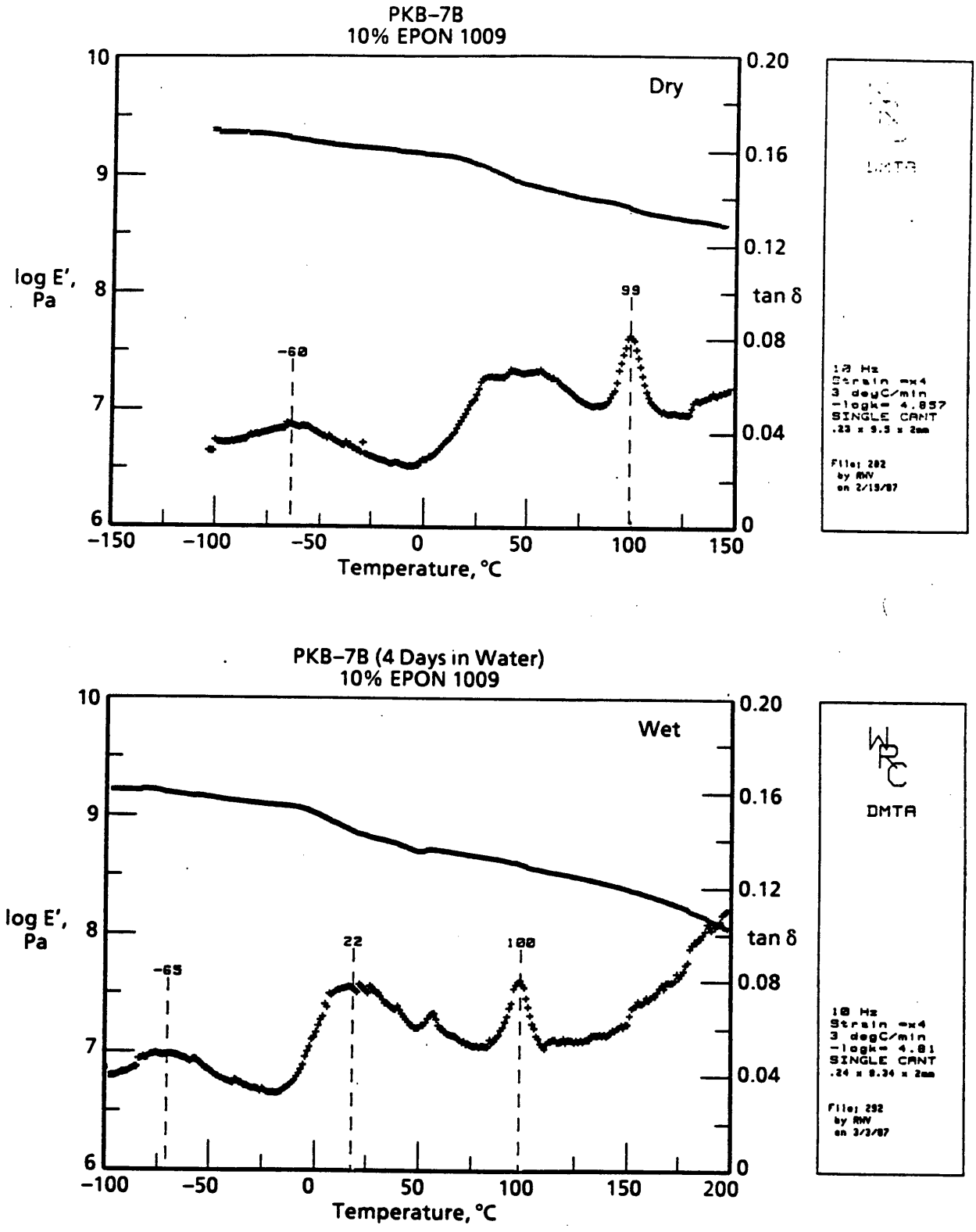

Figure 9-H. DMTA of Epoxide Blend

011882-8

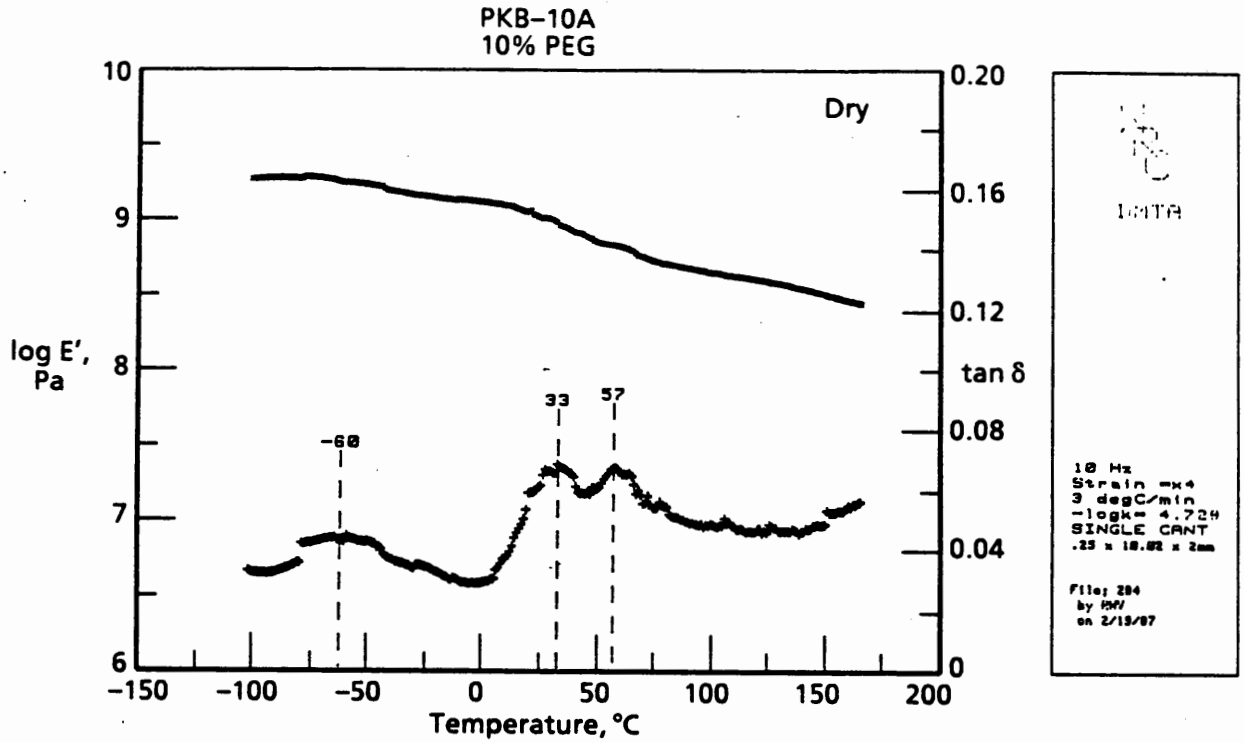

Figure 9-I. DMTA of Polyethylene Glycol Blend

011882-9

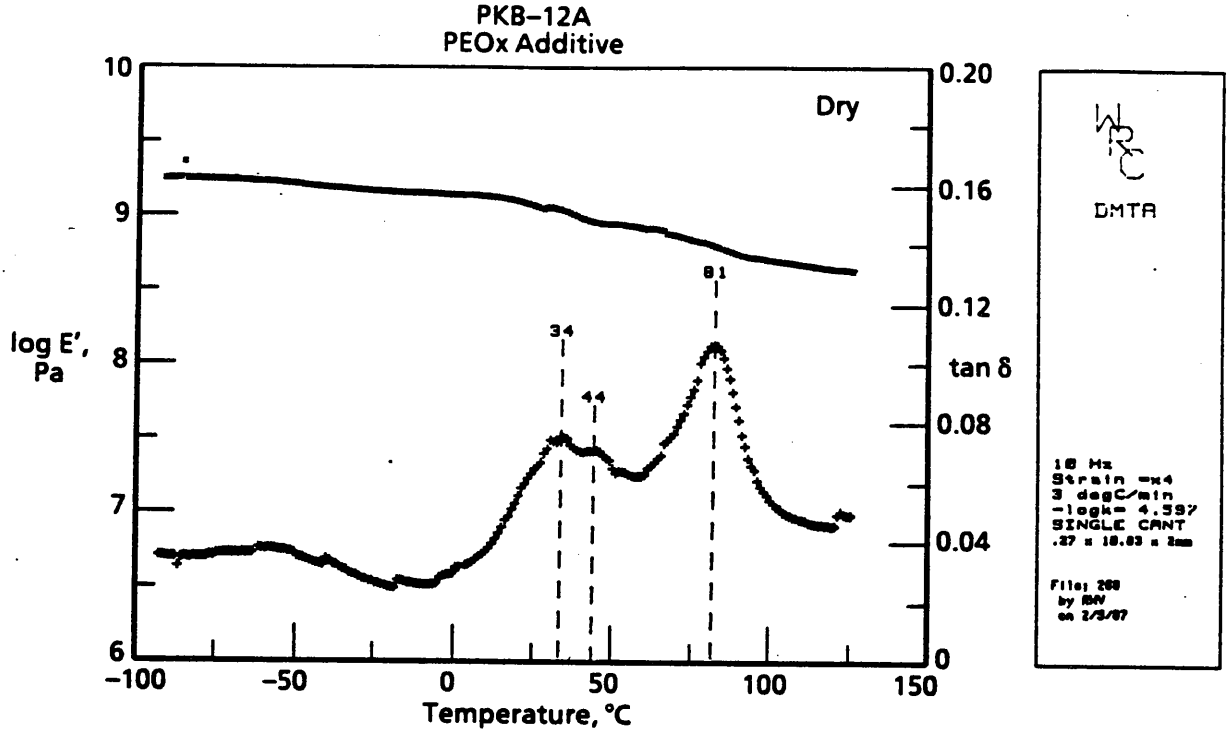

Figure 9-J. DMTA of Polyethyl Oxazoline Blend

011882-10

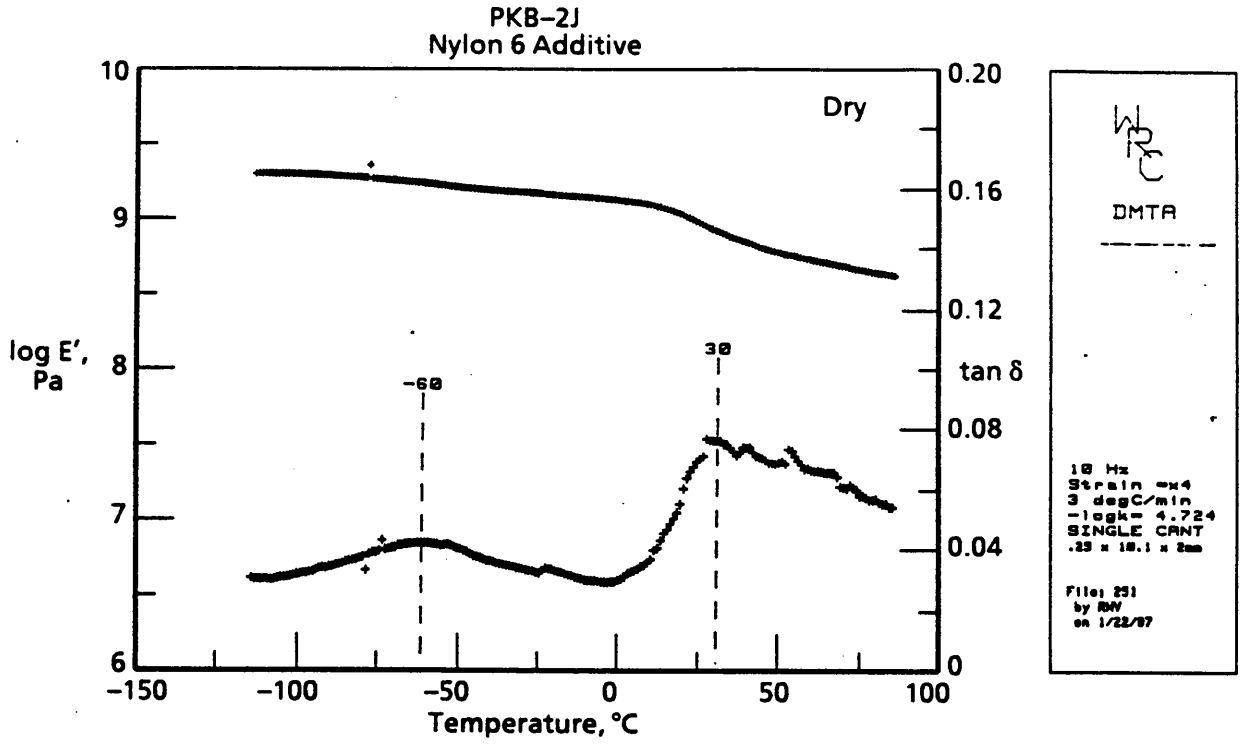

Figure 9-K. DMTA of Nylon 6 Blend

011882-11

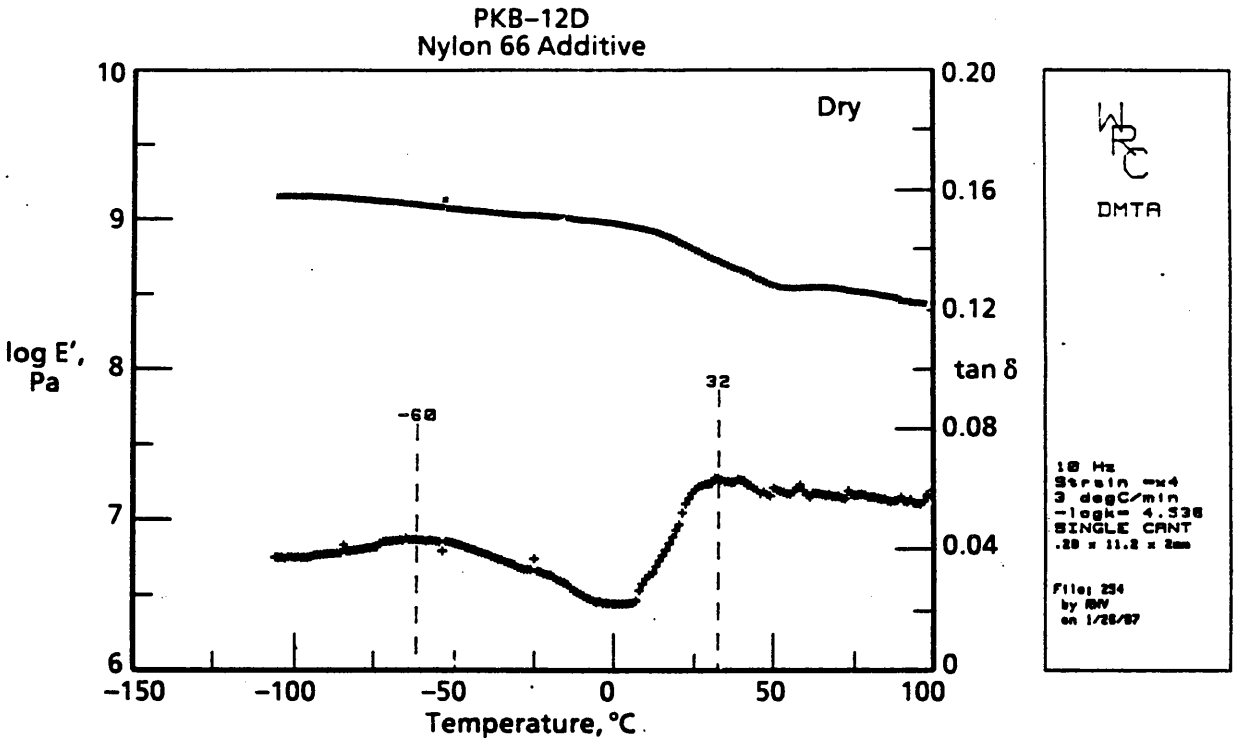

Figure 9-L. DMTA of Nylon 66 Blend

011882-12

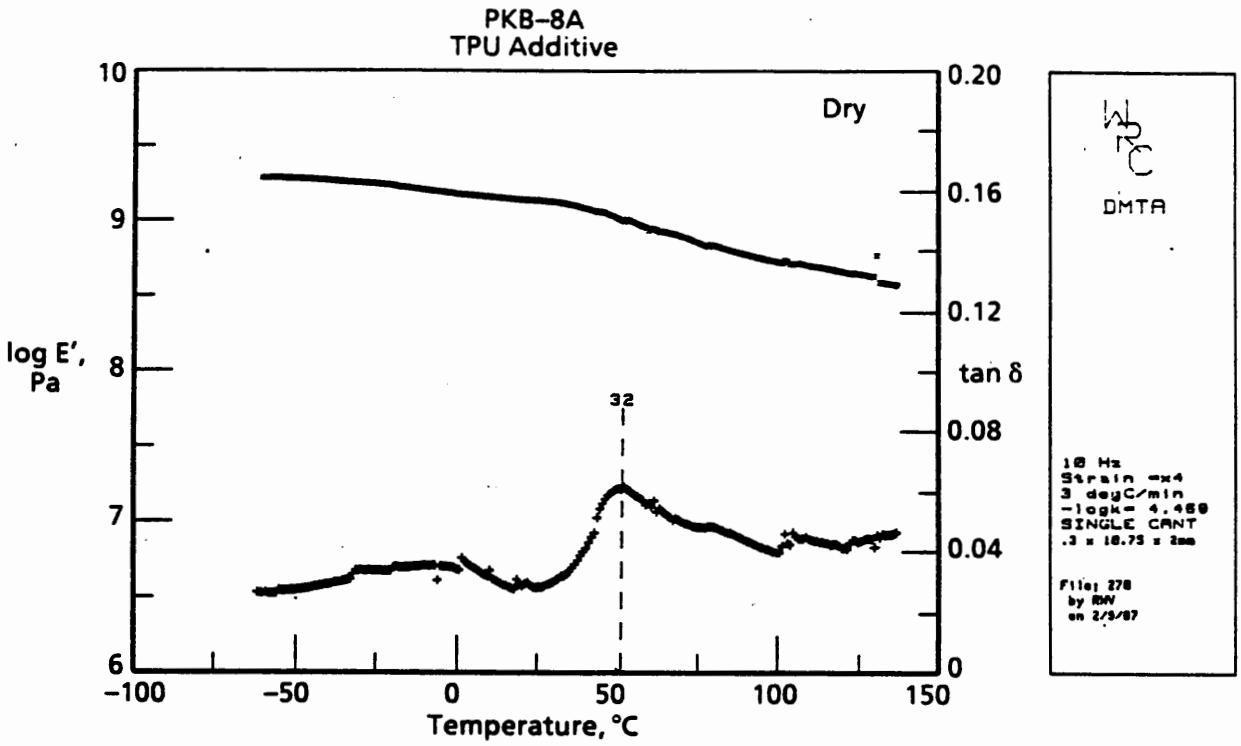

Figure 9-M. DMTA of Thermoplastic Polyurethane Blend

011882-13

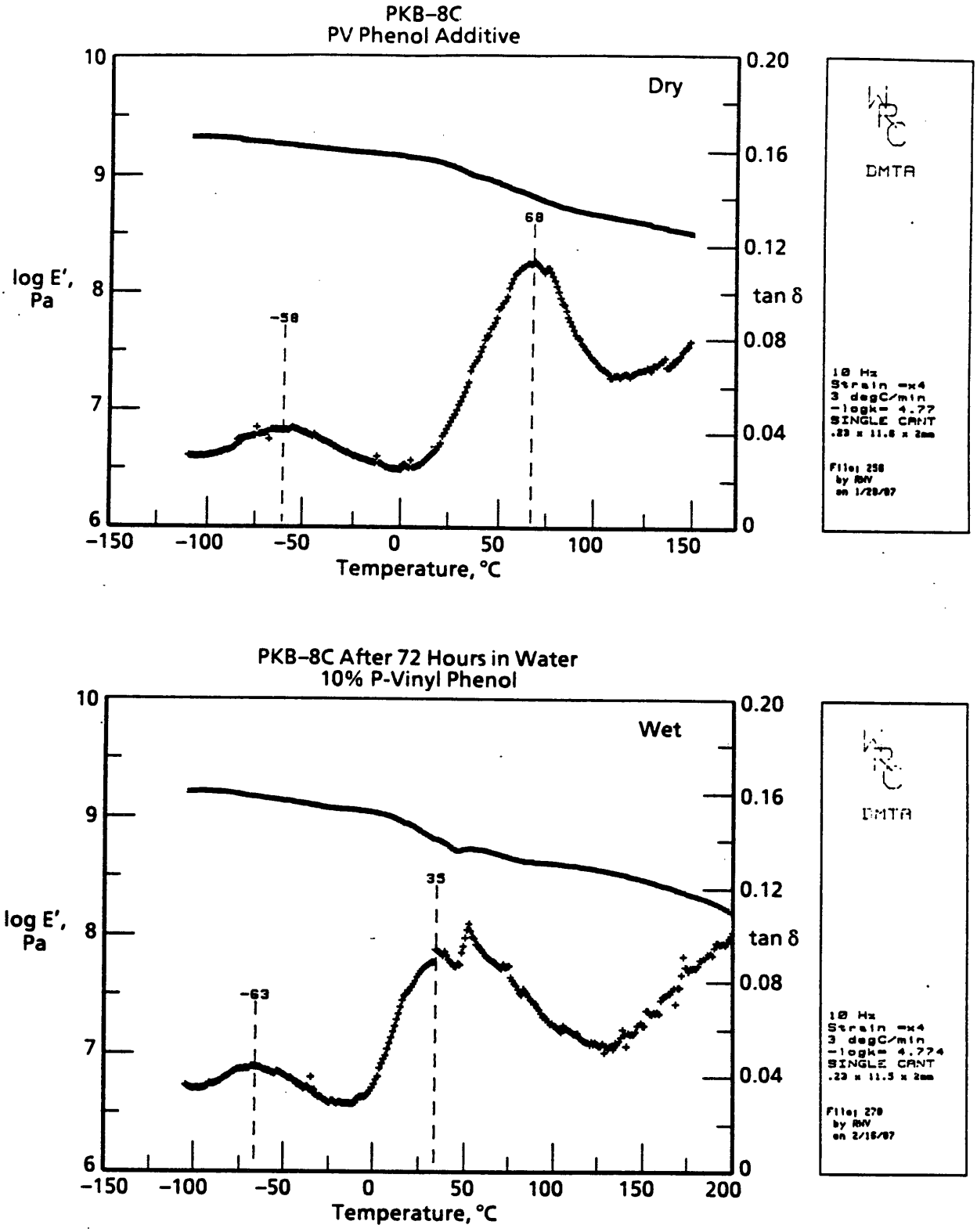

Figure 9-N. DMTA of Polyvinyl Phenol Blend

011882-14

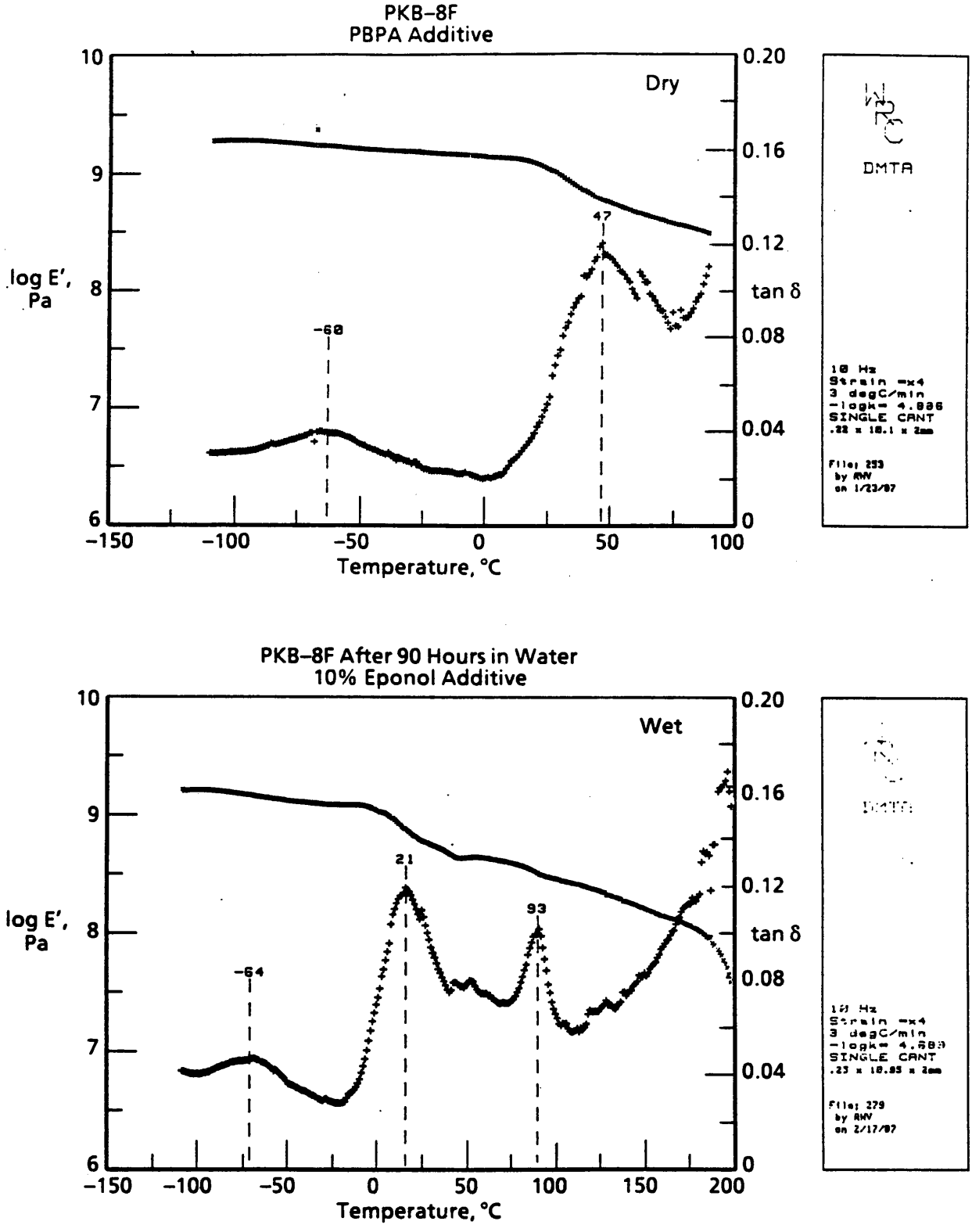

Figure 9-O. DMTA of Poly Bisphenol A Hydroxy Ether Blend

011882-15

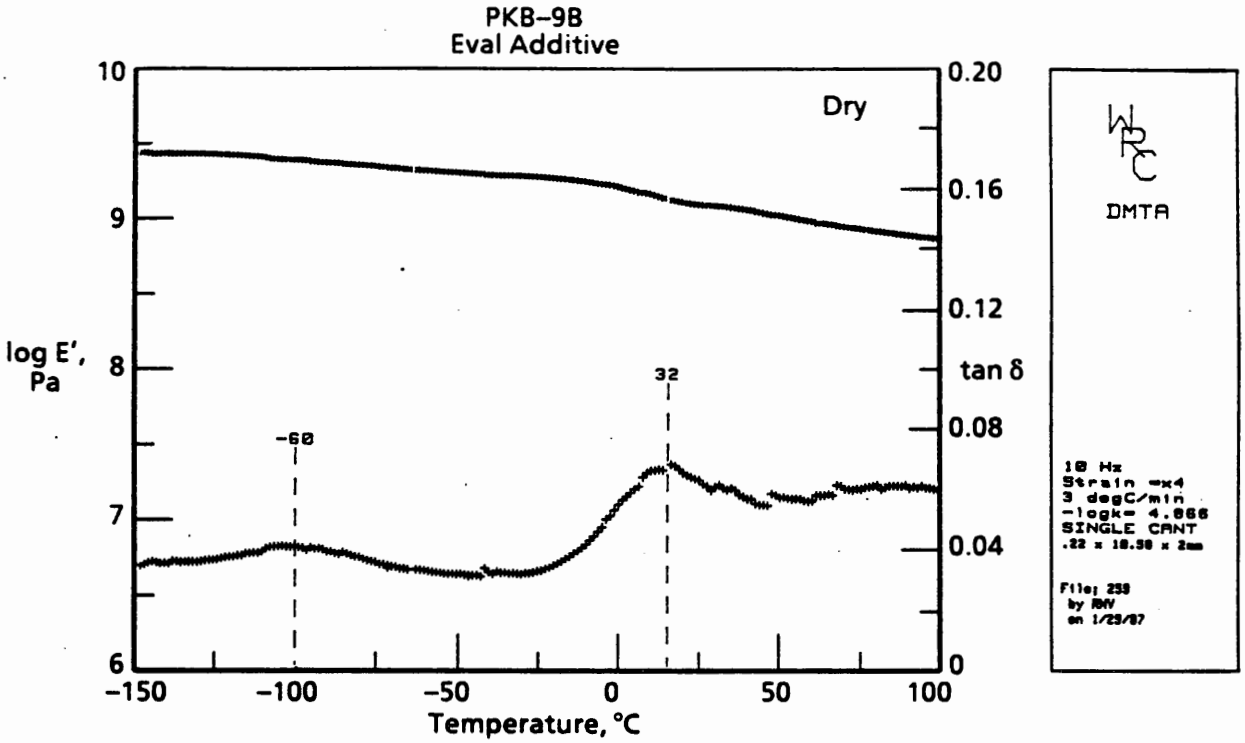

Figure 9-P. DMTA of Polyethylene/Vinylalcohol Blend

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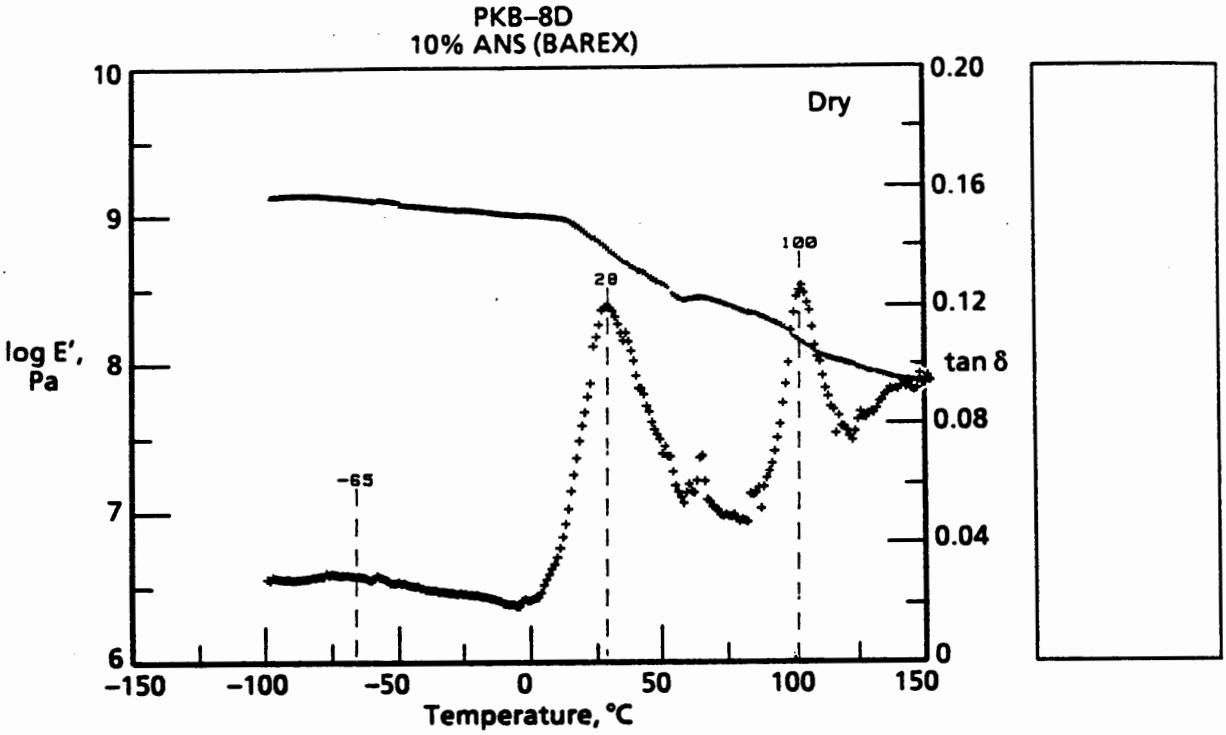

Figure 9-Q. DMTA Polyacrylonitrile/Styrene Blend

011882-17

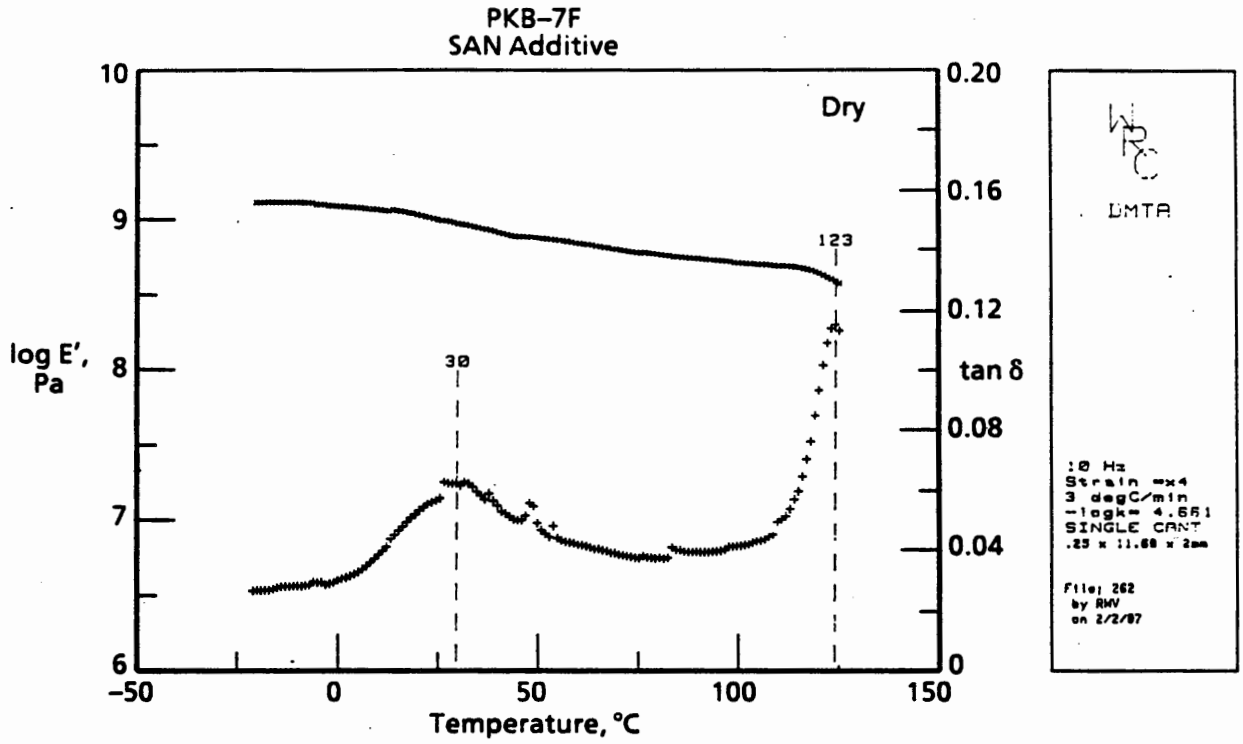

Figure 9-R. DMTA of Polystyrene/Acrylonitrile Blend

011882-18

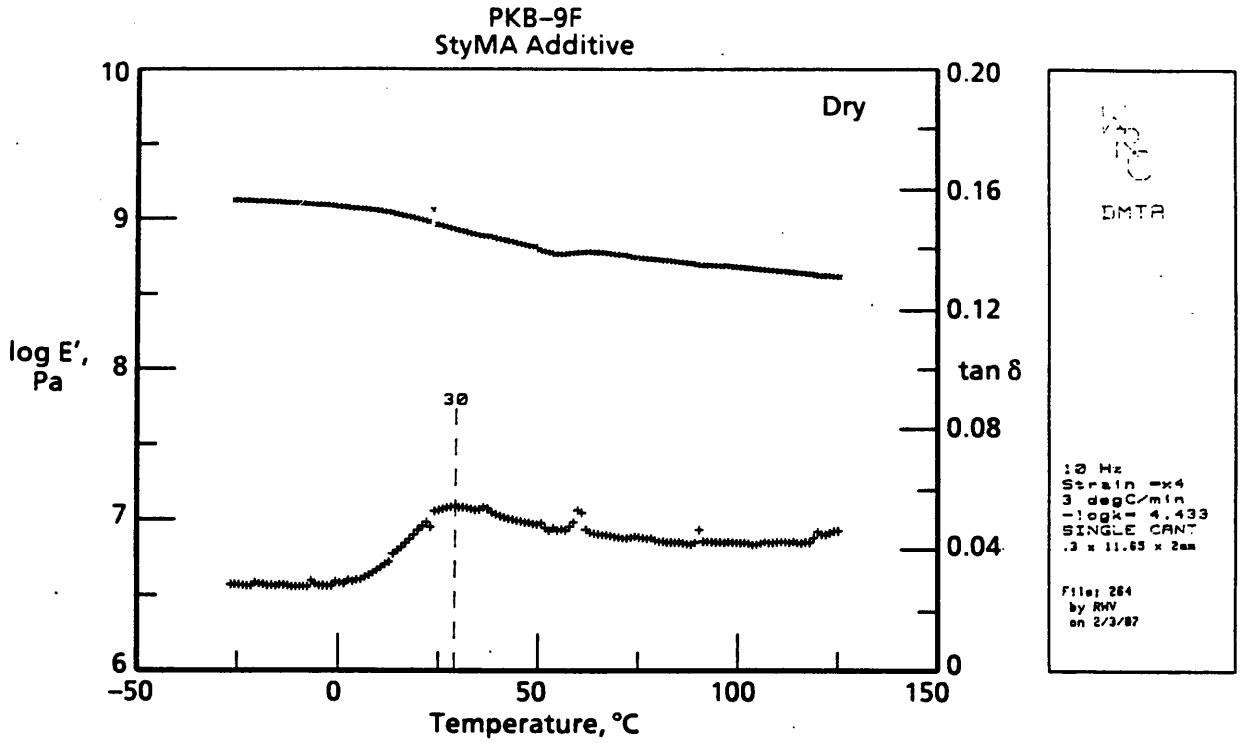

Figure 9-S. DMTA of Polystyrene/Maleic Anhydride Blend

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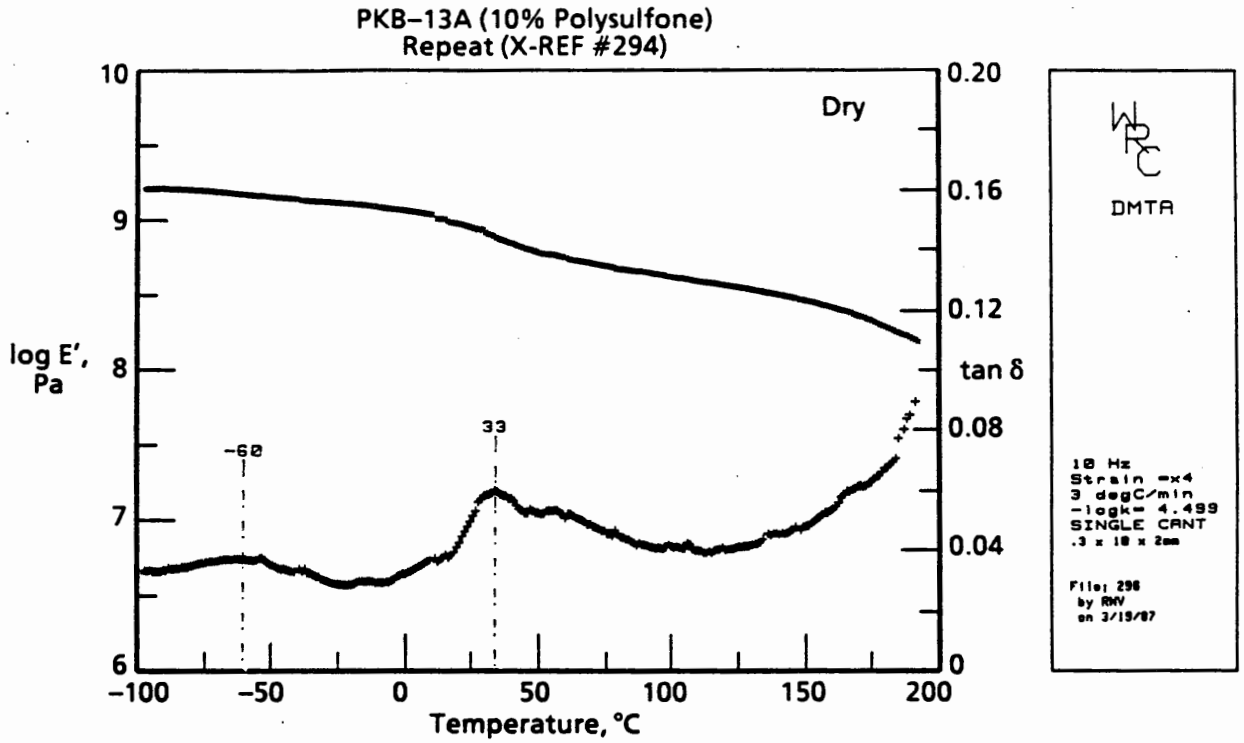
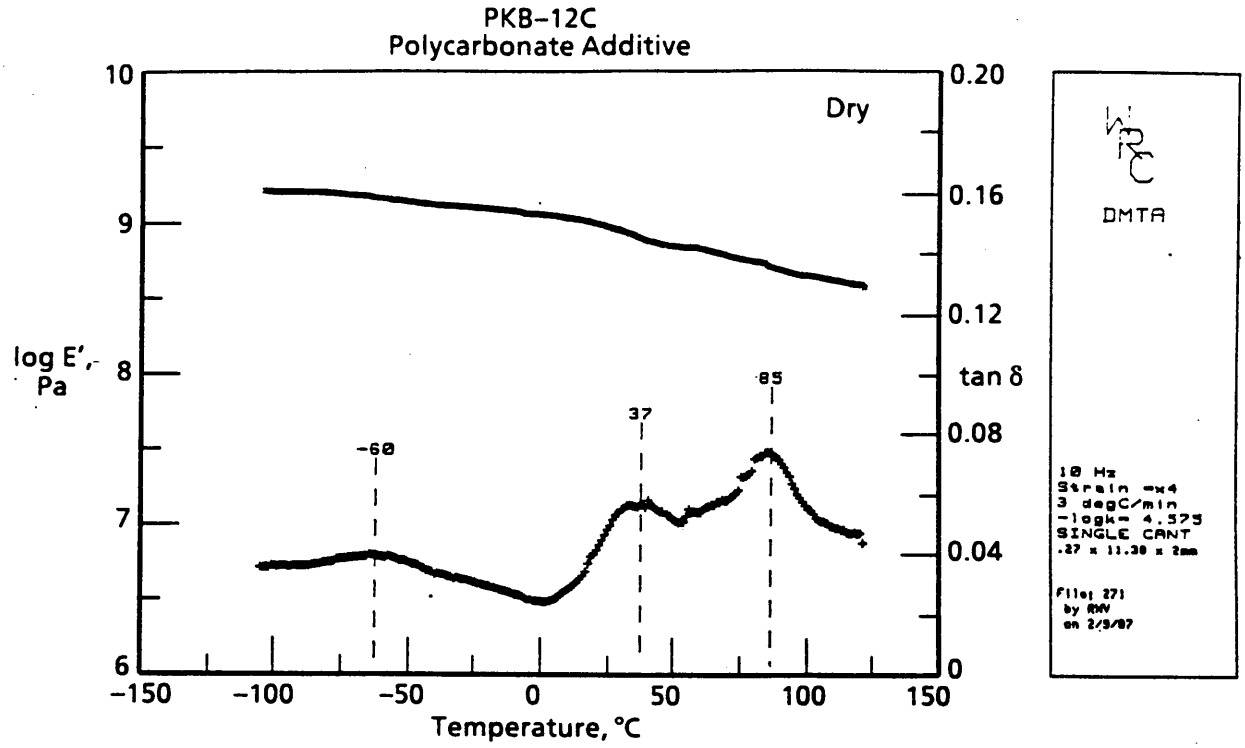


Figure 9-T. DMTA of Polysulfone Blend

011882-20



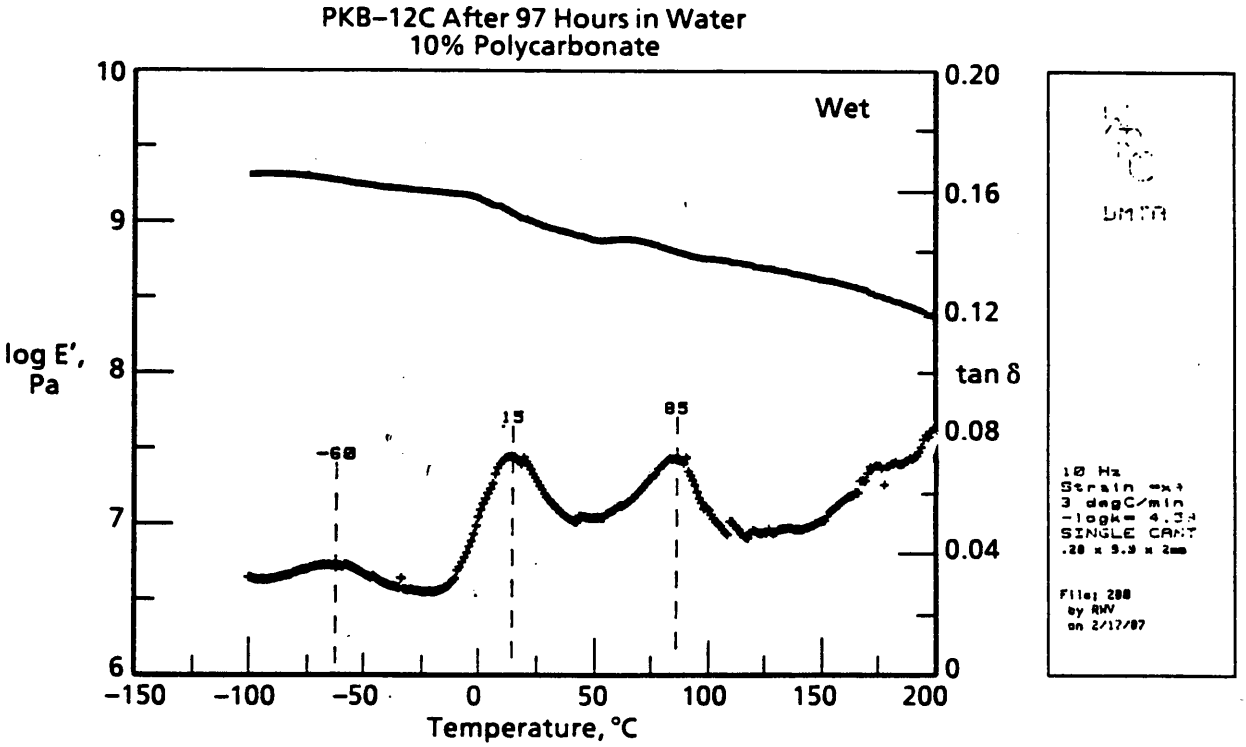


Figure 9-U. DMTA of Polycarbonate Blend

011882-21

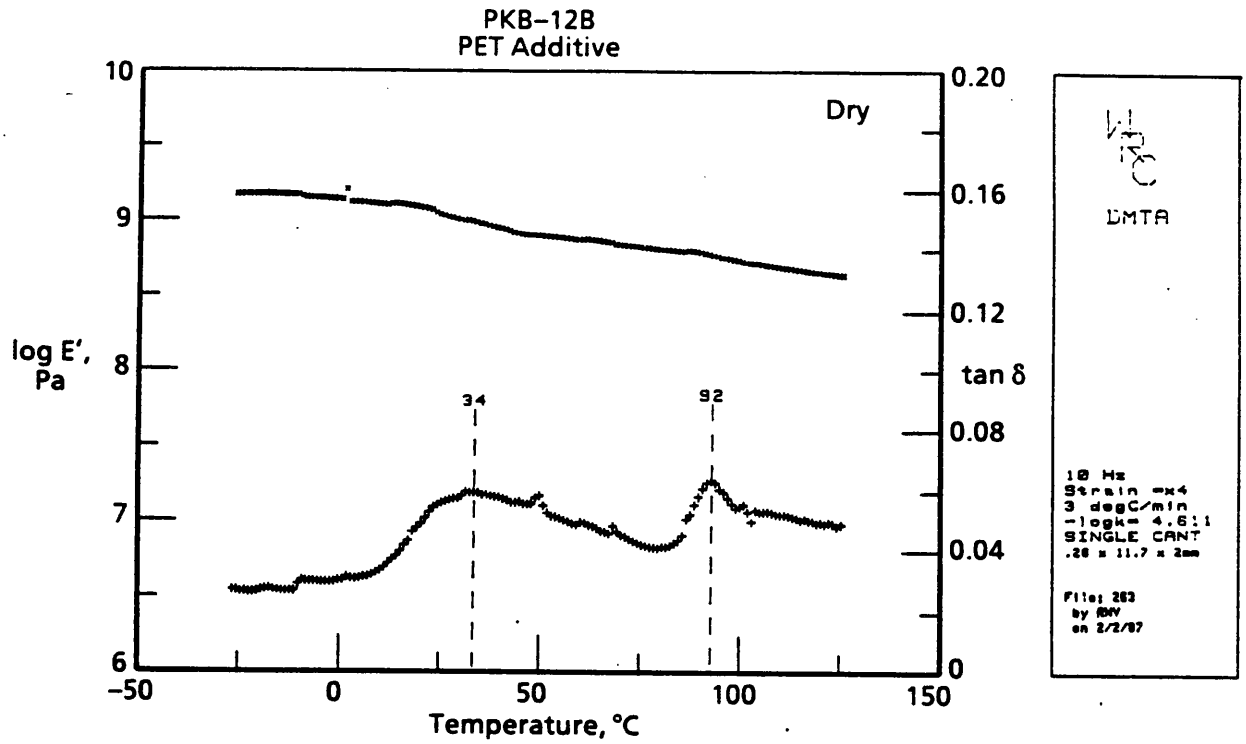
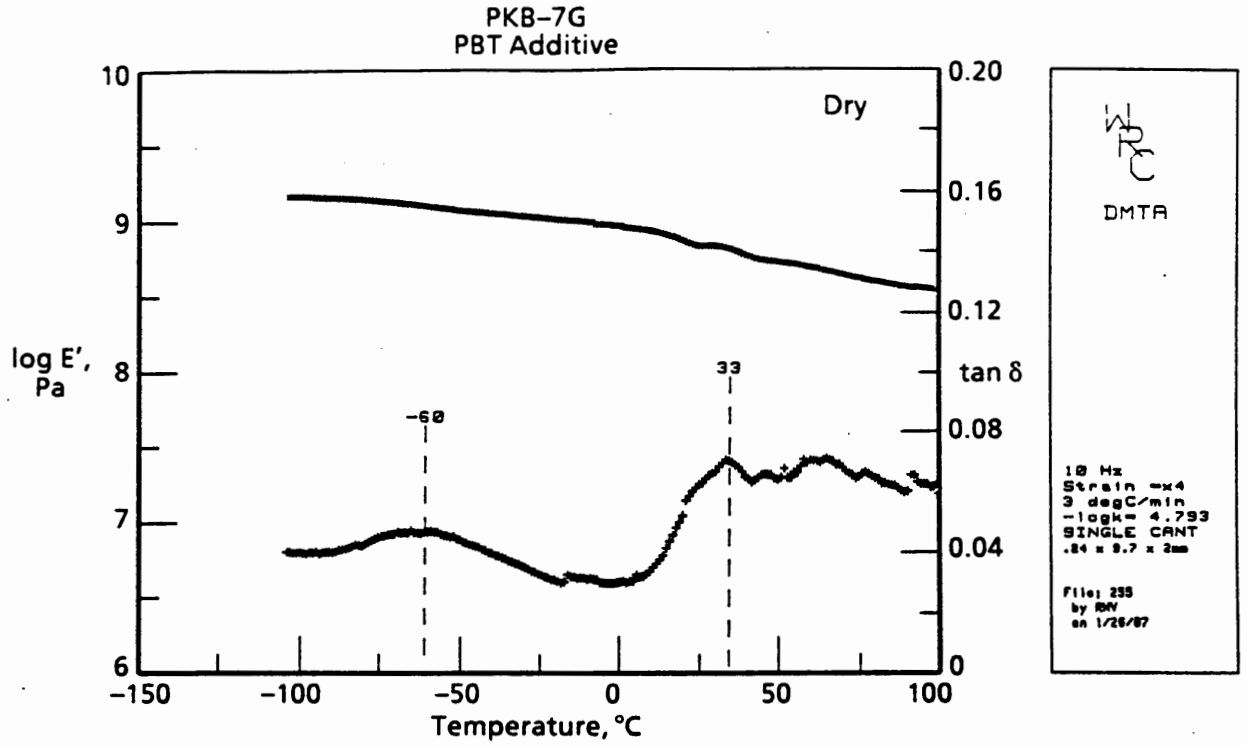


Figure 9-V. DMTA of Polyethylene Terephthalate Blend

011882-22



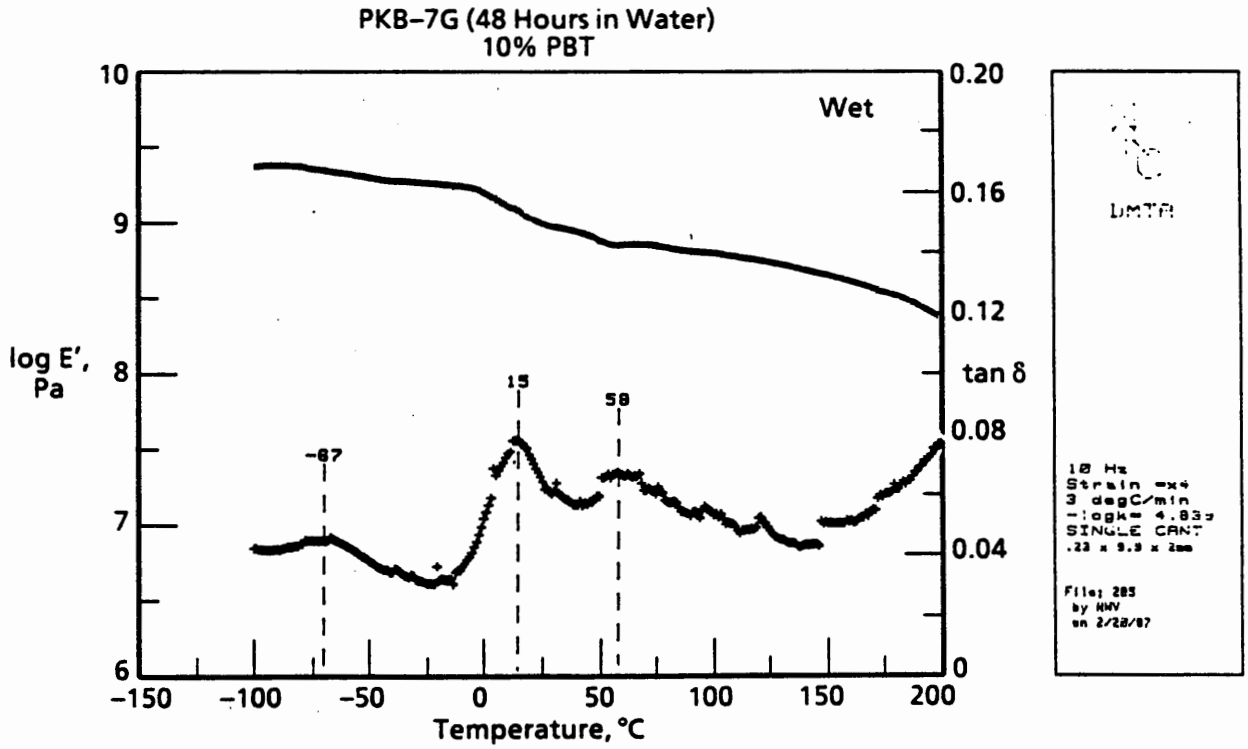


Figure 9-W. DMTA of Polybutylene Terephthalate Blend

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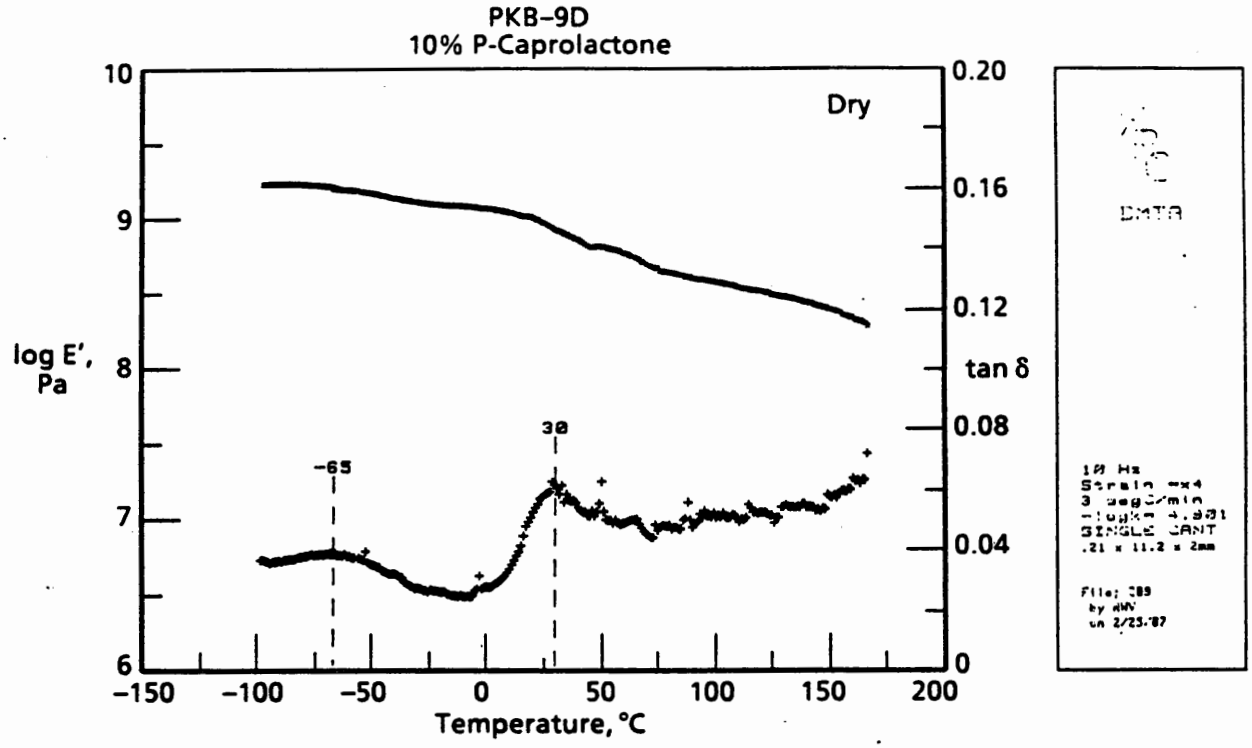

Figure 9-X. DMTA of Poly C_5 Ester Blend

011882-24

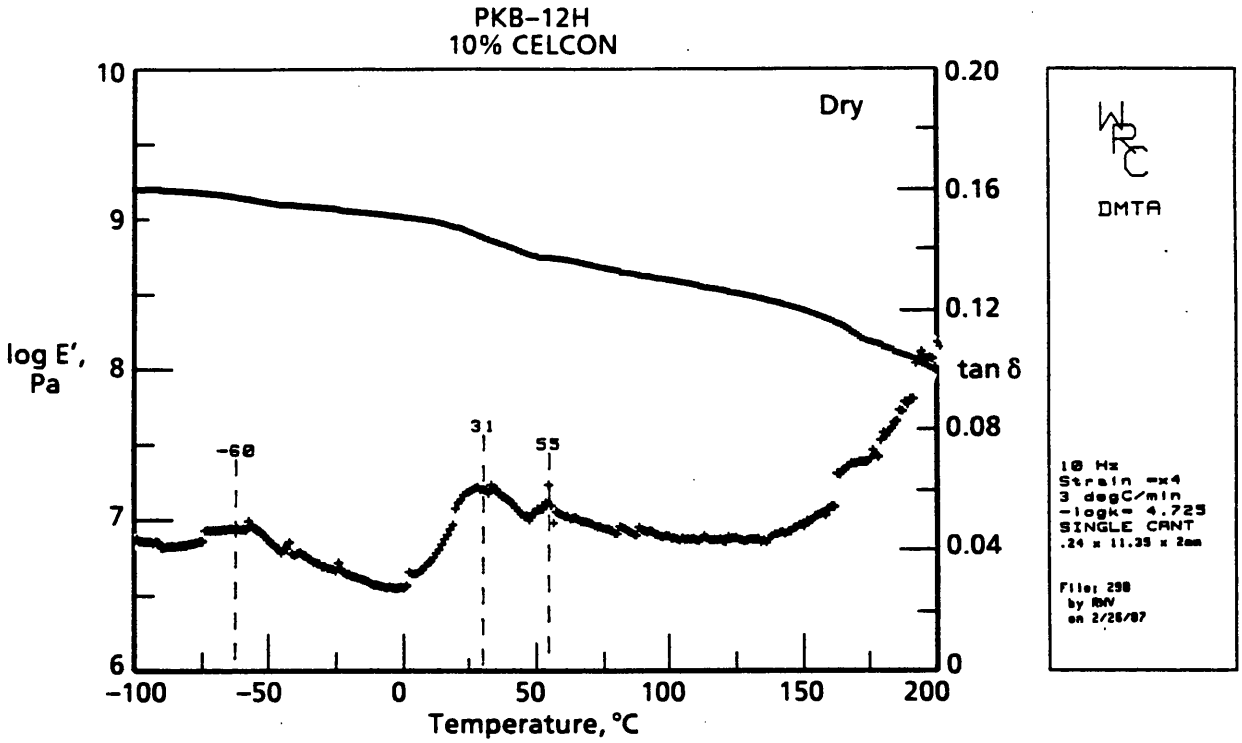

Figure 9-Y. DMTA of Polyacetal Blend

011882-25

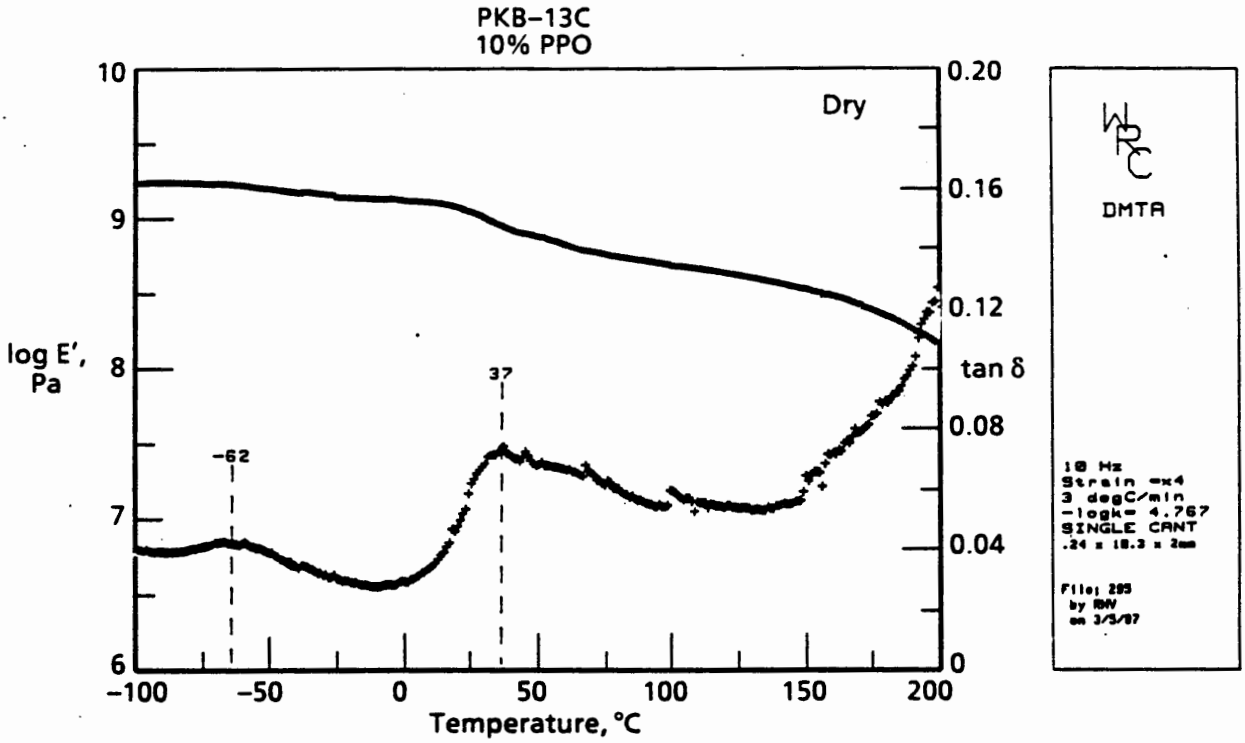

Figure 9-Z. DMTA of Polyphenylene Oxide Blend

011882-26

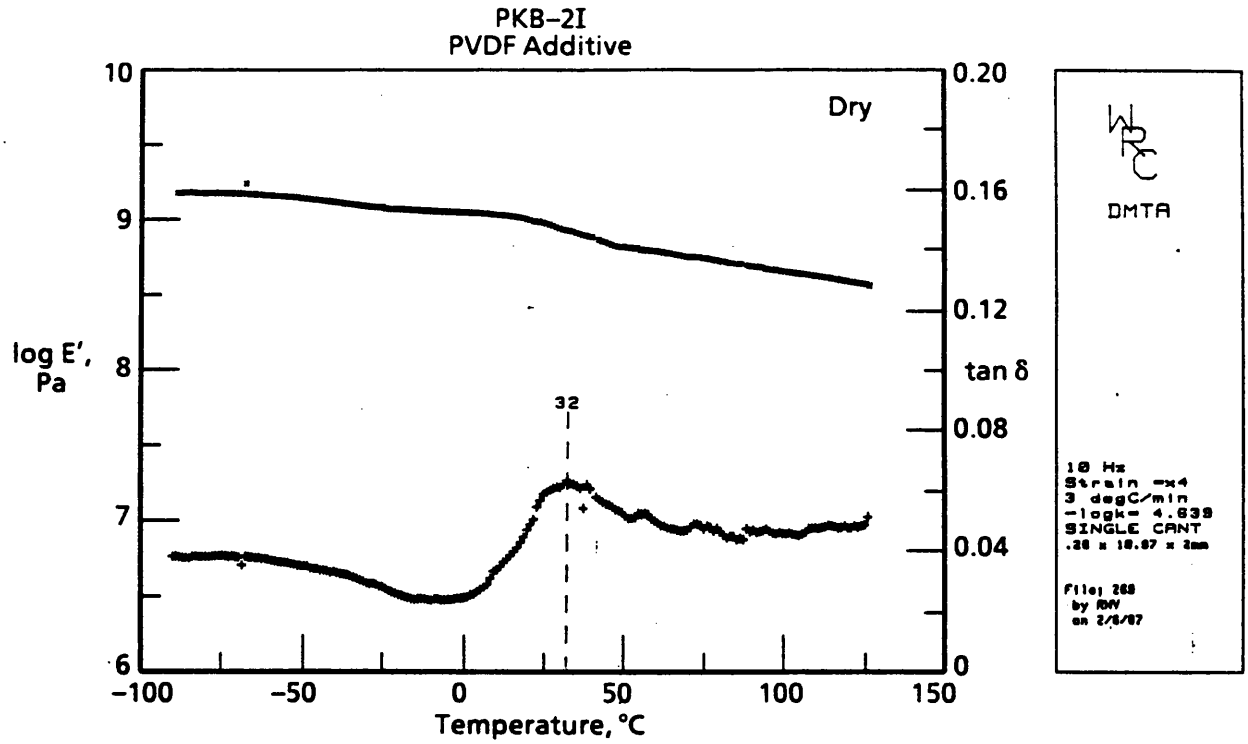

Figure 9-AA. DMTA of Polyvinylidine Fluoride Blend

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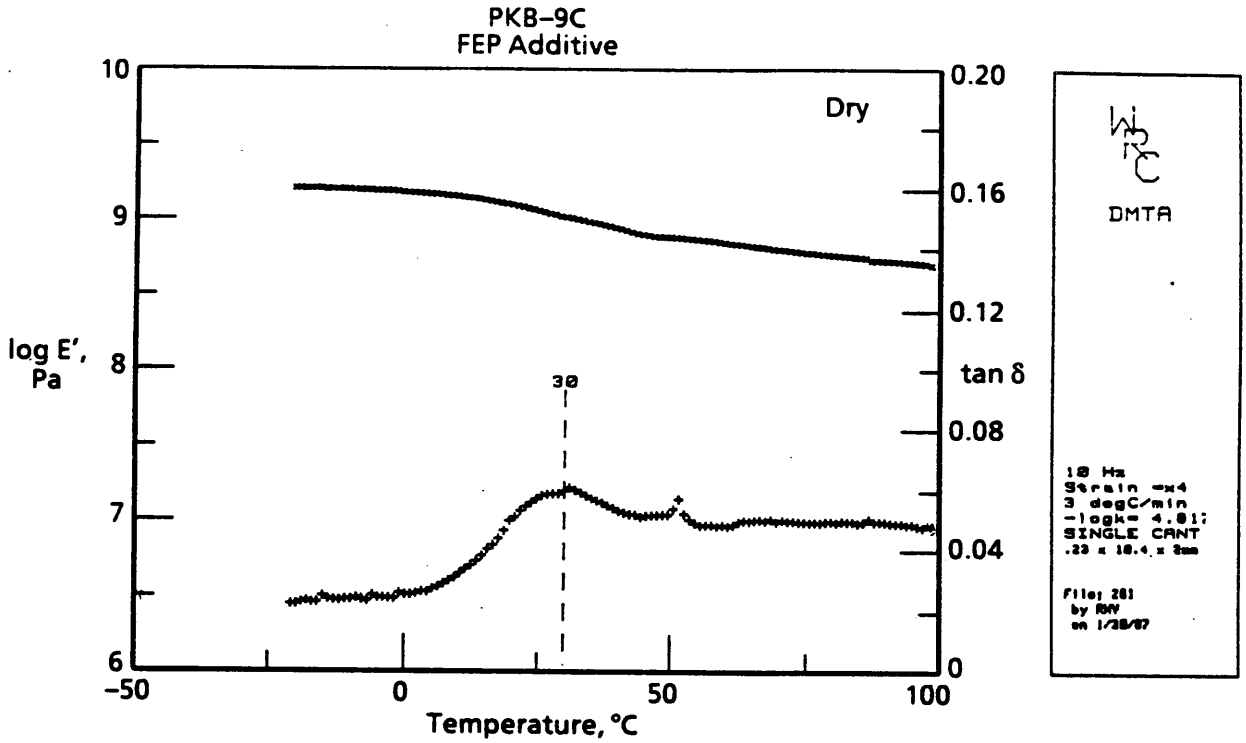

Figure 9-AB. DMTA of Fluorinated Polyethylene/Propylene Blend

011882-28

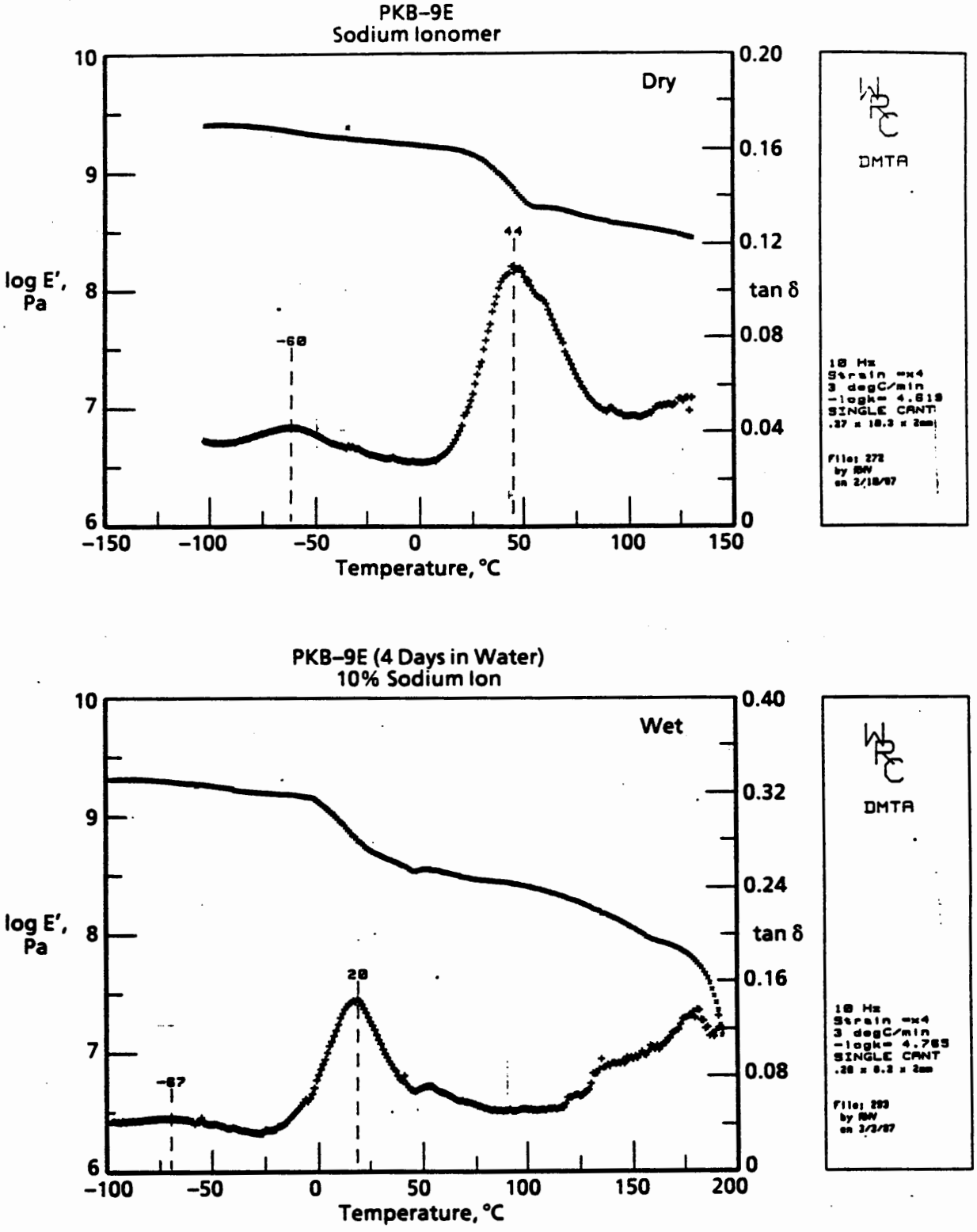

Figure 9-AC. DMTA of Sodium Ionomer Blend

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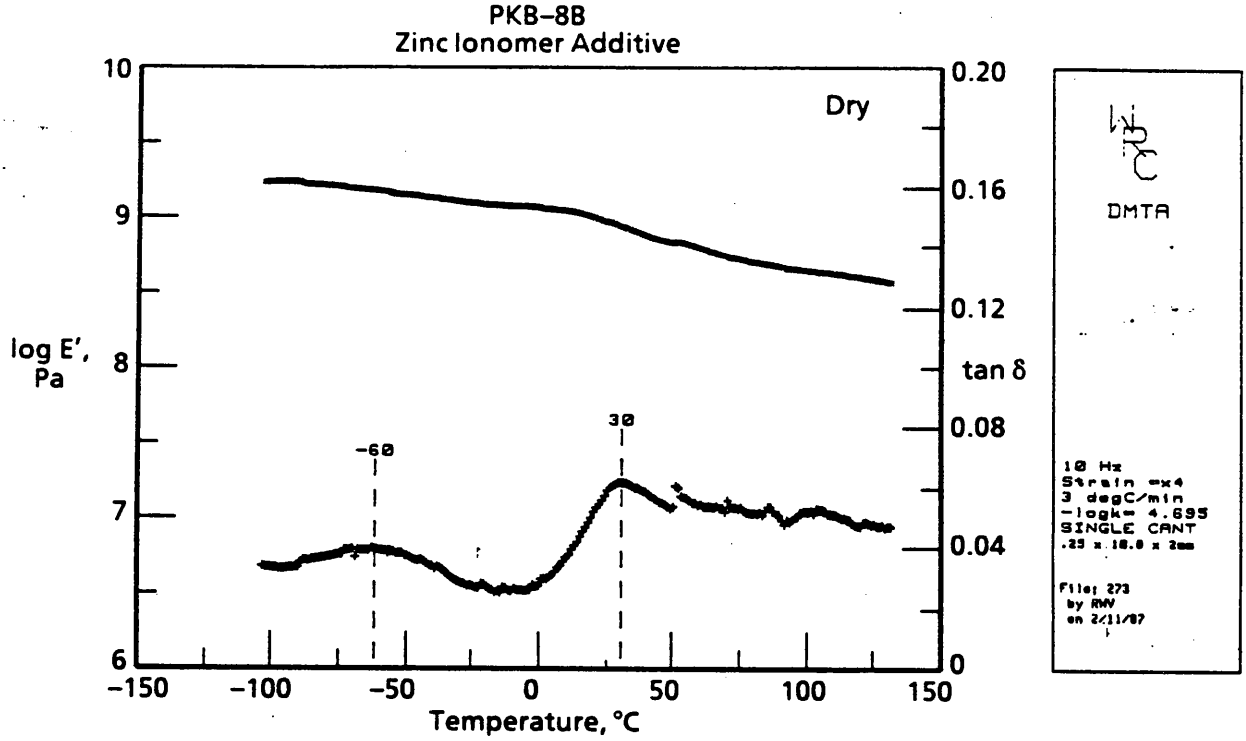

Figure 9-AD. DMTA of Zinc Ionomer Blend

011882-30

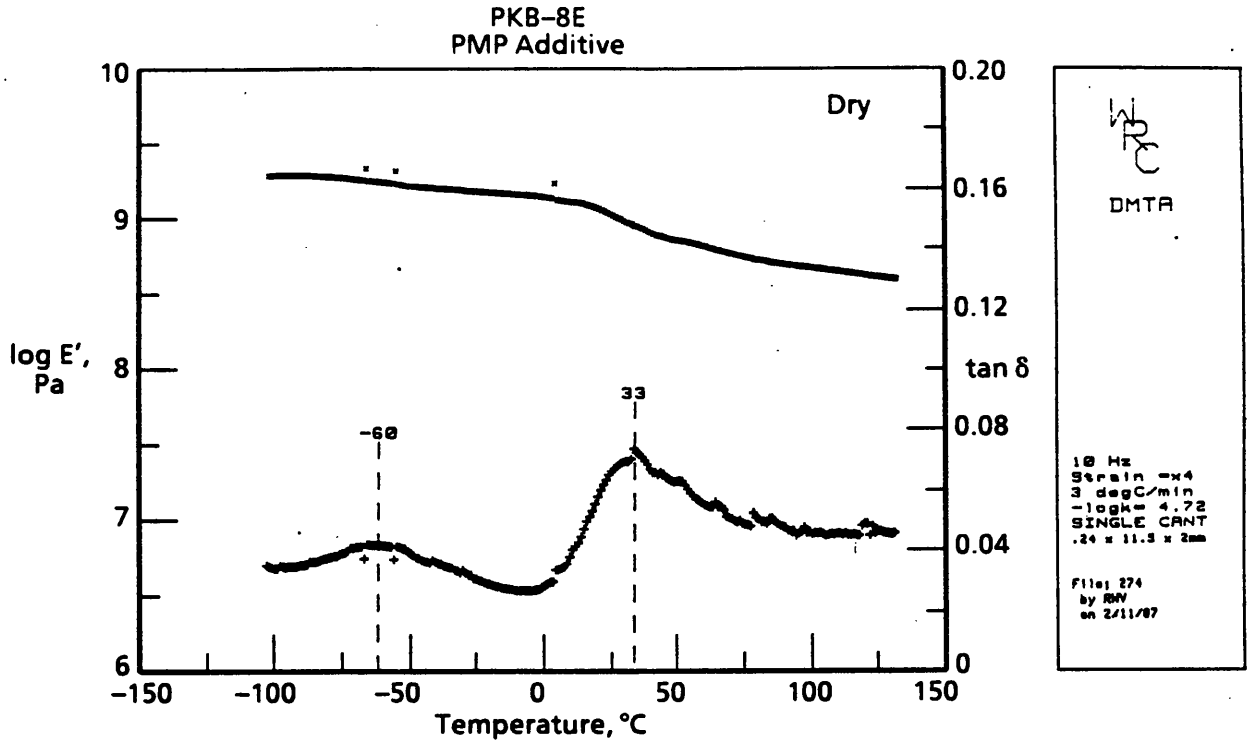

Figure 9-AE. DMTA of Poly-4-Methyl Pentene Blend

011882-31

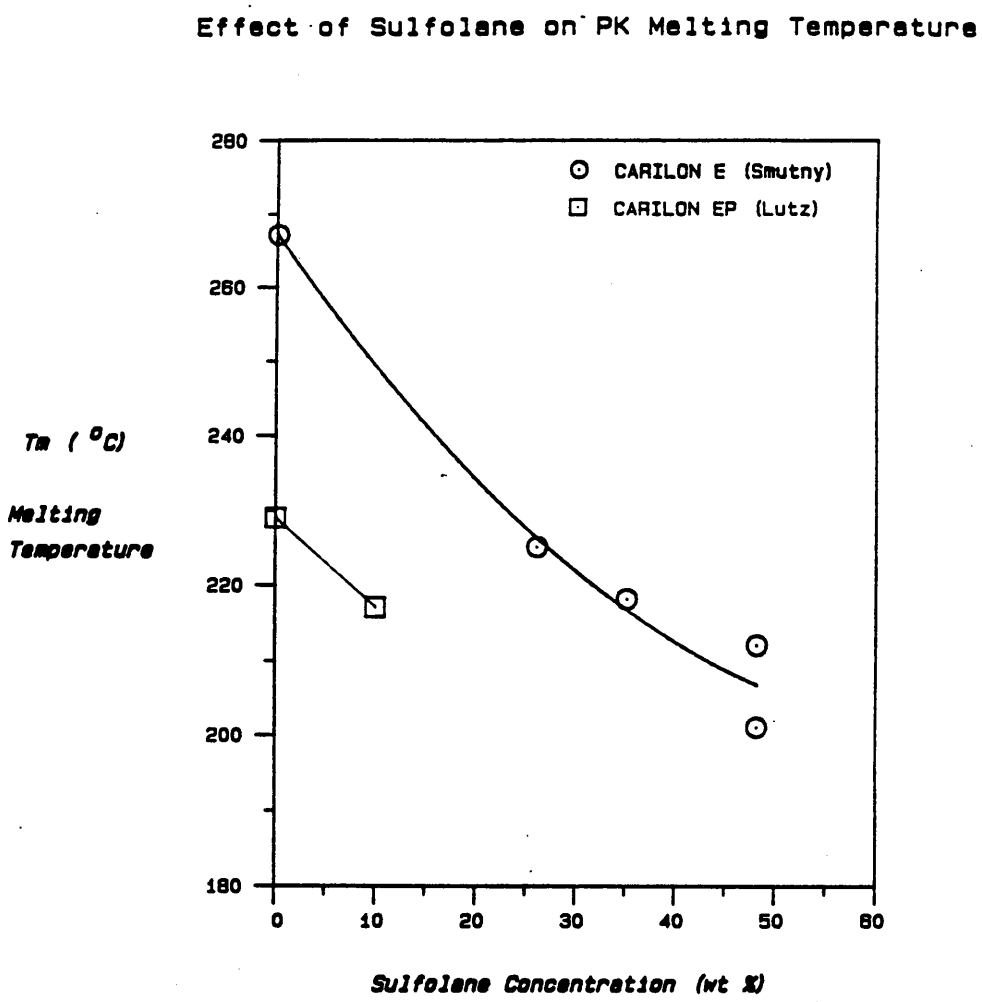

Figure 10. Effect of Sulfone Solvents on Polyketone Melting Temperature

011882

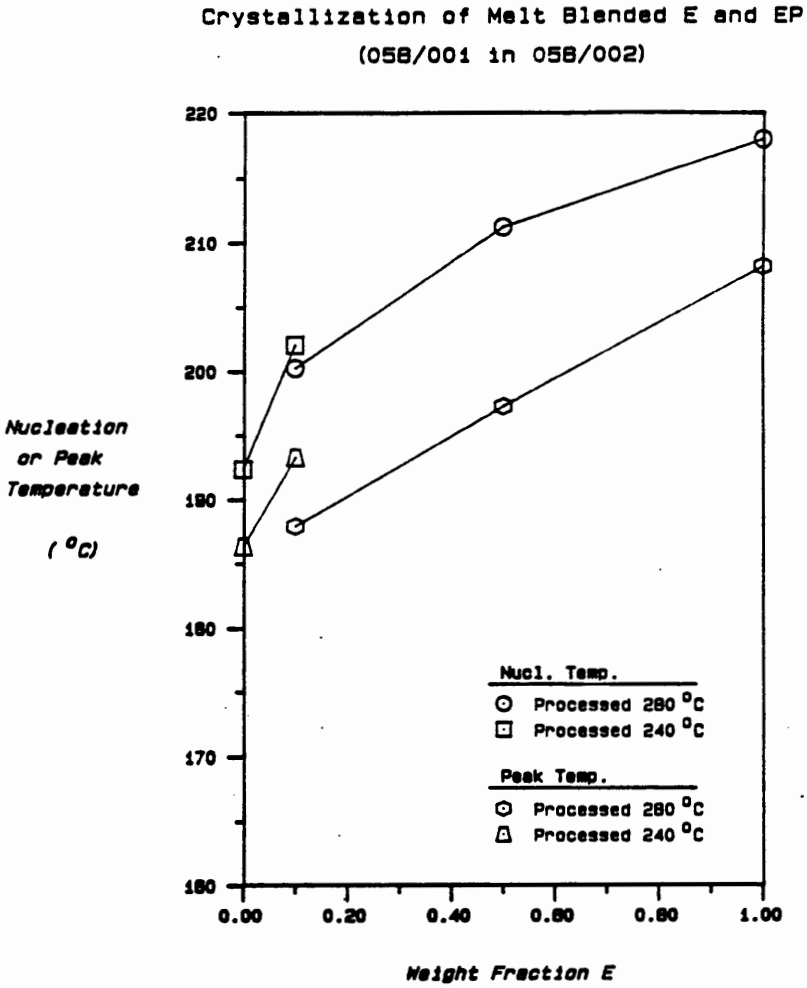

Figure 11. Crystallization Behavior of Polyketone Terpolymer-Copolymer Blends

011882

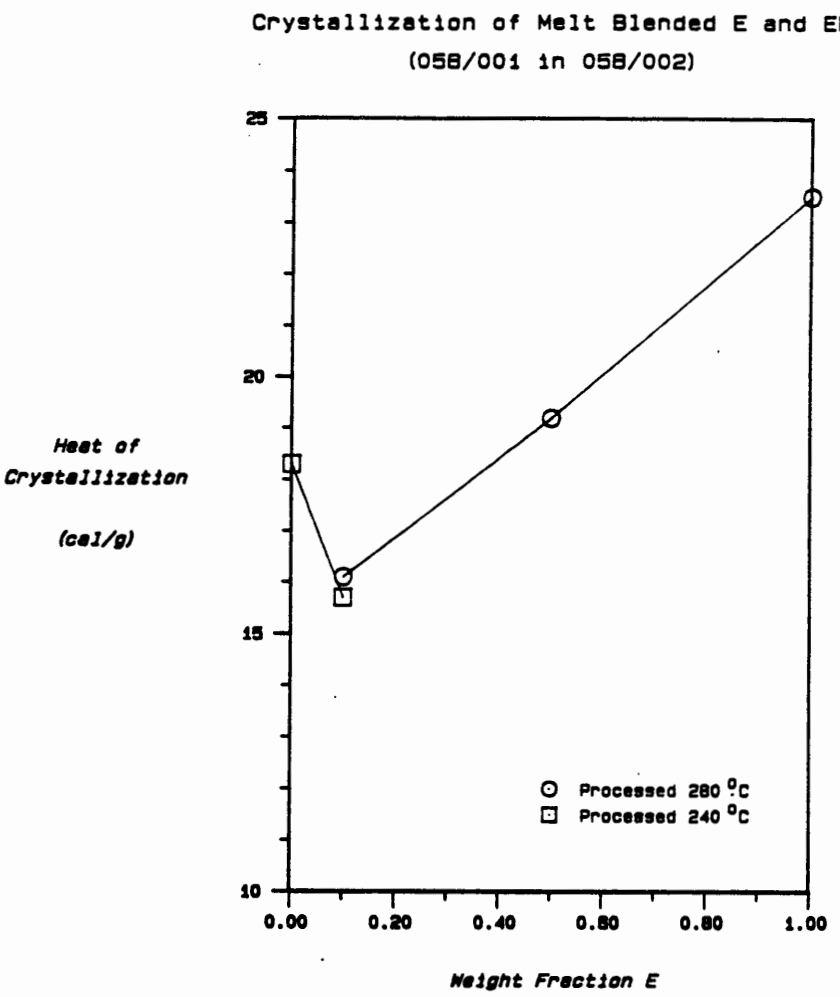

Figure 12. Crystallization Enthalpies of Polyketone Terpolymer-Copolymer Blends

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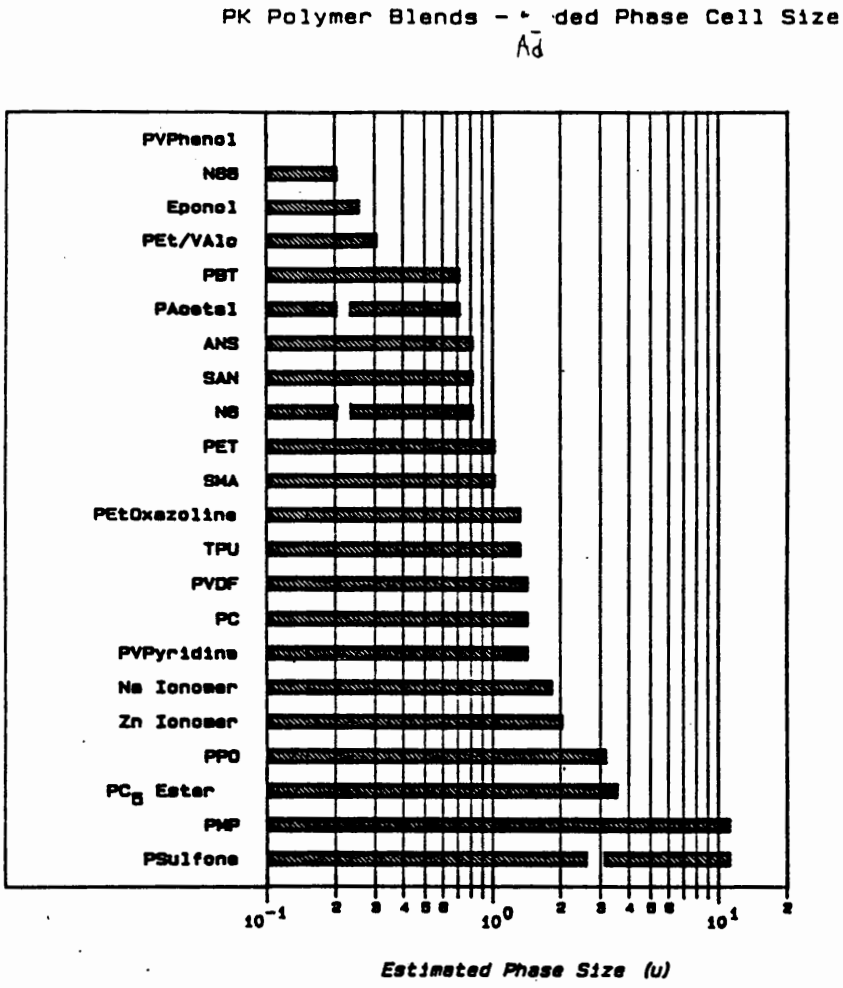

Figure 13. Phase Size of Various 10% Polymeric Additives in Polyketone Blends

011882

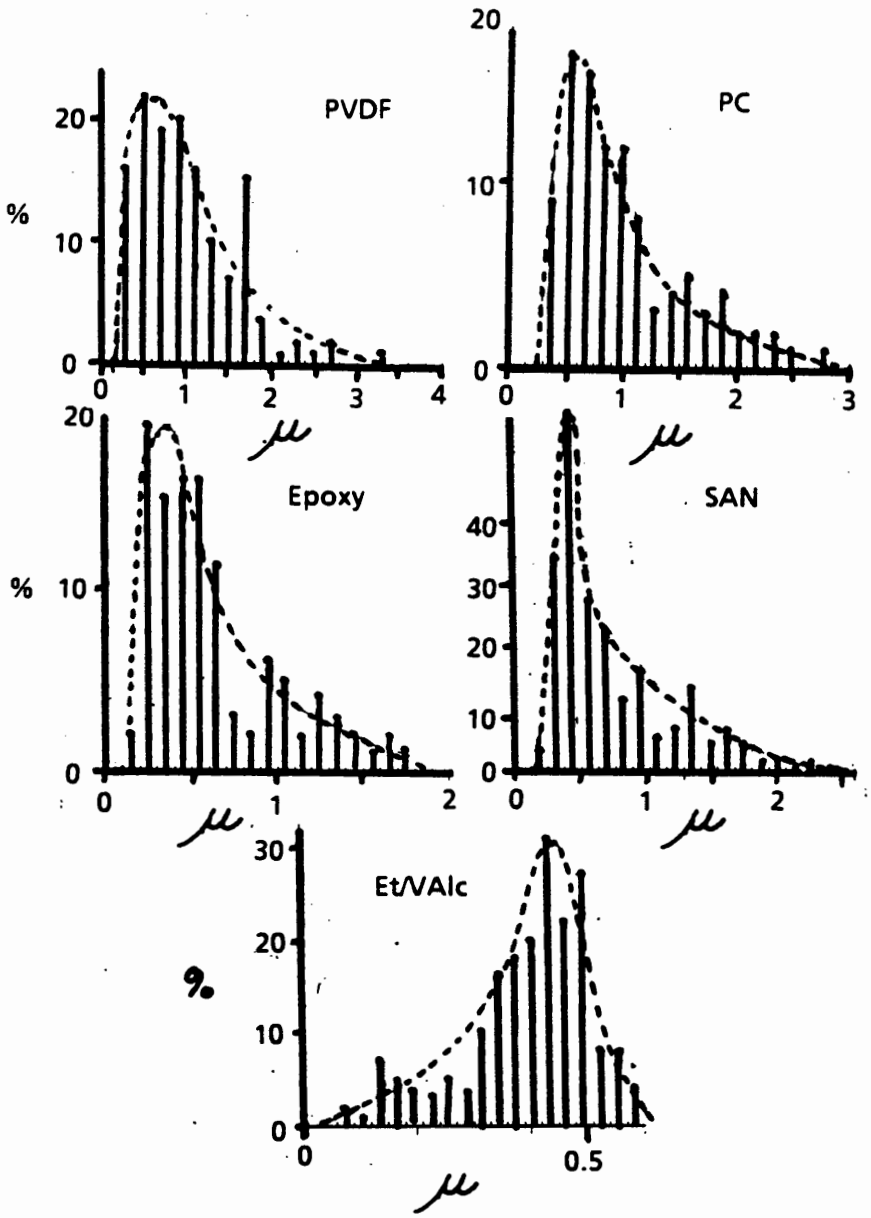

Figure 14. Phase Size Distribution by Image Analysis of Polymeric Additives in Polyketone Blends

011882

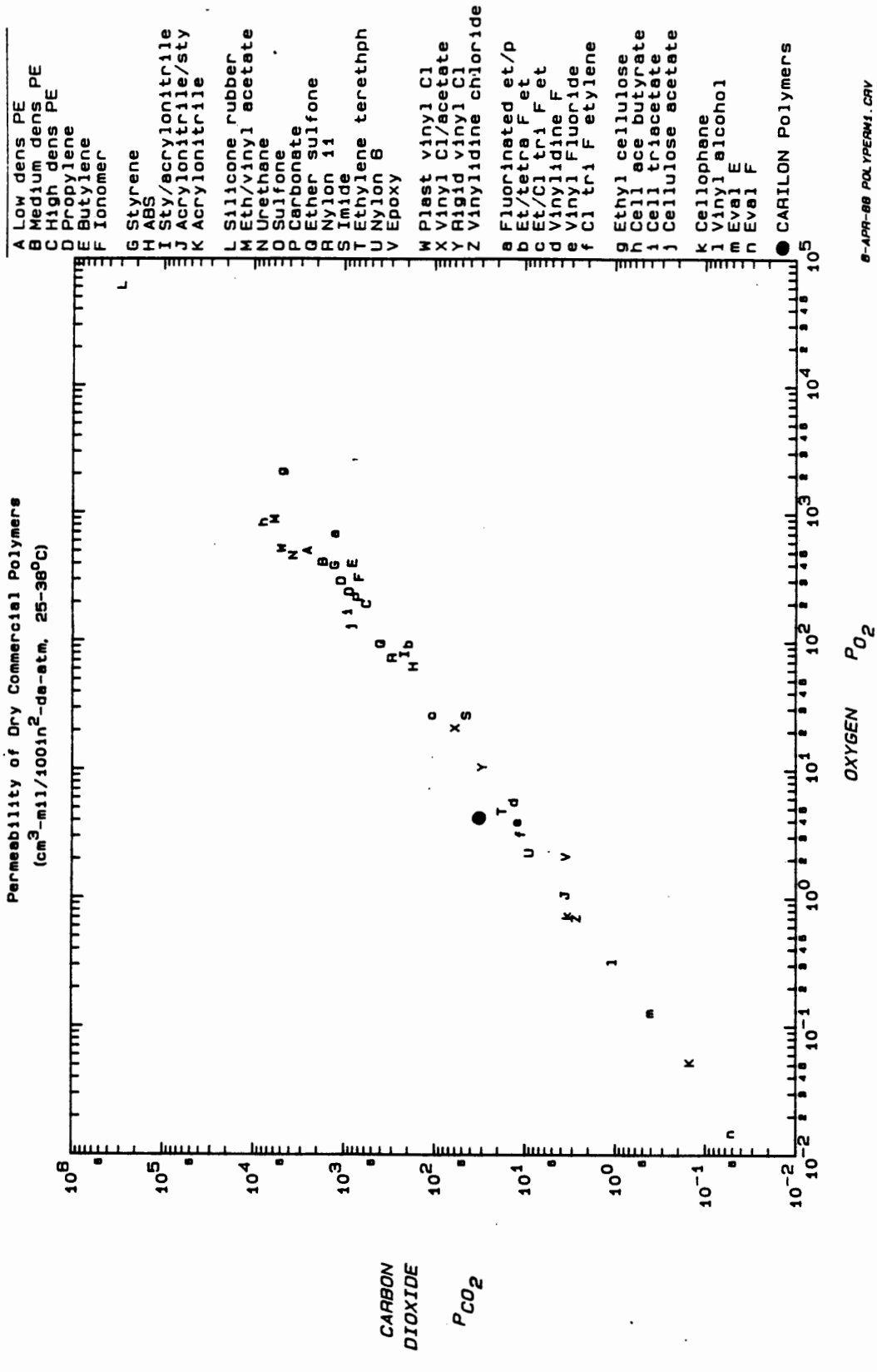

Figure 15. Comparison of Carbon Dioxide and Oxygen Permeability of Polyketone with That of Various Polymers

011882

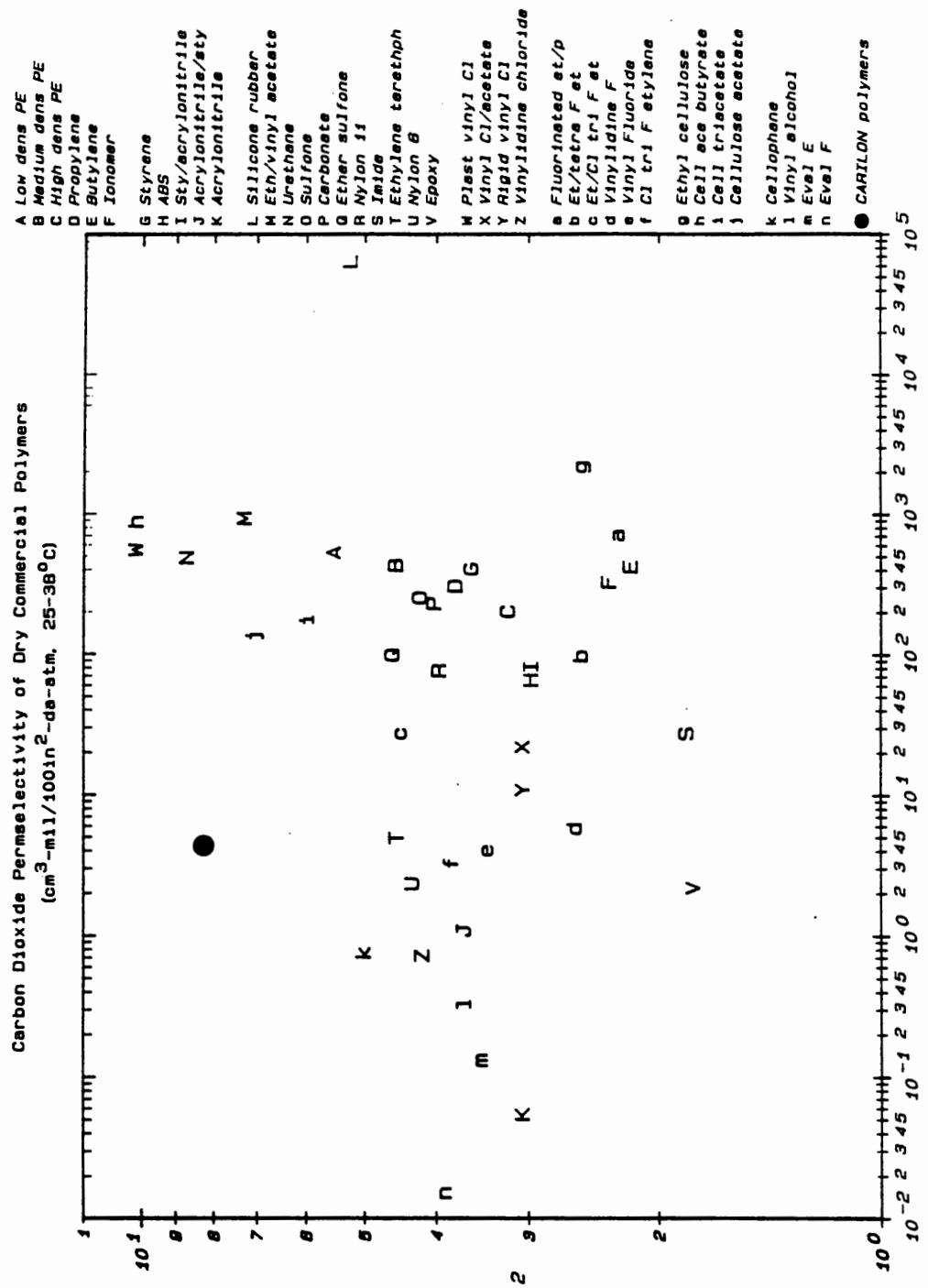

Figure 16. Comparison of Carbon Dioxide and Oxygen Permselectivity of Polyketone with That of Various Polymers

011882

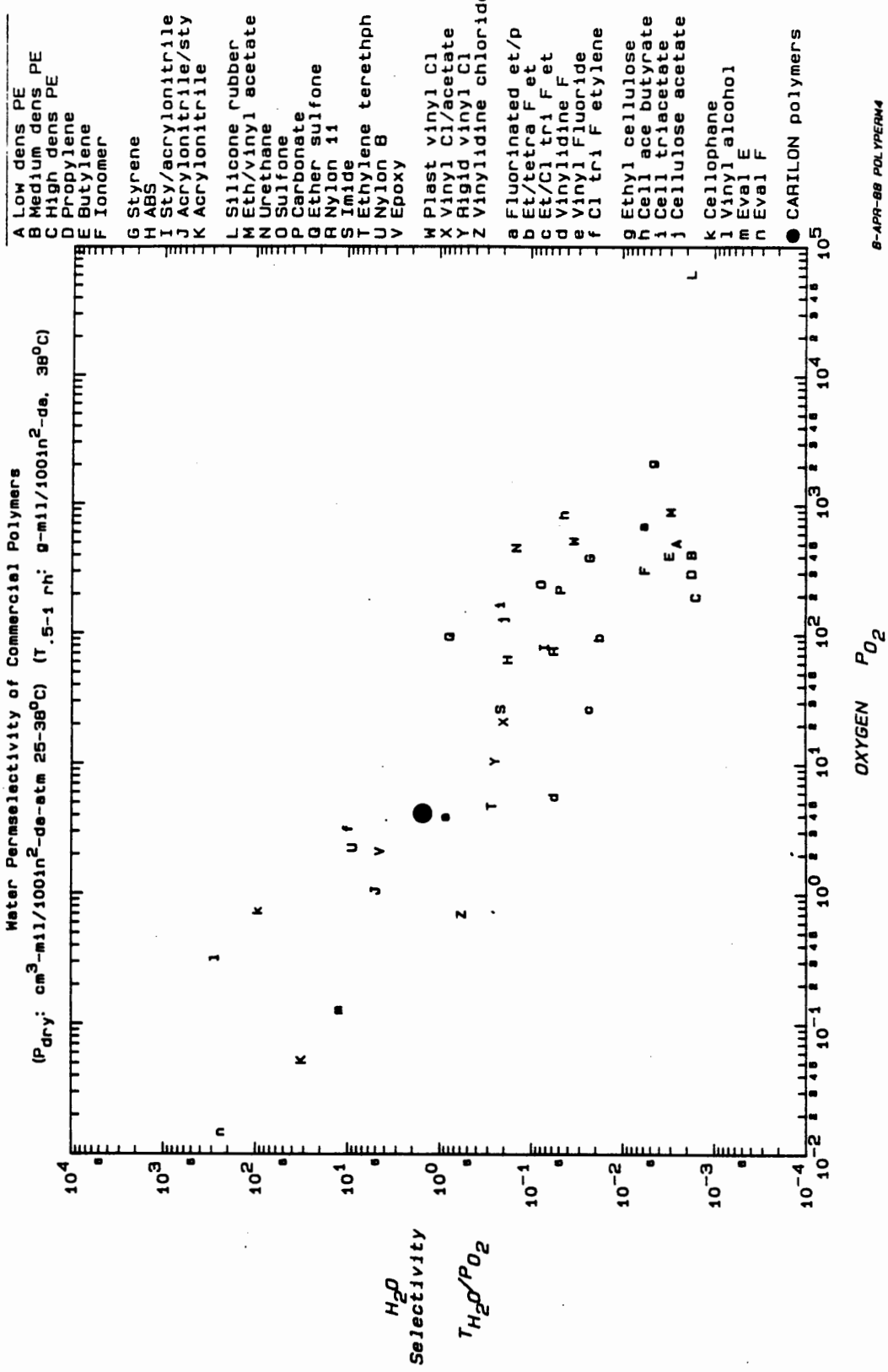

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Figure 17. Comparison of Water Vapor Permselectivity of Polyketone with That of Various Polymers

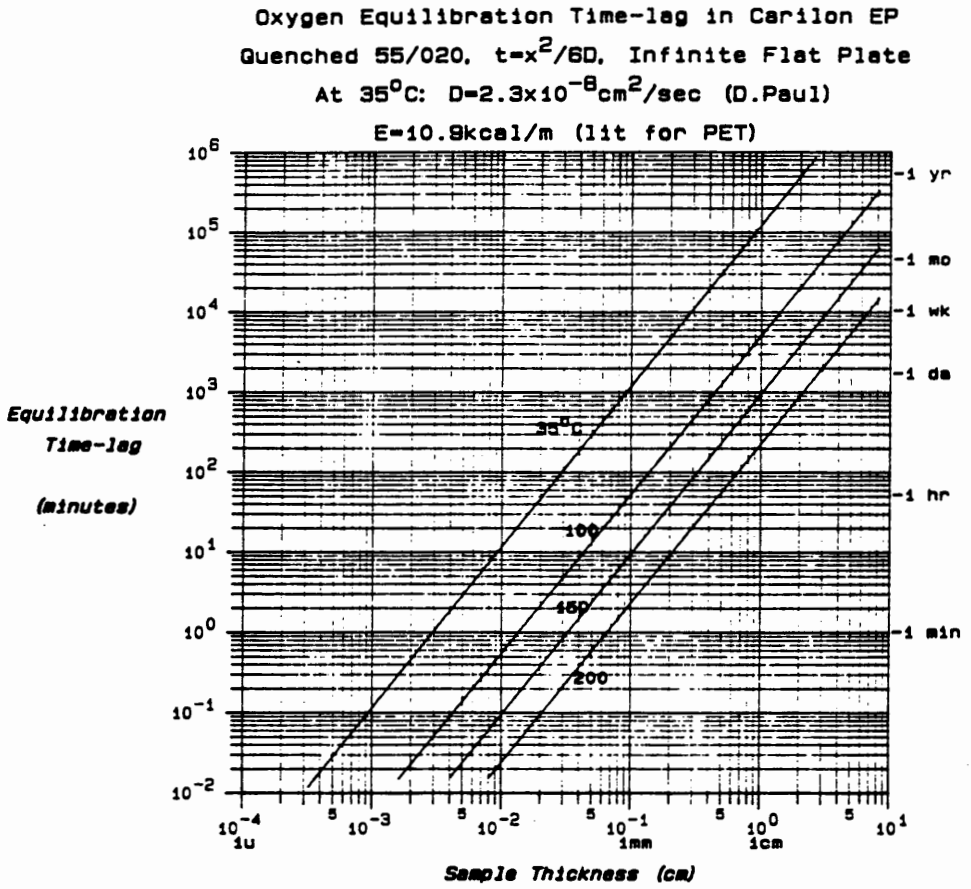

Figure 18. Model for Estimating Equilibration Time of Polyketone Specimens of Various Geometry at Several Temperatures

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Appendix

Appendix

BLENDING

Feed Preparation

The feed to the 15 mm twin screw machine has to be in the form of finely divided particles because of the small size of the hopper and throat. Low density PK powder will feed adequately without compacting. Blends were made by dry mixing PK powder with finely powdered additives. Polymers that come in the form of nibs had to be reduced in size prior to mixing with PK powder. A cryogenic grinder, purchased for this purpose by D. R. Stewart,[7] worked well with all of the polymers included in this study. Stratification of the mixes with PK powder was minimized by the use of an Accu-Rate, "flexible hopper" volumetric feeder, also obtained by Stewart.

When dry feeds were required, the PK portion was dried under vacuum at ambient temperature to prevent thermal degradation, for about 24 hours. Other components usually were dried together with the PK. Where the drying conditions suggested by the manufacturer for an additive were more severe than those used for the PK, that material was dried separately and mixed with the PK powder just prior to blending. Since the PK powder will re-absorb water quickly from the atmosphere, these "dry" runs can be assumed to have contained some low, but undefined level of moisture. One exception was the "bone dry" run, PKB 16F, where extraordinary care was taken to exclude all moisture.

Undried feeds were run without any effort to control moisture content. Generally, in such cases it can be assumed that the sample was probably equilibrated with ambient moisture at around 23°C and 50% relative humidity. This would suggest that the PK contained about 1–1.5% moisture.

Extruder

The extruder was a 15 mm Baker Perkins, low pressure type, twin screw internal mixer.[7] A description of the mechanics and operation of an 80mm BP, from which this version is a scale-down, has been described in detail elsewhere.[8a]

The screw configuration was fast-forwarding, single stage, with 16 cam pairs. Residence time distribution for this machine, running with PK, was established and also has been reported elsewhere.[9] The average residence time for most of the runs in the present screening study was about 30 seconds.

Atmosphere Control

Most of the runs in this study were made with the feed hopper, throat and barrel under an atmosphere of pure nitrogen. This was accomplished by the use of a nitrogen purge, introduced at the point where the feed flights of the extruder can be reached. This stream flowed counter-current to the falling stream of dispersed polymer powder, up the length of the throat, back through the feeder barrel, into the closed hopper and out through a constriction on the hopper lid. Although the blanket may not have been absolutely rigorous, it is believed to have been very effective. Since the feeds were finely divided powders, only a small amount of dissolved oxygen could have made its way into the extruder.

SPECIMEN PREPARATION

Compression Molding

Samples for this study were compression molded by conventional methods to thickness of 10 mil retarded quench or 30 mil rapid quench. The 10 mil samples were used for most of the testing whereas the 30 mil samples were used for burn and rheology measurements.

During earlier IPN studies using small samples of various compression molded polymers, particularly PP and PBT, it had been found by Lutz and R. P. Gingrich that mechanical properties can be dramatically affected by the technique used to solidify the sample and the orientation arising from the location in a plaque where the specimen was removed.

When a compression molded sample of polymer is quenched, the outermost layers are crash solidified. The interior regions, on the other hand, are much slower to cool because of the insulating effect of the outer incremental layers of polymer. As film thickness is reduced, the insulated, slow cooled "center cut" is progressively eliminated, eventually leaving only the outer skins to dominate the properties.

For compression molded specimens of polypropylene homopolymer which had been quenched against heavy aluminum, heat-sink plates for example, it was found that the Young's modulus dropped from its usual 200,000 psi to half that value as the film thickness was reduced to around 10 mils or less. This indicated that the quenched material is much more ductile than slow cooled polymer. In both PP and PBT, such results were traced to the formation of transcrystalline skins on the outer surfaces of the samples.

It was found that if the cooling rate of PP was about 20°C/min or less in the temperature region of crystallization, the low modulus skins did not form and the full modulus was obtained. This rate is similar to that of the standard cooling rate used in a DSC recrystallization. A "retarded quench" method was then developed that provides about the correct cooling rate and simulates the thermal history of a much thicker specimen.

Since the quenching method used for this type of specimen can be critical to morphology and degree of crystallinity, it was thought desirable to use a modified solidification technique for polyketone, where such effects have not been studied. Ten mil samples were preferred because they are more readily made bubble-free then thicker samples, although recent samples of PK are less prone to form bubbles during molding than the early materials. Also, Handlin has since shown that with PK the retarded quench often will not change the mechanical properties by very much from those obtained with a standard quench.[13]

Injection molded specimens are always highly oriented because the melt is being quenched while the material is flowing into the mold. It is often assumed that no significant orientation exists in compression molded films since the melt is more or less quiescent for a period of time prior to solidification. However, it was found during the PP and PBT studies that considerable residual orientation does remain in thin compression molded films, even with moderate molecular weight polymers, especially when a very long quiescent holding time is not being employed.

This amount of orientation can effect all mechanical properties. Apparently, complete melt relaxation requires a considerably longer time than is normally used. For PK especially, a long hold time in the melt is not feasible because of the severe degradation that would occur.

Physical property test results on compression molded polymer will depend on the mechanical test-direction relative to the melt flow-direction during molding, a function of exactly how the specimens are cut from the plaque. The portion of a plaque at the center, where the original mass of sample was placed in the mold, and the outer edges or any other poorly defined flow regions, should be discarded. Thus, only the remaining ring of material having uniform, well defined flow direction is suitable for testing.

The flow direction is from the center outward, perpendicular to the edges of the usable ring of material. In the PP/PBT studies, specimens were cut so that the test strain would be at an angle of 45° to the in-mold flow direction for all routine work, approximating an average of the perpendicular and parallel directions.

The retarded quench protocol used in all the blend screening experiments to simulate the center portion of a 1/8 inch thick, quenched specimen, giving a cooling rate of around 20°/min, is as follows:

Plates:	Chromium ferrotype, with 4 mil aluminum foil inserts.
Temperature:	240°C for terpolymer, 280°C for PK copolymer and other blends with high melting components.
Time:	1.5 minutes in the press, total.
Thickness:	Use large, 10 mil spacer window.
Quench:	The plates containing the molten film are taken from the press and quickly sandwiched between 1/8 inch Teflon sheets that had been preheated to the molding temperature. This configuration is then quenched by insertion between 1/2 inch aluminum plates at 22–25°C.
Specimens:	If mechanical properties are to be measured, special effort must be made to cut samples with consistent orientation with respect to flow direction, from the center outward. The center and edges of the plaque must be avoided.
Storage:	Specimens to be tested for mechanical properties were kept dry-as-molded by being sealed directly into paint cans containing molecular sieve. The can seals then are not breached until testing is to be carried out.

Moisture or Oxygen Equilibration

There often is a need to estimate the time required to equilibrate a specimen with water or oxygen. If anaerobic tests are to be performed, it is often desirable to diffuse all residual oxygen out of a sample. Because moisture is a plasticizer for water absorbing polymers, its presence can dramatically alter physical properties. In the interest of obtaining meaningful data, a known level must be maintained in such test specimens. Further, the water in a specimen must be uniformly distributed throughout the test piece.

For example, once a typical injection molded bar of nylon is exposed to significant amounts of moisture, the outermost incremental layers will be plasticized by absorbed water. Subsequently, it may require many months to a year at room temperature for the sample to completely re-equilibrate.[8d] The process can be speeded up by conditioning at elevated temperatures, but this procedure superimposes thermal annealing on the already complex sample history.

Polyketone not only is plasticized by up to about 3% water, but the time-temperature positions of the second order transitions are affected by water content. Profound effects of moisture on ultimate properties should be expected and results cannot be interpreted unless moisture is properly managed. With PK, increasing the temperature to speed equilibration also will speed chemical degradation processes, in addition to inducing physical annealing.

Since the equilibration time-lag will be proportional to the square of the sample thickness, specimen conditioning times can be very long indeed. Based on data from a number of sources, the diffusion constants and activation energies for oxygen and water in PK are believed to be similar. Using such data, and taking an activation energy from other similar polar polymers, it has been possible to construct an approximate diagram of 0.95 equilibration time, expressed as a function of specimen thickness and temperature, shown in Figure 18. (Of course, diffusion constant will be a

function of incremental water content, making the time-lag somewhat dependent on the particular conditioning sequence.)

Apparently, at ambient conditions, one can expect a 2 mm nib to equilibrate in about a week and a 10 mil film in several hours. Since the equivalent film thickness in a low bulk density PK reactor powder has been estimated from surface area to be on the order of 400A, or 4×10^{-6} cm, equilibration of a single powder particle with its surroundings will be essentially instantaneous. Thick beds of powder, of course, will require longer periods to equilibrate.

ANALYTICAL PROCEDURES

DSC

Many difficulties with the DSC technique were experienced during the course of the present studies. Various known and suspected substrate effects on PK melt made it difficult to select the proper DSC pan material for routine thermal analysis. Finally, the use of aluminum pans that had been "passivated" with a fluorophosphate treatment[16] was adopted, on the basis of extensive but still incomplete understanding of these substrate effects. This practice has since been abandoned in favor of untreated aluminum, and some of the repeat DSC results reported here were made with plain aluminum pans.

A protocol for sample preparation was adopted in which the polymer powder or very thin slices of consolidated material were to be exposed to a dry nitrogen atmosphere for 24 hours prior to being sealed into the DSC pans, still under nitrogen.

The 20°C/min thermal cycle was to be from ambient to 285°C, followed immediately by return to ambient, then again to 285°C where a 10 min isothermal soak was carried out, followed again by return to ambient.

The initial heat should indicate the condition of the sample resulting from its prior history. The quick excursion to 285°C was to obtain a clean cooling curve with only a short melt history, from approximately the processing temperature required for the high melting PK copolymer. The heat soak was intended to simulate a very severe processing history, albeit without contact with the ripened steel innards of a processing machine.

A type of DSC apparatus was used for these thermal analyses that did not have a capability for automated programming. Unfortunately, the thermal analysis group did not fully appreciate the subtleties of using the DSC as a chemical kinetics reactor. It is true, of course, that most common polymers submitted for analysis are chemically stable in the melt and heat soaking can be carried out in connection with nucleation. However, for the PK runs, reaction times at 285°C were not well controlled. As a result, much of the data eventually became suspect.

Repeat runs were carried out on many of the blends that originally showed poor recrystallizability after heat cycling. Wherever these gave higher results, they were substituted for the originals. Far too much had been invested in the hundreds of analyses to justify repeating them all. Therefore, the DSC results in this report must be taken with reservations, especially where melt instability is indicated by low recrystallizability. Also, the use of non-fluorophosphate passivation has not been tracked in the DSC data given in this report.

Another problem that was encountered with the DSC results was a higher enthalpy on solidification than on the preceding melting, sometimes by as much as 20%. Normally one would expect about 5–10% lower values, due to delayed crystallization and annealing. This must have been caused by some peculiarity in the DSC traces that prevented analogous placement of the baselines, on which areas under the peaks are based.

Severe baseline drift and slope was also encountered throughout the period when data were being gathered for the present study. This problem not only reduced the accuracy of results, but sometimes resulted in incorrect or uninterpretable enthalpies of crystallization or fusion.

It has subsequently been established that the fluorophosphate pan treatment caused fouling of the DSC calorimeter, resulting in at least some of the erratic baseline behavior.[16] This fouling required frequent clean-out and recalibration, a laborious and time consuming chore. The policy at this writing is to use plain, untreated aluminum pans for PK thermal analysis.

As is common with other polymers, nascent powders and samples crystallized from solvent solution have higher degrees of crystallinity than melt recrystallized analogues, even in the absence of any melt degradation.

However, many of the PK DSC thermograms have features that are not readily explained. Strange shoulders, odd small peaks and narrowing of the peaks have been observed with many of the PK samples examined. Among other consequences, these subtle changes in peak shape alter the temperature positions reported for the peaks. The samples have seen various treatments, or no treatment, and no satisfactory explanations to explain these features has been forthcoming.

Rheology

Rheology measurements were carried out on a Rheometrics parallel plate rheometer. Most were run using aluminum plates that had been passivated with the fluorophosphate treatment mentioned under the DSC procedure,[16] an expedient practice but one with uncertain consequences to melt chemistry. The technique, still under development by W. P.Gergen, will be reported in detail in the future.

Oven Life

Oven life was determined by the finger bend embrittlement test first adopted by H. J. Syrier, KSLA, for quick screening of PK samples. 10 mil specimens were aged in a circulating oven with high make-up, ambient, laboratory air. Temperatures were held to within less than 1°C except for the brief periods when the oven doors were opened to remove samples. Overshoot when the oven re-equilibrated after opening was determined to be minimal. Samples were examined for embrittlement each day, after having been allowed to cool to ambient temperature for 15 min.

The oven life was reported as one day prior to the day on which failure was determined to have occurred. Measurements were made at 100, 120 and 140°C. However, only the 100°C measurements are used in this report. Accuracy of the test has been determined to be $\pm$ 1 day.

Color

Color measurements were carried out on a Gardner XL-800 tristimulus colorimeter. A special 1 cm orifice was made from flat black paper and the device standardized by reflectance through this orifice to the white calibration plaque. Yellowness index was then determined on 10 mil polymer films, backed with the calibration plaque.

Burn

Combustion was carried out in a standard ASTM Limiting Oxygen Index apparatus, using a non-standard test procedure. The test samples were half centimeter wide strips of 30 mil thick compression molded polymer. The retarded quench was not used for making these films. The samples were mounted vertically and lighted at the top with a small gas flame.

All burns were made in 19.5% oxygen atmosphere, which had first been determined to give marginal burning rates, but still extensive total combustion using control PK samples. It was assumed that any significant flame retardant activity in the blends would be detectable.

Solubility

Solubility in HFIPA was determined by placing small pieces of the 10 mil thick polymer films in vials containing the solvent at room temperature, for 24 hours. The solutions or suspensions then were examined subjectively for appearance.

Electron Microscopy

Microtoming, decorating and preparation of the STEM photomicrographs were carried out by J. E. Cox. Notes on the STEM results on natural and Ru stained microtomed samples are shown in Table 9. At first, samples of PK and its blends were microtomed from the extruded nibs either at ambient temperature or cryogenically. Since the cold-cut samples gave consistently better results, the cryo-technique was subsequently adopted as standard.

Where electron absorption is higher or lower in the added polymer than in PK, unstained cuts gave good contrast. Ruthenium tetroxide staining, instituted at WRC by D. L. Handlin, was found to markedly darken the PK polymer phase, while affecting the added polymers to varying degrees. This treatment usually gave good or adequate contrast with the other polymer phases if the natural contrast was insufficient. However, in the case of FEP, the electron opacity of both the natural and stained blends were similar, and the phases could not be well resolved by either technique.

Many of the micrographs appeared to have consistently good contrast and appeared to be suitable for automated computer analysis. Indeed, five of the blends were examined successfully by image analysis, as discussed in the text under Results, Polymer Additives, Phase Size, and shown in Figure 14.

Dynamic Mechanical Spectroscopy

The DMTA mechanical spectrometer was purchased, and its adaptation to PK was carried out by D. L. Handlin.[14] Several problems had not been completely resolved when the tests reported here were carried out. The most severe, had to do with the mechanical clamping of the 30 mil thick specimens. Slippage caused some erratic behavior in the results and also prevents the determination of absolute modulus.

When samples were to be run dry, it was necessary to get the specimens mounted and the temperature lowered very quickly. This is necessary because of the rapidity with which equilibration of 10 mil films with ambient humidity occurs at room temperature. Mounting of the specimens took only about two minutes. That, together with subsequent cooling to -80°C where the tests were begun, was completed in less than about 10 min.

MATERIALS

Polyketone Polymers

grade	type	CARILON polyketone form	LVN_{60}	T_m (°C)	Antioxidant
055/022	terpol	p	2.33	233	> 0.2 Irg 1076
056/001	copol	p	2.46	257	> 0.2 Irg 1076
056/002A	terpol	p	1.48	221	> 0.2 Irg 1076
056/002B	terpol	p	1.72	225	> 0.2 Irg 1076
056/003	anaerobic ter	p	1.72	223	> 0.2 Irg 1076
087/002	terpol	n	1.29	220	> 0.5 Irg 1076, 0.2 Ionol (plus 0.3 added Ethanox 330 in this report)

p = powder
n = nibs

Particulates

$CaCO_3$ Pfeizer MM, extremely fine - ~700 angstroms.
Basic Al_2O_3 Aldrich 19944-3 (G. B. Klingensmith)
Acidic Al_2O_3 Aldrich 19996-6 (G. B. Klingensmith)
Zinc oxide grade unknown.
Talc Cypress Minerals, Beaverwhite
TiO_2 du Pont, TiPure R-101
Carbon Black Whitco, Cotinex N330 Neutralized to pH 8. (Andrei Filippov, Brent Ruggles, WRC)
Bentonite untreated clay, grade unknown.
Graphite Thiocol, Alpha Prod. 00641 t2N5 (E. J. Smutny)

Chemicals

Irganox Ciba Geigy:
- 565 (hindered phenol-thioether-triazole)
- 1010 (hindered phenol-ester)
- 1076 (hindered phenol-ester)
- 1425 (hindered phenol-Ca phosphonate)
- MD 1024 (hindered phenol-hydrazid)

Tinuvin Ciba Geigy:
- 770 (aliphatic, (hindered) secondary amine)
- 327 (hindered phenol-triazole)
- 144 (hindered phenol-hindered amine-ester)

Ethanox 330 Ethyl Corp (hindered phenol)
Ionol 330 Uniroyal
Stearamide Ashland Chem., Adogen 58
EDTAA Ciba Geigy, Sequestrene AA (supposedly ethylene diamine tetraacetic acid, but our sample was the sodium salt.)
NBC du Pont, Trylex 86752
Zn Stearate ICN Biomedicals, 20030x
Na Stearate ICN Biomedicals, 22828x

Solvents and Oligomers

	Estimated Mole Wt.	T_g (C)	T_m (C)
pentaerythritol Aldrich, P474-5 (aliphatic alcohol)	136		260
C4 sulfone Shell Chemical Sulfolane W (aliphatic sulfone) (E. J. Smutny, WRC)			XXX
diphenyl sulfone Aldrich, P 3535-9 (aromatic sulfone) (E.J.Smutny, WRC)			125
epoxy Shell Chem, EPON 1009 (EPCH-BPA oligomer)	4,000	86	-
PEG Polyethylene glycol, 5000 (E. J. Smutny, WRC)	5,000		69

Asphalt (C. L. Nielsen, WRC):

- sour Shell Oil, W-36 Wood River AC-20 paving asphalt ex Maya/West Texas mixed sour.
- blown Shell Oil, L 1712 W-370 air blown to 229°F softening point.
- flux Shell Oil, W-370 Deer Park roofing flux ex Yates crude.

Polymers

	Estimated Mole Wt.	T_g (C)	T_m (C)
PEOx Dow, XAS-10874.01 (Poly ethyl oxazoline)		59	
N6 Allied, Capron 8552 (nylon 6)			225
N66 du Pont, Zytel 101 (nylon 66)			258
TPU Dow Pellethane 2103 80AE (thermoplastic p urethane)	40,000	-	159
PVPhenol Polysciences, Cat.# 6527 (polyvinyl phenol((D. L. Handlin, WRC)	4,000	150	-
PVPyridine MP-Dajac, Cat.# 8573 (polyvinyl pyridine)		71	-
PBPA Shell, Eponol 53-L-32 (solvent removed) (linear polyhydroxy ether of BPA)	80,000	100	-
PEt/VAlc Kurray, Eval F (copolyethylene/vinyl alcohol)	80,000	-	189
ANS Sohio, Barex 210 (copolystyrene/~2/3 acrylonitrile)	100,000	88	-
SAN Dow, Tyril 100-27 (copolystyrene/~1/3 acrylonitrile)	120,000	112	-
SMA Arco, Dylark 332 (maleic anhydride derivatized polystyrene)		XXX	
PSulfone Carbide, Udel P-1700 (poly aryl ether [BPA] sulfone)		190	
PC Mobay, Merlon M-40 (BPA polycarbonate)			149

Polymers (Cont'd)

	Estimated Mole Wt.	T_g (C)	T_m (C)
PET Celanese, Celenex 2113 (polyethylene terephthalate)		90	259
PBT GE, Valox 310 (polybutylene terephthalate)	30,000	(36)	228
C5 Ester Carbide, PCL P-300 (polycaprolactone)			58
PAcetal Celanese, Celcon M-90 (polymethyl ether copolymer)			XXX
PPO GE, 0.46IV (no polystyrene) (polyphenylene oxide)		215	
PVDF Pennwalt, Kynar 460 (polyvinylidine fluoride)			165
FEP Polysciences, 4615 (fluorinated ethylene propylene polymer)			260
Na Ionomer du Pont, Surlyn 8528 (Na salt/free carboxylic acid ionomer of PE)	100,000	-	101
Zn Ionomer du Pont, Surlyn 7930 (Zn salt/free carboxylic acid ionomer of PE)	100,000	-	101
PMP Mitsui TPX MX 004 (poly 4-methyl pentene, contains processing aids)	150,000	-	228

GLOSSARY

ANS	Copoly AcryloNitrile/Styrene.
AO	AntiOxidant, usually hindered phenol.
CARILON® polymer	Shell tradename for linear, alternating polymers of carbon monoxide and olefin(s).
dynamic vulcanization	Crosslinked in a shear field, breaking down the gel to "rheological units", see *e.g.* M. Mooney, J. Appl. Phys., **25**, #9, 1098 (1954), and **27**, #7, 691 (1956).
C_5 Ester	Polycaprolactone.
cell	Unit of dispersed phase observed by electron microscopy.
DMTA	Dynamic mechanical spectrometer, see reference [14].
DSC	Differential Scanning Calorimetry.
EDTAA	Ethylene Diamine TetraAcetic Acid.
ETP	Engineering ThermoPlastic.
FEP	Fluorinated Ethylene-Propylene polymer.
HFIPA	HexaFluoro IsoPropyl Alcohol.
IPN	Interpenetrating Polymer Network.
KG-MA	KRATON® G Elastomer – Maleic Anhydride graft polymer.
KRATON G 1651	The highest molecular weight grade of S-EB-S, does not undergo viscous flow even above 300°C (S-EB-S I in reference [6]).
LVN_{60}	Limiting Viscosity Number, 60°C in m-cresol. Conversions are as follows: LVN_{100} (m-cresol) x 0.81 = LVN_{60} (m-cresol) LVN_{HFIPA} (35°C in HFIPA) × 0.91 = LVN_{60} (m-cresol)
matrix morphology	Microscopic structural component having concave surface, see reference [8c].
N6	Nylon 6.
N66	Nylon 6/6.
NBC	Nickel diButyl dithio Carbamate.
OIT	Oxidation Induction Time by a high temperature DSC technique.
P–	Poly–
PB	Poly Butylene
PBPA	Poly BisPhenol A hydroxy ether, EPONOL resin.
PBT	Poly Butylene Terephthalate.
PC	PolyCarbonate.

GLOSSARY (Cont'd)

PE	Poly Ethylene
PEG	Poly Ethylene Glycol.
PEOx	Poly Ethylene Oxazoline.
PET	Poly Ethylene Terephthalate.
PEt/VAlc	CoPoly Ethylene/Vinyl Alcohol.
PMP	Poly 4-Methylene Pentene.
PP	Poly Propylene
PPO	Poly Phenylene Oxide.
PS	Poly Styrene
PV-	Poly vinyl-
PVDF	Poly VinyliDine Fluoride.
PK	CARILON PolyKetone.
SAN	Poly Styrene/AcryloNitrile.
shear-plane lubrication	Flow of crosslinked or "yield stress" particles in a small amount of incompatible, low viscosity fluid. (see reference [5].)
skeletal morphology	Microscopic structural component having concave surface, see reference [8c].
SMA	Poly Styrene-Maleic Anhydride.
STEM	Scanning Transmission Electron Microscopy.
TPU	Thermoplastic PolyUrethane.
UL Oven Life	Underwriter's Laboratory, "Continuous Service" or long term service temperature (often extrapolated to 1 year – see reference [1]).

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