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Assessment of CARILON® Thermoplastic Polymers Product Technology

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Project No. 62177, 62182
CARILON® Thermoplastic Polymer

PRINTED: September 1988

APPROVED BY: R. G. Hayter

REFERENCE: Based on work through July 1988

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ABSTRACT

Product research and development programs at WRC and KSLA over the past two years have led to an emerging understanding of the competitive advantages (and drawbacks) of CARILON™ Thermoplastic Polymers. This report is a summary of the current status of this understanding against the background of a rapidly growing and evolving body of technical information. The conclusions presented here are, therefore, subject to change.

The inherent properties of CARILON™ Thermoplastic Polymers place it in the general class of engineering thermoplastics. The CARILON™ Thermoplastic Polymers have a higher heat distortion temperature and lower creep response compared to most engineering polymers. This has been confirmed in product development work carried out in cooperation with Ford on painted exterior body panels and with Heinz on retortable food containers. Both potential customers confirmed the unique advantages of CARILON™ Thermoplastic Polymers in these applications. Further cooperative work in these and related applications is in progress to build on these advantages. We anticipate that additional advantaged products will emerge as we explore reinforcement, flame retardants and toughening technology and the potential ability to achieve clarity and strength through orientation, each of which have been demonstrated in a preliminary manner.

By blending CARILON™ Thermoplastic Polymers with other polymers, the opportunity for further product differentiation is emerging. Uniquely in CARILON™ Thermoplastic Polymers, toughening can be achieved close to the transition in toughness with increasing molecular weight. Low levels of toughening polymer are, therefore, very effective and other mechanical properties are largely retained. Blends with nylon, in particular, are showing advantaged properties at both ends of the compositional spectrum.

Stabilization technology with CARILON™ Thermoplastic Polymer has progressed to the point where continuous use temperatures in the region of 85°C (comparable to that of ABS) has been achieved using combinations of conventional antioxidants. Leads towards higher temperatures are being pursued using less conventional stabilizers such as aluminas, acrylic acid copolymers and metal ion derivatives of Surlyn. Stability under processing conditions approaches commercial requirements for injection molding, but further improvements are needed for extrusion, fiber spinning, etc. Although there are leads towards improvements in ultra-violet stability, no useful system for, say, fiber applications is yet in hand. Overall, much improvement is still required in stabilization technology.

July 1988

**STRUCTURE - PROPERTY
RELATIONSHIPS**

W. P. GERGEN



I. STRUCTURE-PROPERTY RELATIONSHIPS

OVERVIEW

CARILON™ Thermoplastic Polymers are polar, linear semi-crystalline polymers with molecular weights similar to those of polymerized alpha-olefin polymers such as polyethylene or polypropylene. Since the chemical structure of these polymers is capable of strong molecular interactions, CARILON™ Thermoplastic Polymers have high melting points and high strength and modulus. Similar to polyethylene, CARILON™ Thermoplastic polymers crystallize with orthorhombic unit cells and undergo transformation to hexagonal structures at high temperature. The melting point of the linear "copolymer" grade, CARILON™ E Thermoplastic Polymer, is about 260C. By adding defects in the form of a "termonomer" melting points down to about 195C have been achieved. These defects reduce the melting point in accordance with well-known theories and at the same time reduce the total crystallinity of the polymer from about 60% to as low as 30%. As in other semi-crystalline polymers increasing molecular weight tends to decrease the crystallinity. This is a more pronounced effect in CARILON™ E Thermoplastic polymers. Typical 1.8 LVN CARILON™ EP Thermoplastic Polymers are about 37% crystalline and melt at about 220C.

CARILON™ Thermoplastic Polymers absorb water to an extent less than nylon but much more than non-polar polymers. Water absorption is higher in CARILON™ E Thermoplastic Polymer than in the EP versions.

MELT BEHAVIOR AND PROCESSING

At temperatures above the crystalline melting temperature, melt viscosity is related to molecular weight to the 3.4 power. Melt viscosity is non-Newtonian in the same manner as in polypropylene and lies in the range where the polymer can be easily processed by conventional thermoplastic processing equipment, Figure 1. Since CARILON™ Thermoplastic Polymers are non-Newtonian in their viscosity behavior, they have very low viscosity in the high shear zones during injection molding. These polymers are easily molded without sinks under conditions which produce high gloss and excellent detail replication.

The chemical nature of these polymers with so many reactive carbonyl groups makes melt-processing, even with stabilizers, a matter of balancing time and temperature to minimize the crosslinking that occurs on exposure to high processing temperatures, raising melt viscosity eventually to unprocessable levels. The activation energy of the degradation reaction is much higher than the activation energy of flow, so the correct procedure is to minimize the processing temperature rather than the processing time. However, in practice some combination of both works. Crystallization from the melt is very rapid occurring at about 60C below the melting temperature.

STRUCTURAL EFFECTS ON PHYSICAL PROPERTIES

Factors which directly determine or influence the set of physical properties include, the percent crystallinity and the melting temperature, the amount of water absorbed, and the molecular weight.

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Most condensation polymers which melt in the range of CARILON™ Thermoplastic Polymer Tm's, have a thermal-mechanical transition (Tg or Beta transition) arising in the amorphous fraction which lies in the vicinity of 60-80C. Therefore, at room temperature where properties are measured, modulus-related properties are enhanced by both the high modulus composite contribution of the crystalline phase as well as by the glassy state in the amorphous phase. This results in a modulus value which is very competitive with the totally amorphous aromatic engineering resins. When the temperature is raised these semi-crystalline polymers go through a very broad transition and rapidly lose the ability to bear stress. This results in lower heat distortion temperatures. These polymers require some type of reinforcement to maintain the ability to bear stress at temperatures above Tg.

On the other hand, CARILON™ Thermoplastic Polymers have a Tg or Beta transition in the vicinity of room temperature or slightly below, depending on the water content. Like polyolefins that are also not in the glassy state, CARILON™ Thermoplastic Polymers have a somewhat low value of modulus compared to the other engineering polymers. Modulus at this temperature is totally dependent on the crystalline volume fraction. However unlike the polyolefins and also unlike the condensation polymers, this transition is not broad. Above this transition the modulus level is remarkably maintained when measured at very low strain, Figure 2. Since failure in the HDT test occurs at a constant modulus level (providing creep is low) the CARILON™ Thermoplastic Polymers also have remarkably high HDTs. In low stress uses they can survive even in the vicinity of the melting temperatures without reinforcement, Figure 3.

The Beta transition temperature is the same in both CARILON™ E and EP Thermoplastic Polymers. The magnitude of this transition (and the plateau levels of modulus above and below the transition) are related to the amorphous volume fraction. Water displaces the transition temperature toward lower temperatures (acting like a "plasticizer"). This movement in the transition temperature gives rise to the effect of water on the modulus, Figure 4. CARILON™ E Thermoplastic Polymer absorbs more water than the EP version, but the change in modulus depends both on the magnitude as well as on the shift in the Beta transition.

Creep in polymers is a result of a time-dependent relaxation or molecular failure process coupled with the linear elastic response to the applied load. Higher modulus polymers creep less because they produce less deformation under a given load, on the other hand if they are sufficiently close in temperature to a higher temperature transition the creep response will be completely dominated by the changing response as the time equivalency to temperature is achieved. This is the reason that CARILON™ Thermoplastic Polymers show better creep response at room temperature than the semi-crystalline engineering resins which are approaching the transition from the glassy state, Figure 5. CARILON™ Thermoplastic Polymer is uniquely on the higher temperature side of the glass transition and creep response is to a first approximation dependent only on the modulus level. The situation is quite different in amorphous polymers such as polycarbonate which remains in the glassy state throughout their entire useful temperature range and show far less

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creep. On the other hand, CARILON™ Thermoplastic Polymers show a transition which involves a transformation in crystal structure at a temperature of about 150C; creep at somewhat lower temperatures will be strongly affected by this transition. The effective window for creep is significantly more narrow in temperature range than that for modulus.

CARILON™ Thermoplastic Polymers are inherently tough. The toughness, both measured by tensile strength and impact resistance, is a strong function of molecular weight. As molecular weight increases, the tensile behavior of CARILON™ Thermoplastic Polymers goes through stages encompassing brittle fracture to stable drawing and finally to strain-hardening. The tensile yield stress and elongation increase with increasing molecular weight. Tensile strength is greater than that of polycarbonate, PPO/styrene alloys, and polyesters, and is on a par with nylon and polyacetal homopolymers. In addition, ultimate elongation is on a par with that of most polyolefin polymers. In CARILON™ EP Thermoplastic Polymers the onset of drawing occurs at about 1.5 LVN while the polymer shows strain-hardening at a LVN of 2.0.

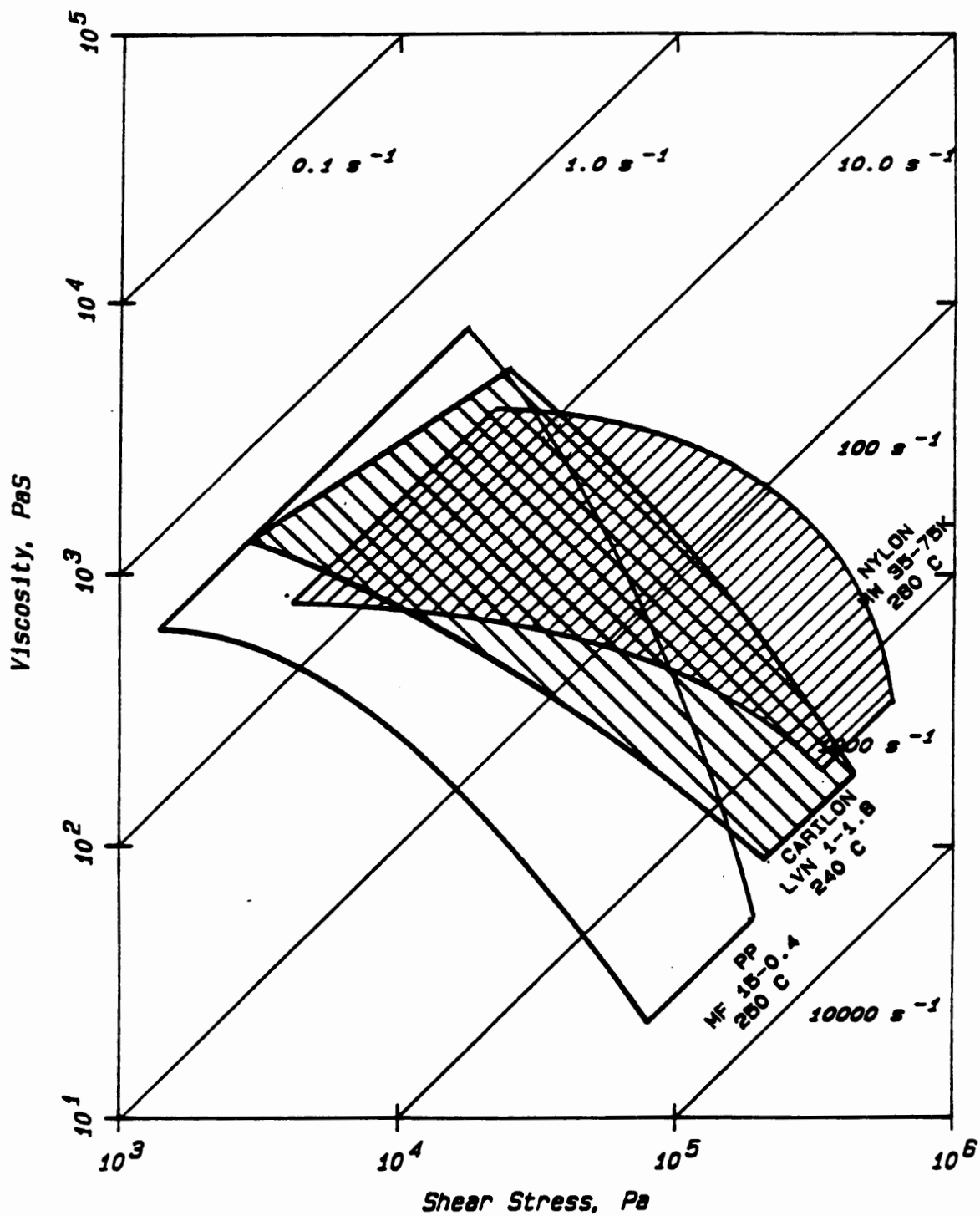
In a similar range of molecular weights, the impact behavior of CARILON™ EP Thermoplastic Polymer also changes dramatically, Figure 6. The change here is a result of shear-banding as the dominant failure mode. Shear-banding is much more energy-absorptive than the less-efficient crazing mechanism. It occurs as the dominant failure mechanism because the shear yield stress is lower than the tensile yield stress. While this condition can occur in most semi-crystalline polymers at sufficiently high molecular weight, CARILON™ Thermoplastic Polymers appear to be unique among engineering polymers probably because they are addition polymers and can be made at sufficiently high molecular weights. The transition occurs in CARILON™ EP Thermoplastic Polymer at a LVN of about 1.8 while in CARILON™ E Thermoplastic Polymer, it occurs at a LVN of about 2.4. The transition shifts toward lower LVN numbers with increasing amount of absorbed water. In the plateau region above the transition, the impact resistance of CARILON™ Thermoplastic Polymers is superior to all other semi-crystalline polymers of normal molecular weight.

CARILON™ Thermoplastic Polymers are unusually solvent resistant. They resist exposure to most organic liquids including limited exposure to gasoline. The polymer will not dissolve or appreciably swell in solvents other than HFIPA or m-cresol. However, the polymer is sensitive to some strong acids and bases which may embrittle and char the polymer. On the other hand, the presence of the carbonyl functionality on the molded surface of CARILON™ Thermoplastic Polymers provides the opportunity for directly decorating those surfaces by painting or plating.

CARILON™ Thermoplastic Polymers have demonstrated barrier properties on a par with those of PET and nylon polymers and with improved and careful morphological control can approach those of conventional barrier polymers such as EVAL. The high chain density resulting from the high carbonyl content coupled with high levels of crystallinity in the CARILON™ E Thermoplastic Polymers should lead to a premium barrier material for O₂ and CO₂ barrier applications.

FIGURE 1

Ranges of Viscosity-Shear Stress for
Polypropylene, Nylon 6 and Carilon EP Thermoplastic Polymer



Fig_1

FIGURE 2
MODULUS-TEMPERATURE BEHAVIOR OF ENGINEERING PLASTICS

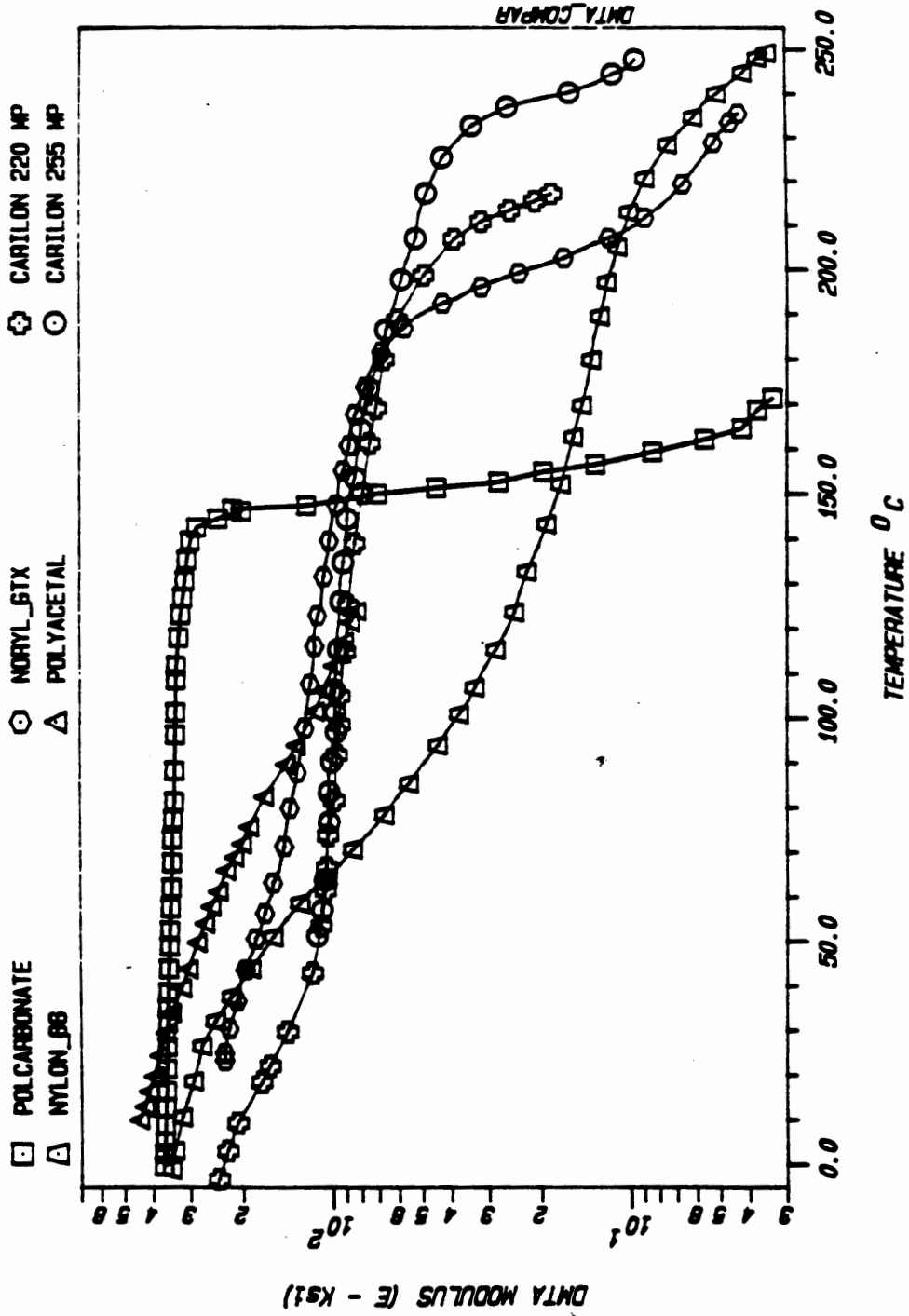


FIGURE 3
 LOAD BEARING TEMPERATURE
 INCLUDING HDT 264
 FOR CARILON THERMOPLASTIC POLYMERS

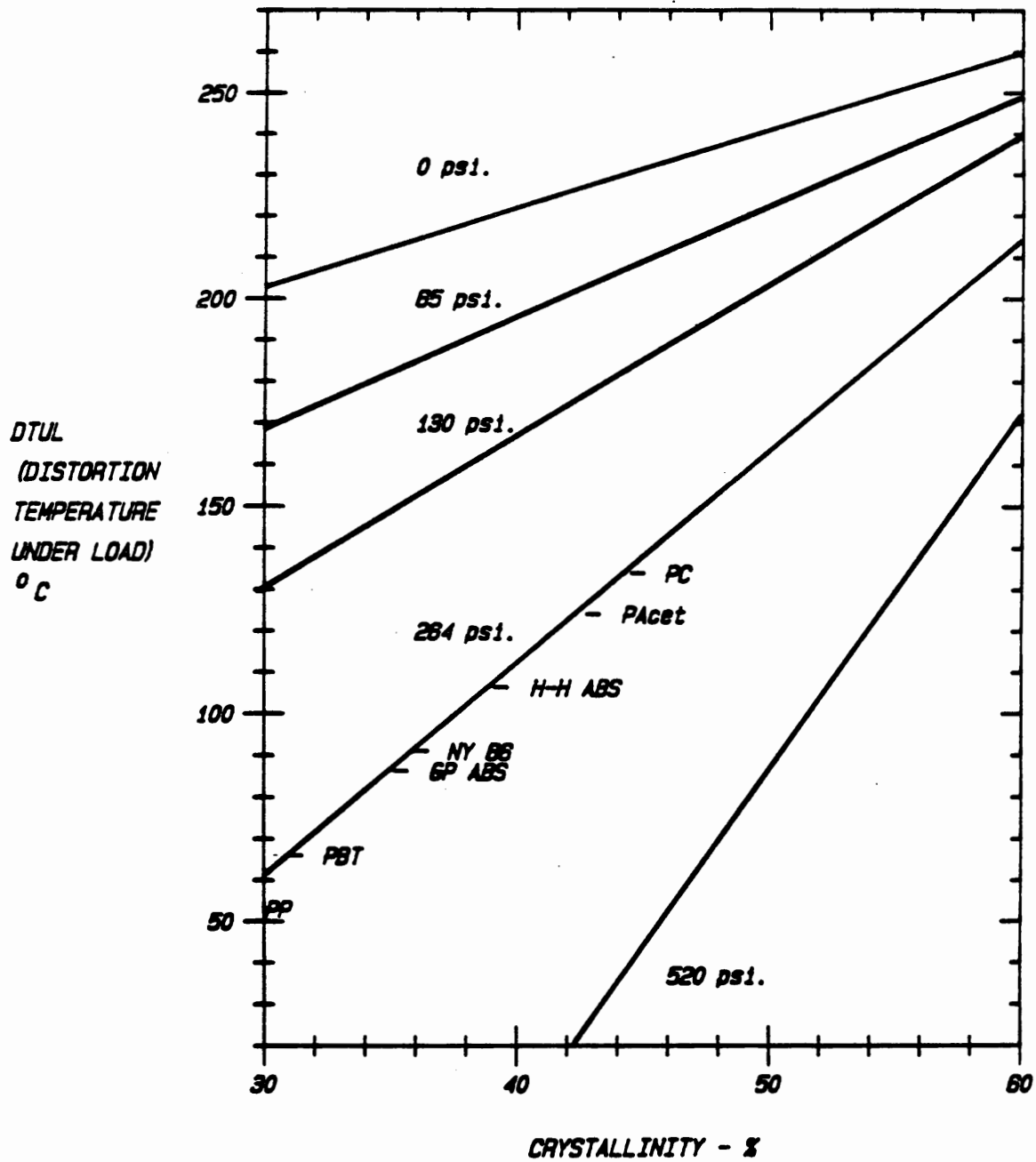


FIGURE 4

EFFECT OF WATER ON MODULUS OF CARILON EP

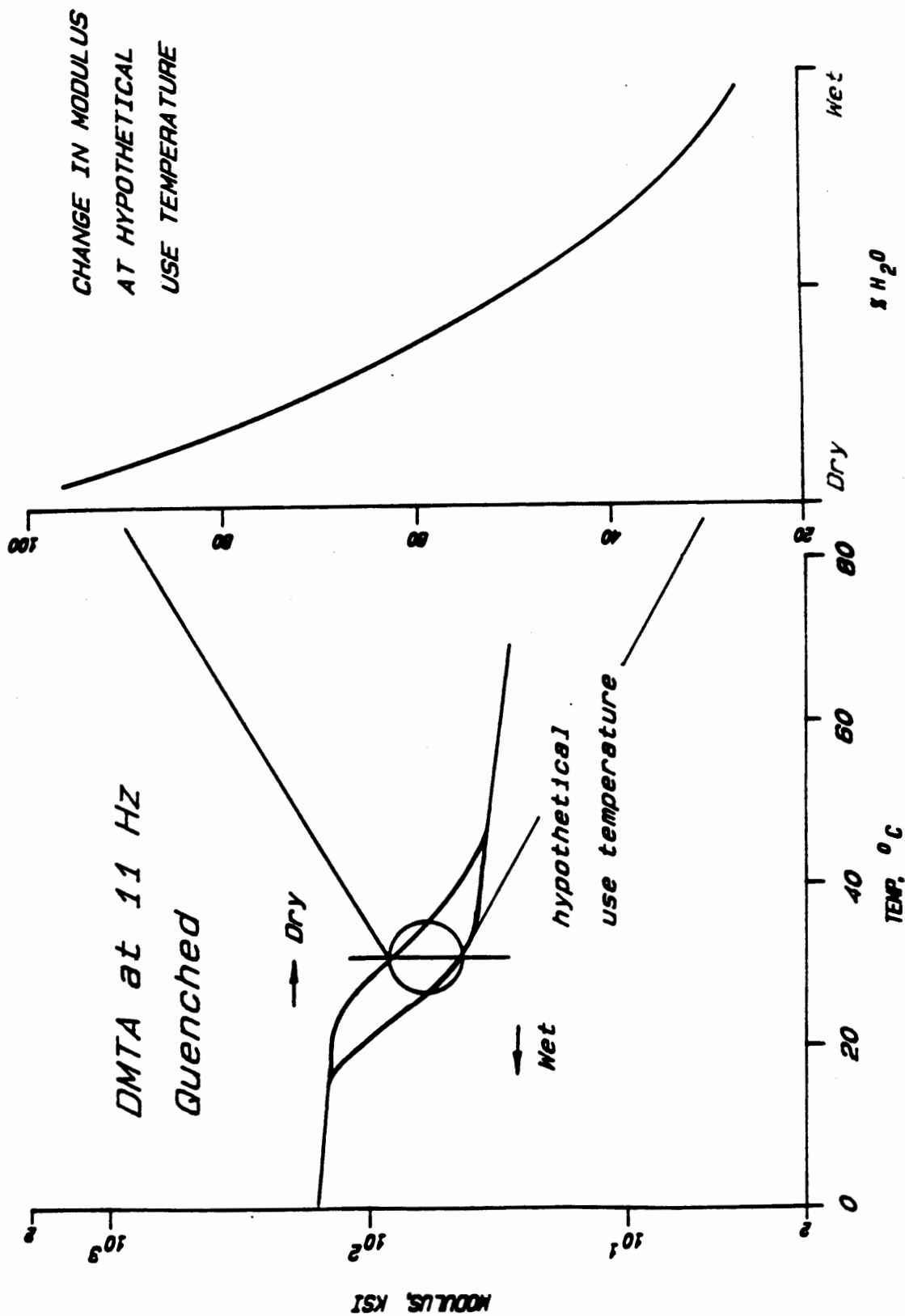


FIGURE 5

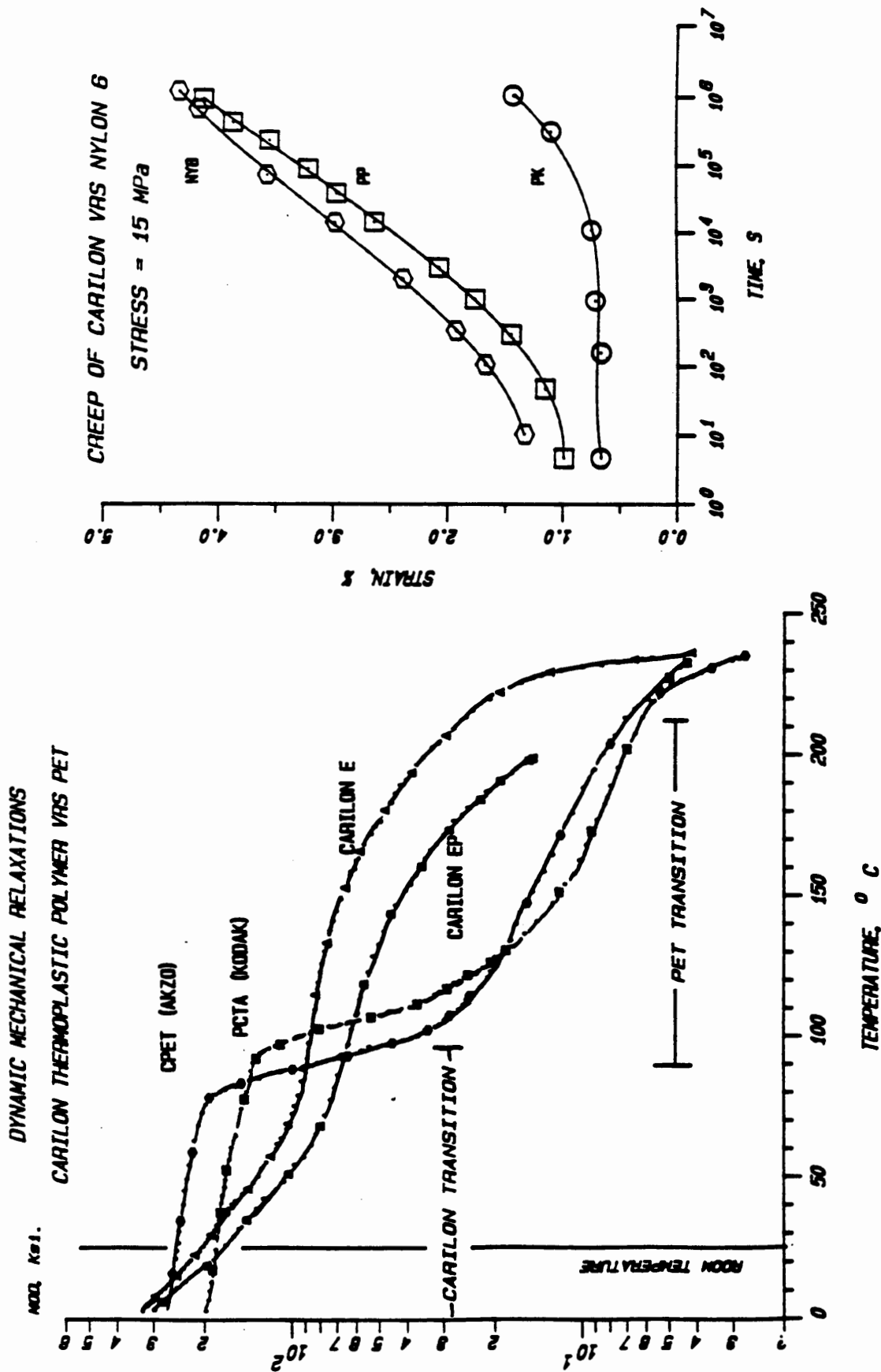
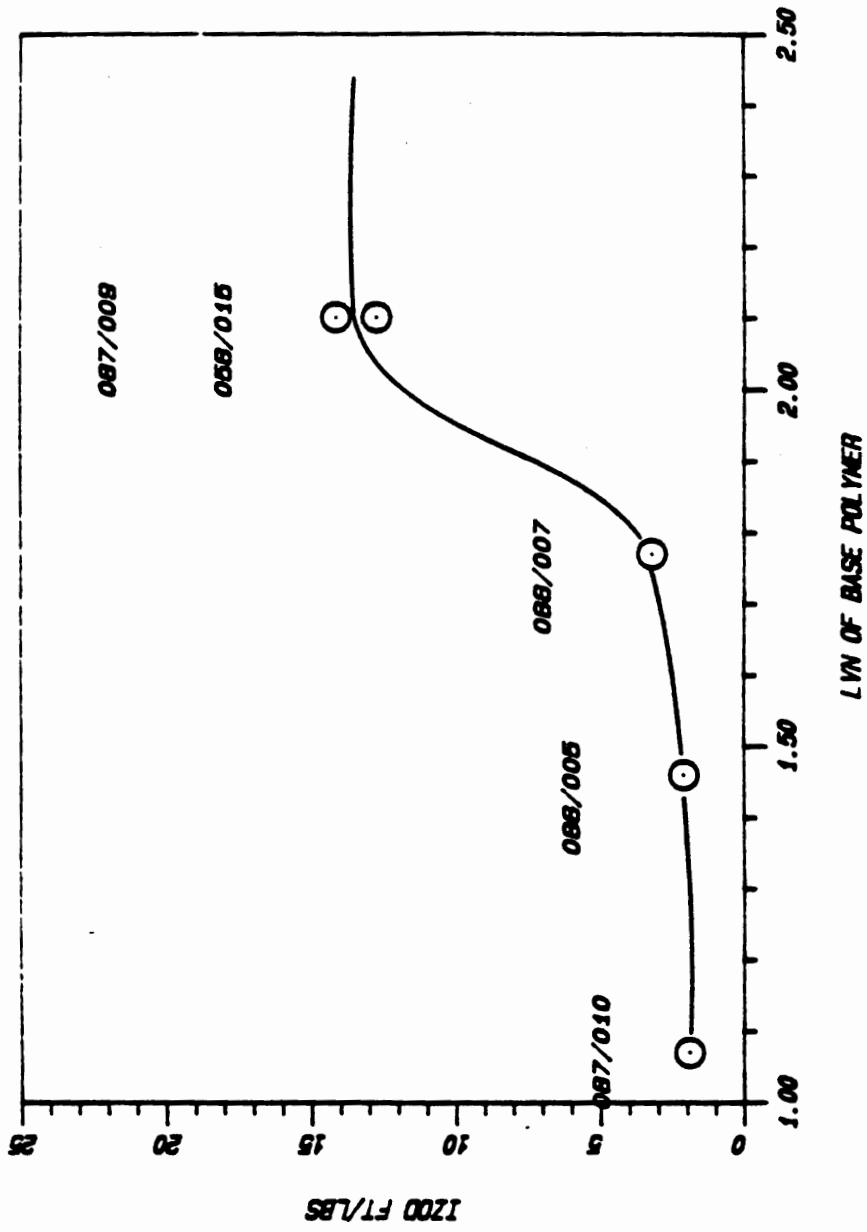


FIGURE 6
IZOD IMPACT AS A FUNCTION OF LVN



**CARILON™ THERMOPLASTIC POLYMERS
IN
ENGINEERING APPLICATIONS**

R. L. DANFORTH

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II. CARILON™ THERMOPLASTIC POLYMERS IN ENGINEERING APPLICATIONS

BASIC POLYMER CHARACTERISTICS

For applications in the end-use areas satisfied by Engineering Thermoplastics (ETPs), Shell's CARILON™ E and EP Thermoplastic Polymers provide a unique balance of physical and processing properties not available in any single ETP polymer on the market today. These products have the stiffness/impact balance and excellent thermal properties typical of amorphous polymers such as polycarbonate coupled with the solvent resistance and electrical properties normally associated with crystalline polymers such as nylon, Figure 1. In addition these polymers have excellent processing characteristics--similar to olefins like polypropylene.

It should be further noted, that CARILON™ E and EP Thermoplastic Polymers are just the first products developed using this new Shell polymerization technology. We see the use of other monomers and modifiers leading to a portfolio of products, tailor made for a wide range of applications including those now served by the High Performance ETP's like polysulfone.

In addition to the key engineering properties mentioned above, CARILON™ Thermoplastic Polymers also have many other areas where the best characteristics of both amorphous and crystalline materials are present in a single polymer. In surface properties, they have high hardness and excellent gloss typical of amorphous polymers which lead to parts with good mar resistance and class A finish. CARILON™ Thermoplastic Polymers also have an active, polar surface which promotes direct paintability and excellent bonding characteristics. Parts made from CARILON™ Thermoplastic Polymers have better dimensional stability than crystalline materials and show no evidence of any hydrolytic instability.

MODIFICATION VIA COMPOUNDING

A. Toughening

CARILON™ Thermoplastic Polymers can be modified with many other polymers to enhance their impact properties, Figure 2. This allows the development of compounds with a variety of property sets, many of which will have a unique balance of stiffness and ductile failure over a wide service temperature range.

B. Reinforcement

CARILON™ Thermoplastic Polymers accept fiber and mineral reinforcing materials readily (demonstrated up to 50%w), allowing development of products with high strength and stiffness, Figures 3-9. As with most thermoplastics, proper surface modification of added fillers is required for optimum properties. The response of CARILON™ Thermoplastic Polymers to reinforcement coupled with the wide spectrum of impact modifiers provides a bases for compounds within the high stiffness and ductile failure desired in many end-use applications.

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The use of fibers and mineral fillers also provide avenues to control shrinkage, coefficient of thermal expansion and warpage.

C. Flame Retardancy

CARILON™ Thermoplastic Polymers respond to commercially available flame retardant chemicals extremely well. Compounds with V-0 ratings have been obtained using non-toxic additives at levels 50% lower than that required by many crystalline polymers, Table 1. This allows cost effective development of products for many applications with excellent property sets and usually at a lower density. In addition, the olefinic character of CARILON™ Thermoplastic Polymers leads to low smoke generation.

D. Processing

When properly stabilized, CARILON™ Thermoplastic Polymers have melt processing characteristics similar to olefins such as polypropylene. Clamp requirements of 2 to 2.5 ton/sq-in are typical compared to the 3 to 5 tons/sq-in required for many ETP materials. CARILON™ Thermoplastic Polymers products also have excellent flow characteristics which result in fast fill times and excellent mold replication. Rapid crystallization allows CARILON™ Thermoplastic Polymer parts to be ejected quickly resulting in fast cycle times. In our molding trials to date we have observed 10 to 30% cycle time reductions over other ETP materials using common molds and equipment.

E. Grade Development

During the evaluation and development of the CARILON™ Thermoplastic Polymers we selected certain specific target applications for compound development of products with property sets aimed at "real world" specifications. Some of the compounds developed include:

1. Vertical Exterior Painted Auto Panels:

The property balance of CARILON™ Thermoplastic Polymers make them uniquely suitable for painted automobile exterior panels and fenders. Both neat and glass reinforced compounds have been developed that have a combination of stiffness and impact equal to or better than other ETP materials, Table 2. This combined with the compound's high HDT properties (which allow ELPO treatment without distortion) make it a better product for this application than other polymers and blends currently available. The surface properties of parts molded from the compounds are excellent (Class A) and the polarity allows direct in-line painting with conventional equipment and coatings. The CARILON™ Thermoplastic Polymers' ability to handle some loading of fillers and to maintain a Class A surface provides a method of controlling shrinkage and warpage not available to most of the other ETP materials that exhibit poor surface quality when filled. A low moisture absorption for CARILON™ Thermoplastic Polymers also contributes to better dimensional stability.

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The excellent processing characteristics allow the use of smaller molding machines (low clamp requirements) and fast cycle times. Both of these lead to lower fabrication costs. These products meet material specifications for body panels at both Ford and General Motors, Table 3. Ford Taurus front fenders have been molded in tooling made for Noryl GTX 910 with excellent results. In addition, the CARILON™ Thermoplastic Polymer compounds were molded with cycle times 10 to 15% faster than the PPO material. A production trial at Buick is planned for this summer.

2. Under-the-hood

a. Rocker Arm Cover

This part was chosen to demonstrate the value of a CARILON™ Thermoplastic Polymer compound in applications where a high service temperature in the presence of a solvent or oil is required. A glass and mica filled product was developed that meets all listed specifications for a Jeep engine, Table 4. The extra value of a CARILON™ Thermoplastic Polymer based compound in this application results from those properties similar to those of amorphous polymers. Nylon is used for its heat properties and oil resistance. Weaknesses are creep at temperature, dimensional stability and warpage. CARILON™ Thermoplastic Polymer is superior to crystalline polymers in these properties. This product also molded well and at a reduced cycle time compared to the glass filled nylon currently in use. Evaluation in use on a real engine is planned.

b. Radiator End Tank

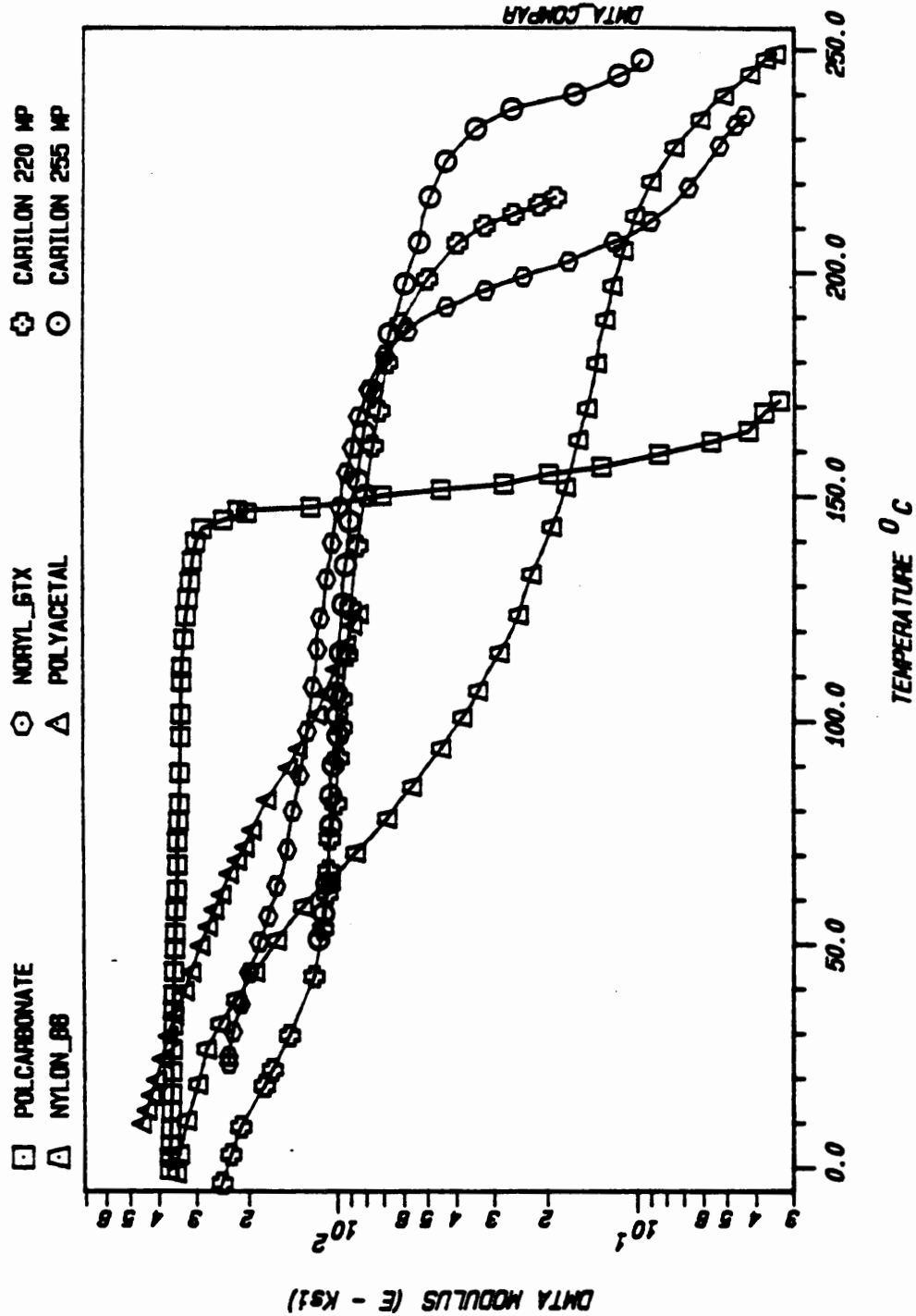
This application was chosen to demonstrate service in temperature/pressure (17 lbs of steam) application. This applications also requires resistance to the chemicals in radiator coolant systems. Again CARILON™ Thermoplastic Polymer compounds should be superior to the nylon currently used because of better creep and dimensional stability. A 30% glass filled system was developed that meets the material specifications, also in Table 4. The product has been molded and will be tested under operating conditions.

3. Future

Under consideration now are compounds to demonstrate functional applications in both transportation and industrial areas as well as some specific applications in small appliance housings.

FIGURE 1

MODULUS-TEMPERATURE BEHAVIOR OF ENGINEERING PLASTICS



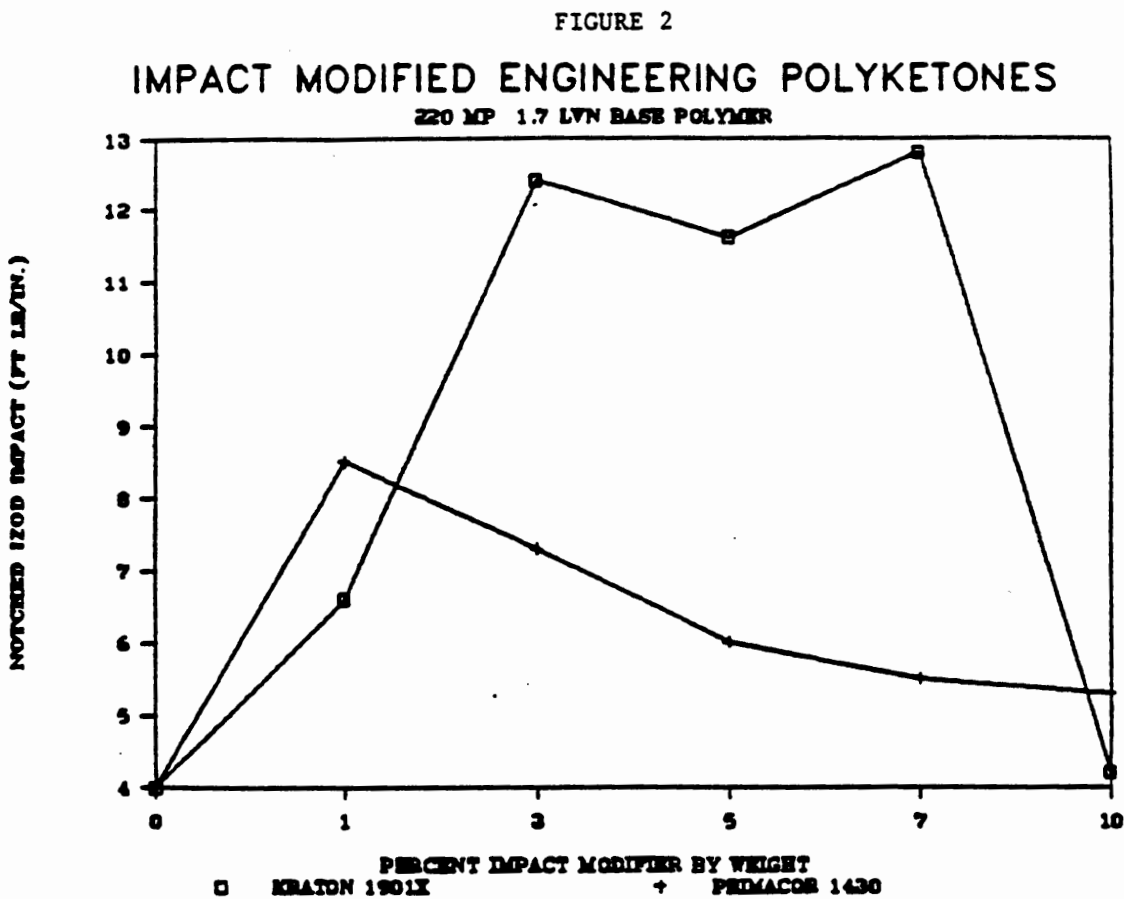


FIGURE 3
FIBERGLASS REINFORCED POLYKETONES

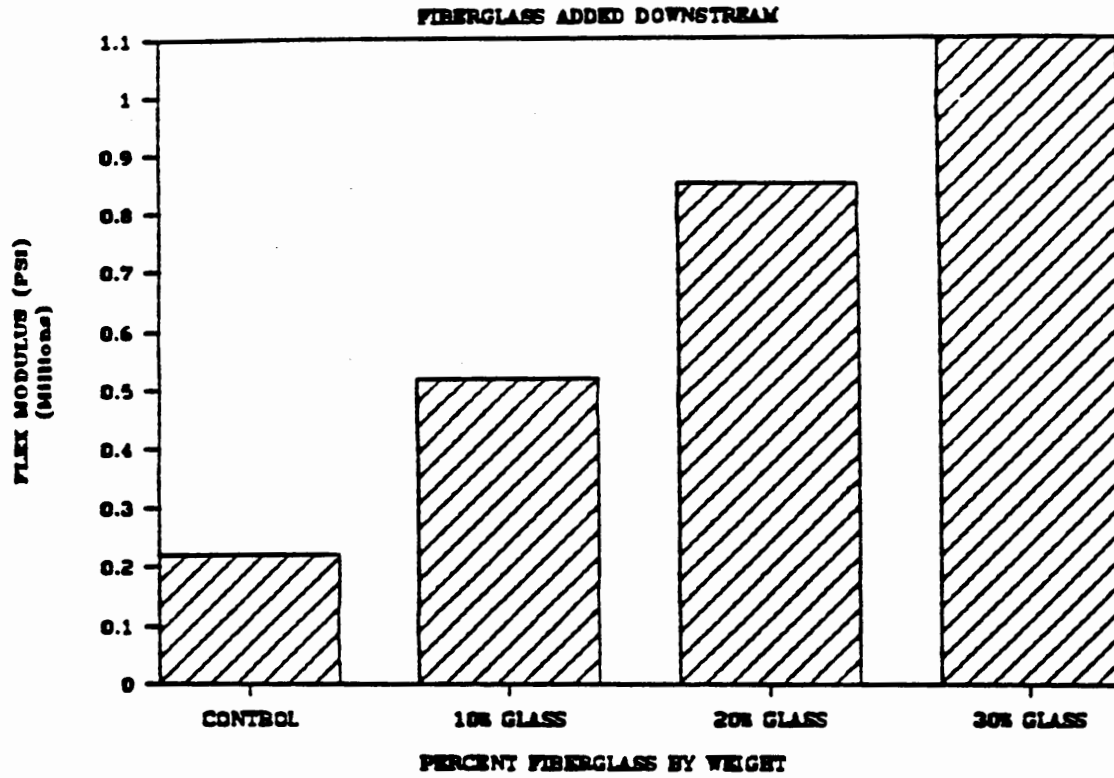


FIGURE 4
FIBERGLASS REINFORCED POLYKETONES
BDT AT 264 PSI

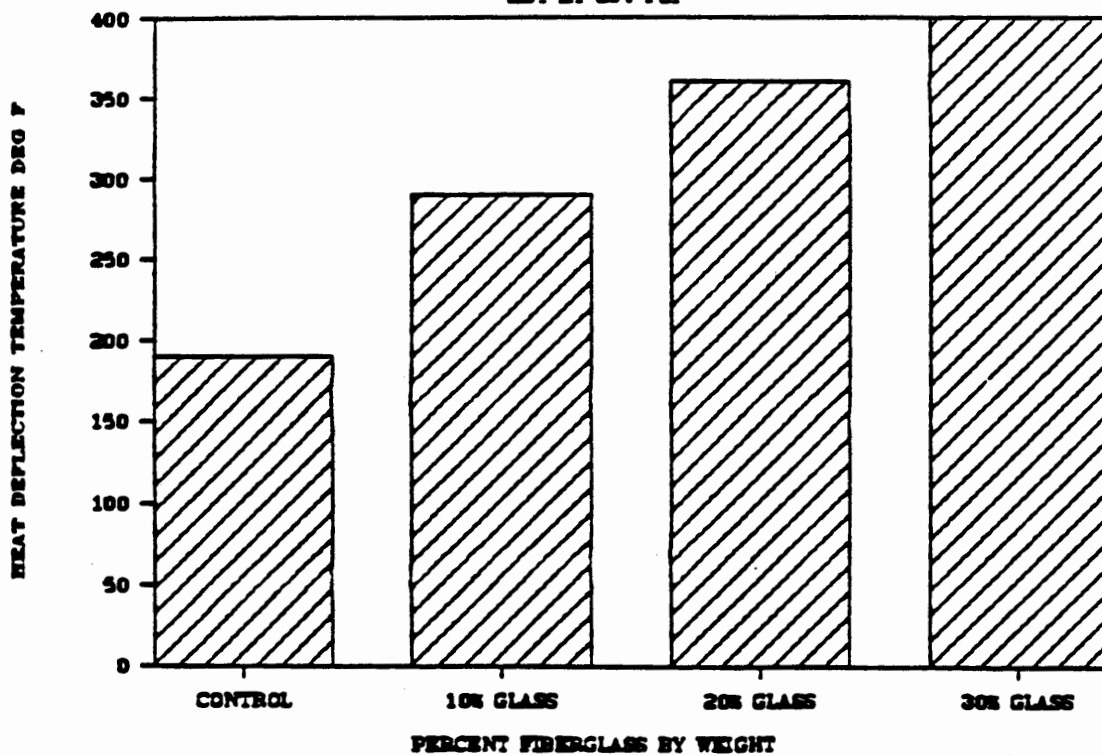


FIGURE 5
MICA-FILLED POLYKETONES
ASPRALOK 100

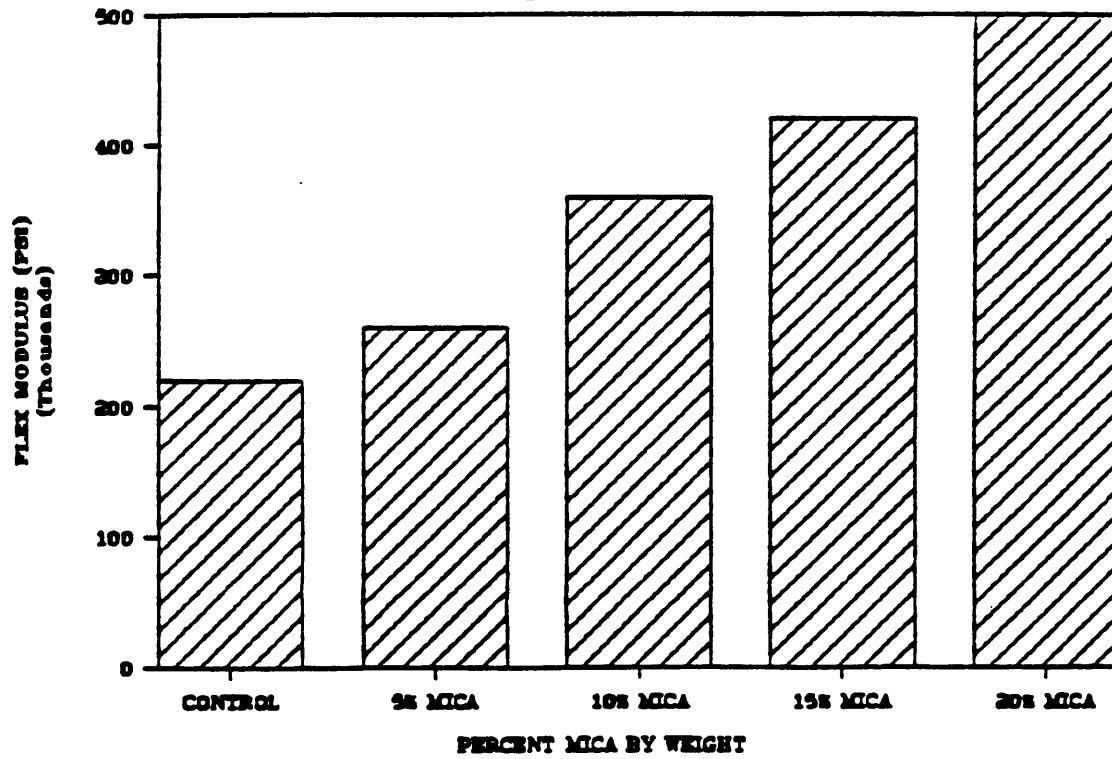


FIGURE 6
MICA-FILLED POLYKETONES
EDT © 264 (PST)

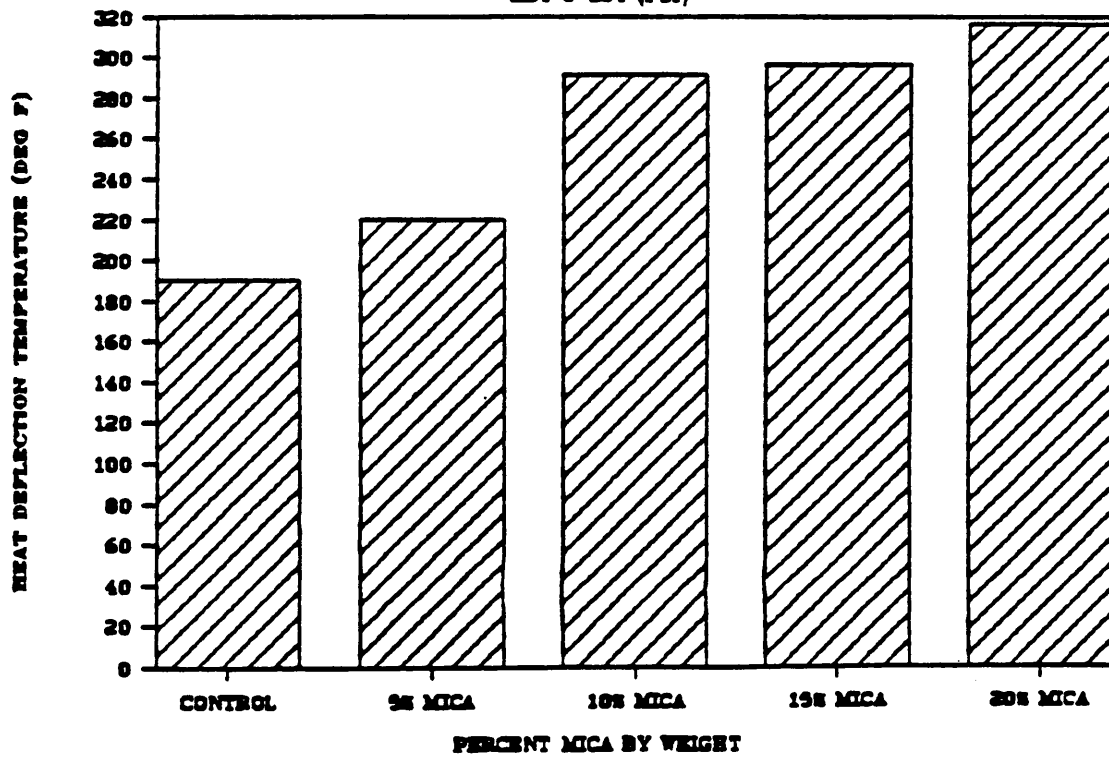


FIGURE 7
REINFORCED ENGINEERING POLYKETONES

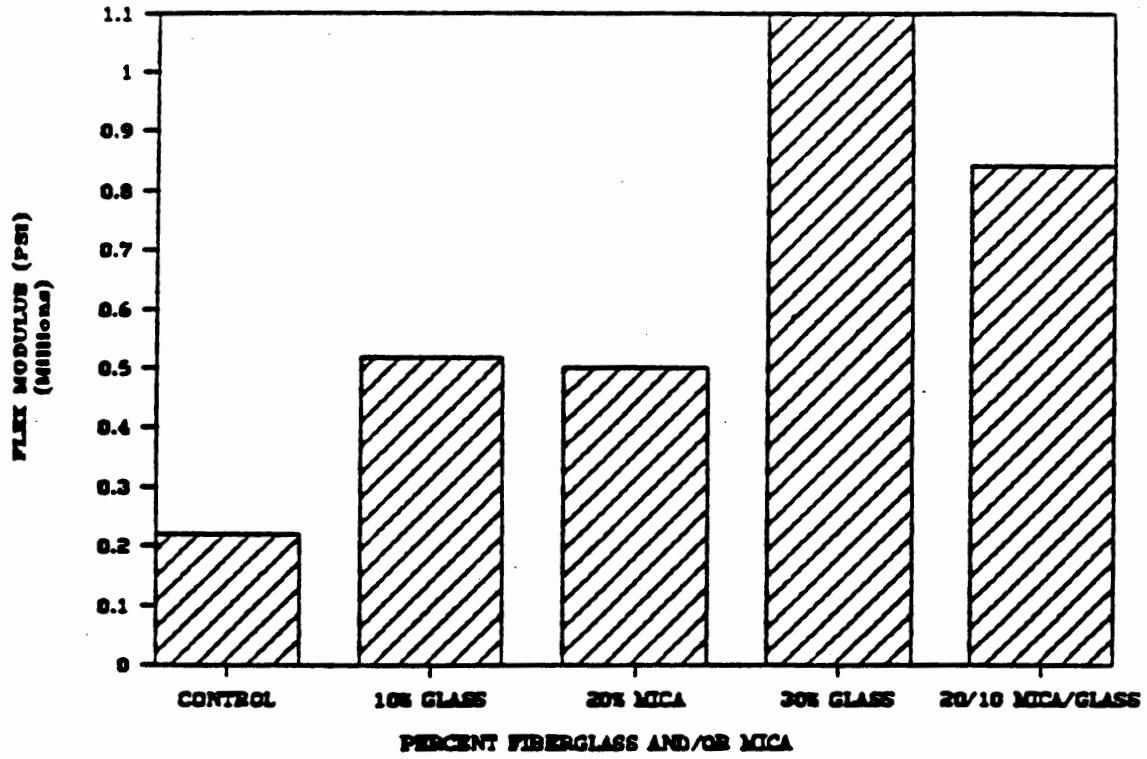


FIGURE 8
REINFORCED ENGINEERING POLYKETONES

EDT@ 264 PSI

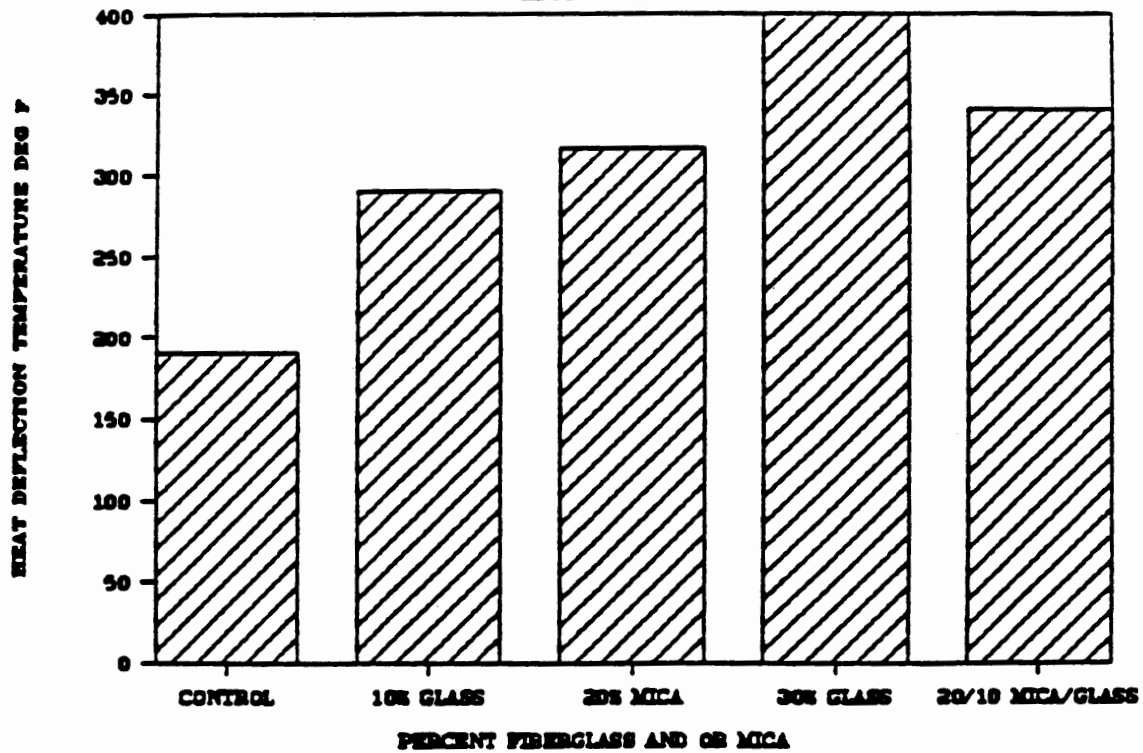


FIGURE 9
 REINFORCED ENGINEERING POLYKETONES
 CLTE (25C-200C)

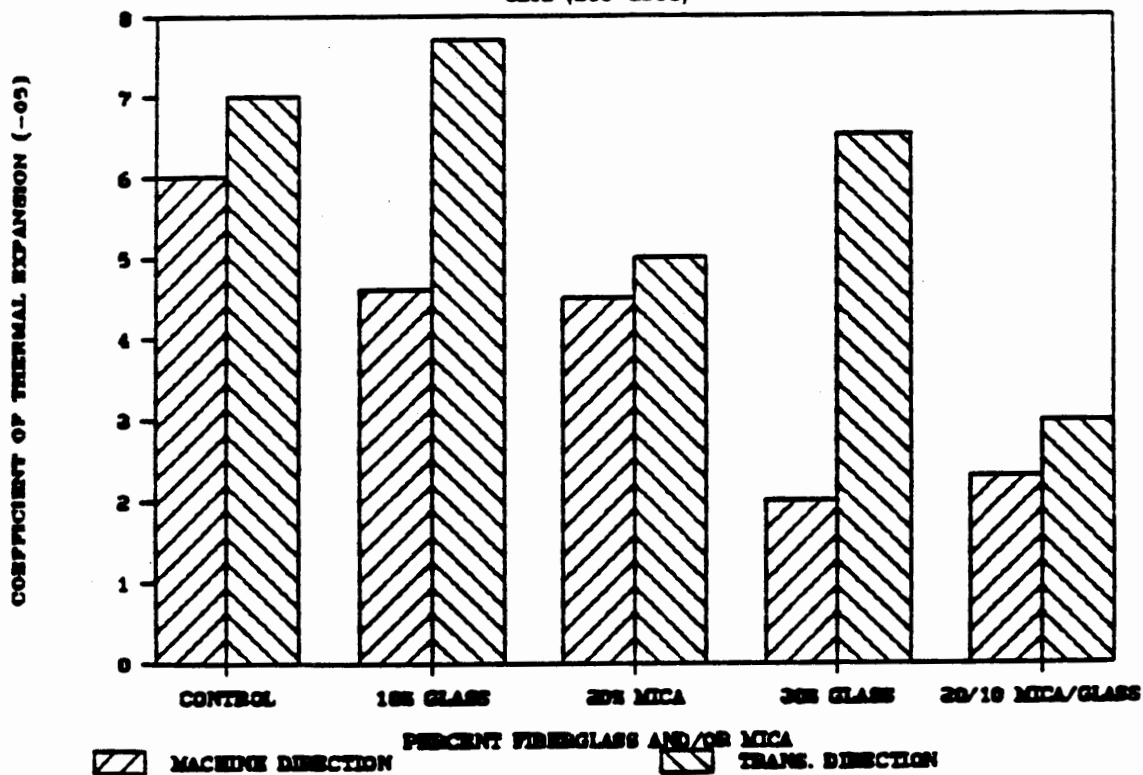


TABLE 1
PROPERTIES OF FLAME RETARDANT CARILON™ POLYMER

<u>COMPOSITION</u>	<u>NOTCHED IZOD FT-LB/IN</u> <u>AGED 7 DAYS</u> <u>AT 100 DEG C</u>		<u>FLEXURAL</u> <u>MODULUS, PSI</u>	<u>LOT, %</u>	<u>UL 94 TEST</u> <u>BURN TIME, SEC</u>	<u>RATING</u>
	<u>ORIGINAL</u>	<u>3.0</u>				
CARILON™ POLYMER (BATCH 88/005/006 BLEND)	3.0	3.0	260,000	17.5	-	-
CARILON™ POLYMER/ ZERODEN/CAO ₃						
80/10/10	1.5	1.3	335,000	29.5	61	V-1
70/20/10	1.6	1.4	390,000	30.5	22	V-0
60/30/10	1.2	1.1	430,000	34.5	10	V-0
80/20/0	1.8	1.7	340,000	30.5	26	V-0
70/30/0	1.8	1.8	370,000	31.5	15	V-0
60/40/0	1.7	1.3	405,000	35.5	7	V-0

TABLE 3

COMPARISON OF CARILON™ POLYMER COMPOUNDS FOR AUTOMOTIVE BODY PANELS

<u>COMPOSITION</u>	<u>FORD COMPOUNDS</u>		<u>GM COMPOUNDS</u>	
	<u>NEAT</u>	<u>GLASS</u>	<u>NEAT</u>	<u>GLASS</u>
CARILON™ POLYMER, %W	92.5	84.5	91.5	80.5
FIBERGLASS (OCF492AA), %W	-	8.0	-	5.0
MICA (ASPROLOK 100), %W	-	-	-	10.0
PRIMACOR 1430, %W	5.0	5.0	-	-
NUCREL 010, %W	-	-	2.0	2.0
KRATON 1901X	-	-	5.0	-
EVA GRAY	2.5	2.5	2.5	2.5
<u>PROPERTIES</u>				
TENSILE STRENGTH, PSI	7,500	8,000	9,200	7,500
FLEXURAL MODULUS, PSI	245,000	360,000	265,000	400,000
ELONGATION TO BREAK,%	104	96	200	69
NOTCHED IZOD, FT-LB/IN	4.5	4.4	10.0	1.8
HDT, 264 PSI, DEG F	230	250	200	240

TABLE 4

PROPERTIES OF REINFORCED CARILON™ POLYMER COMPOUNDS

<u>COMPOSITION</u>	<u>COOL VENT AND RADIATOR END TANK</u>	<u>ROCKER ARM COVER</u>
CARILON™ POLYMER 87/015, %W	67.5	-
CARILON™ POLYMER 88/005/006, %W	-	67.5
FIBERGLASS (OCF 492AA), %W	30.0	10.0
MICA (ASPROLOK 100) %W	-	20.0
NUCREL 010, %W	2.0	2.0
EVA BLACK, %W	0.5	0.5
<u>PROPERTIES</u>		
FLEXURAL MODULUS, PSI	1,100,000	830,000
FLEXURAL STRENGTH, PSI	15,100	17,500
NOTCHED IZOD, FT-LB/IN	1.6	1.3
TENSILE STRENGTH	8,500	11,000
ELONGATION TO BREAK, %	21	14
CLTE, IN/IN/DEG F X 10 ⁻⁵		
FLOW DIRECTION	1.9	2.3
TRANSVERSE DIRECTION	6.5	3.0
HDT, DEG F AT 264 PSI	398	340

**CARILON™ THERMOPLASTIC POLYMERS
IN
PACKAGING**

J. R. KASTELIC

III. CARILON™ THERMOPLASTIC POLYMERS IN PACKAGING

SUMMARY

The fundamental physical properties of Shell's CARILON™ Thermoplastic Polymers make the resin highly suited for applications in food packaging. The most notable characteristics are high temperature capability, potentially good organolytics and high oxygen barrier. These attributes are combined in this rapidly crystallizing resin permitting fast cycle fabrication of both molded and thermoformed/pressure-formed high barrier containers. If sufficient orientation is imparted during the fabrication step, such as by Solid Phase Pressure Forming (SPPF), attractive contact clarity is attained. Properties are such that monolayer processing techniques are usually applicable. In the case of small containers, a coating is necessary to reduce moisture loss and to prevent undue weight loss if long shelf life is required. CARILON™ Thermoplastic Polymer containers are proving their capability in the most challenging food packaging application viz., low-acid, oxygen-sensitive retorted foods.

OXYGEN BARRIER

Oxygen permeability of this new resin is a strong function of crystallinity, Figure 1. Barrier performance of fabricated monolayer containers is sufficient for high oxygen sensitivity foods. This is attained by optimization of crystalline fraction and avoidance of degradation during processing. Although the permeability is not low enough to allow direct substitution for Saran or Eval in multilayer constructions, it is adequate for use of the polymer as a simple monolayer. This presents significant advantages by eliminating the need for costly and complex multilayer fabrication equipment and regrind recycle streams.

In retort applications, the oxygen barrier performance of CARILON™ Thermoplastic Polymer monolayer containers matches that of advanced desiccant technology, such as used in Omni containers and exceeds that of non-desiccant PP/EVOH/PP multilayer containers, Table 1. The moisture sensitivity of the oxygen permeability is much lower in CARILON™ Thermoplastic Polymers than in Eval and is not significantly changed by retorting. Even the asymmetric multilayer structures experience increased oxygen permeability for a significant period after retorting. Consequently, the exposure of the food product to oxygen is lower in CARILON™ Thermoplastic Polymer monolayer containers than in a conventional multilayer container over the life cycle of the food product.

MOISTURE BARRIER

The moisture barrier of CARILON™ Thermoplastic Polymers falls in line with PET and the better nylons. Calculations show that this is adequate in the case of large containers but is insufficient for small containers intended for long shelf life. Water permeation at typical 4-8 oz single serve sizes results in a shelf weight loss which may be unacceptably high in a one year time frame so moisture barrier must be augmented by some means.

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Several materials possess sufficient moisture barrier in thin gauges to remedy the excess water loss of small containers. Polypropylene is one example but its use requires coextrusion and complicates scrap recycle. Spray or dip coatings, such as used on cans, are favored as the solution. Saran and a proprietary thermoset coating appear best at this time. The thermoset has been successfully retorted in actual pack tests and offers the further advantage of enhanced gloss and clarity. Table 2 lists moisture barrier achieved with coated and uncoated CARILON™ Thermoplastic Polymer containers. Table 3 shows actual weight changes observed in small containers.

FOOD CONTACT PERFORMANCE

In thermoplastics, flavor scalping generally correlates with the permachor value calculated based on the actual chemical structure. Such calculations lead to a high permachor number for CARILON™ Thermoplastic Polymers and to expectations that absorption of polar and nonpolar flavorants will be low. Other polar polymers such as nylon and PET do exhibit excellent flavor retention and for the same reasons.

Staining is a problem for olefins used in food packaging. Retorted tomato products for example strongly stain the PP inner wall in Lunch Bucket and Omni containers. Even polyethylene overcaps which become spattered in microwave cooking become quickly stained and are strongly tinted to hide this.

By contrast, CARILON™ Thermoplastic Polymer containers do not exhibit significant staining. Containers retorted with food products have retained attractive contact clarity in actual test packs. Grease and oil resistance is an area of concern for polycarbonate but presents no problem for CARILON™ Thermoplastic Polymer containers, either oriented or unoriented. CARILON™ Thermoplastic Polymers represent one of the few viable pathways to the all-plastic retort food jar.

DUAL-OVEN AND RETORT PERFORMANCE

The high melting point of CARILON™ Thermoplastic Polymers, in combination with the fast crystallization rate and high level of achieved crystallinity, leads to excellent performance at retort temperatures. Containers made from CARILON™ Thermoplastic Polymers easily pass the requirement of under 3% volume change at normally used report temperatures of 250 to 260°F. Thermoforming must be used in the case of PP to reduce shrinkage to tolerable limits but, the practice introduces cycle rate, sheet handling and container trimming difficulties and precludes attainment of contact clarity.

Figure 2 shows DMA data (modulus only) of CARILON™ Thermoplastic Polymers and CPET. The curves show that both materials are applicable for retort and dual-oven containers, with CARILON™ E Thermoplastic Polymer type resin offering a dual-oven safety margin comparable to GPET. Only CARILON™ Thermoplastic Polymers can be injection molded thus making possible a very rigid, high quality, partitioned eat-out-of tray much like that made from costly thermosets by trans-

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fer molding. CPET trays must be fabricated from sheet and consequently must resort to a formed-in partition which actually behaves as a hinge. This is particularly undesirable during handling after heating of the food. Stability on the oven rack is also compromised.

CARILONTM Thermoplastic Polymer trays can be microwaved, according to our tests, provided thickness is not over about 50 mil. Higher thickness shows a tendency to absorb microwave energy and possibly melt. Oven baking test indicate adequate rigidity up to at least 400°F, but some discoloration (possibly aggravated by contact with particular foods) has been noted on unpigmented containers. Even better performance can likely be achieved when higher melting resin grades are available.

FABRICATION

CARILONTM Thermoplastic Polymers exhibit extremely rapid crystallization kinetics which rival those of olefins. This allows containers to be fabricated at attractively high rates. Also, the economical SPPF forming techniques can be used as have been developed for PP. Unlike the case with PET, no annealing is required to fabricate retort, steam sterilize, and dual oven containers. Tables 4 and 5 list representative conditions for sheet extrusion and forming. Viscosities are available for both processes. Blow molding has been successfully performed at lab scale but at this time little can be said until further development work can be undertaken. Stretch blow molding is proving difficult and success may require considerable development effort and even machine or resin modifications.

CONTAINER ENGINEERING

CARILONTM Thermoplastic Polymers exhibit very good mechanical properties. Strength and flexural modulus is approximately double that of PP, consequently some container down-gaging may be possible. Impact strength is maintained to below -40°F and, unlike PP, no special considerations need to be given to frozen food applications. Table 6 lists the practical range of container types envisioned at this time.

Recently, we have become aware that there may be need for improved all-plastic barrier caps and lids for hot fill and retort. Films, laminates and coextruded thin gage sheet may find uses as flat or formed flexible lids. Mechanical properties are such that screw caps and other engineered closures might be alternative packaging applications.

In terms of flexible lidding for CARILONTM Thermoplastic Polymer containers, nylon heat seal layers are looking very promising. Lower melting CARILONTM Thermoplastic Polymers grades are being considered as another attractive alternative. Foil or Saran will be required to provide barrier in thin gage flexible lidding. Double seamed containers should be possible in the future and, due to the basic monolayer structure, might be made through injection molding. In addition to added freedom in container design, the precision which can be achieved by molding may offer significant advantages in seam reliability also.

TABLE 1

OXYGEN PERMEABILITY OF THERMOPLASTIC CONTAINERS

	<u>OXYGEN PERMEABILITY (CC/CONTAINER-DAY)</u>	
	<u>BEFORE RETORT</u>	<u>AFTER RETORT¹⁾</u>
CARILON POLYMER	0.002	0.002
PP-EVOH-PP WITH DESSICANT (OMNI)	0.003	0.003

1) MEASURED 12 HOURS AFTER RETORT

TABLE 2
WATER PERMEABILITY OF CARILON POLYMER CONTAINERS

<u>COATING</u>	<u>THICKNESS</u>	<u>WATER PERMEABILITY</u>	
		<u>BEFORE RETORT</u>	<u>AFTER RETORT</u>
UNCOATED	-	0.029	0.029
VICLAN 834	0.5 MIL	0.013	0.013
PPG	1.0 MIL	0.005	-

WVTR GIVEN AS GM/CONTAINER-DAY, 4.2 OZ SIZE, 25 DEG C

TABLE 3

WATER LOSS THROUGH CARILON™ POLYMER CONTAINERSUNCOATED CONTAINERS

<u>CONTENTS</u>	<u>WEIGHT LOSS PER YEAR, %¹⁾</u>
BABY FOOD (CHICKEN)	21.5
KETCHUP	14.3
OIL AND VINEGAR	12.7
SATURATED SALT SOLUTION	4.4

COATED CONTAINERS (DARAN 820 PVDC)

BABY FOOD (CHICKEN)	3.9
SATURATED SALT SOLUTION	0

COATED CONTAINERS (PPG D)

BABY FOOD (CHICKEN)	2.1
SATURATED SALT SOLUTION	0

1) 4 OZ CUP, FOIL LID

TABLE 4

CONDITIONS FOR EXTRUDING CARILON™ POLYMER SHEET

EQUIPMENT: TWO INCH TWO STAGE SINGLE SCREW EXTRUDER

CARILON POLYMER: 40% 1.7 LVN, 232 DEGREE C MELTING POINT
60% 1.5 LVN, 224 DEGREE C MELTING POINT

EXTRUDER SET POINTS:

ZONE 1	246 DEG C
ZONE 2	254 DEG C
ZONE 3	240 DEG C
ZONE 4	232 DEG C
ADAPTER ZONE 1	204 DEG C
ADAPTER ZONE 2	227 DEG C
DIE	227 DEG C
MELT TEMP	238 DEG C
RPM	70

ROLL STACK SET POINTS:

TOP ROLL	138 DEG C
CENTER ROLL	182 DEG C
BOTTOM ROLL	93 DEG C

TABLE 5

CONDITIONS FOR FORMING CARILON™ POLYMER SHEET

EQUIPMENT: ILLIG 37/10 CONTINUOUS THERMOFORMER

CARILON POLYMER: 40% 1.7 LVN 232 DEG C MELTING POINT
60% 1.5 LVN 224 DEG C MELTING POINT

FORMER SET POINTS:

PREHEATER	230 DEG C
ZONE 1	OFF
ZONE 2	OFF
ZONE 3	383 DEG C
ZONE 4 TOP	353 DEG C
ZONE 4 BOTTOM	335 DEG C
ZONE 5 TOP	374 DEG C
ZONE 5 BOTTOM	383 DEG C
ZONE 6	423 DEG C
ZONE 7	OFF
ZONE 8	OFF
PLUG	250 DEG C
TOOL	25 DEG C
STROKES/MIN	5

TABLE 6

POTENTIAL CARILON™ THERMOPLASTIC POLYMER
RIGID PACKAGING APPLICATIONS

(DECREASING ORDER OF TECHNICAL COMPLEXITY)

- * INJECTION BLOW MOLDED CLEAR WIDE MOUTH JAR
- * INJECTION BLOW MOLDED CLEAR WIDE MOUTH JAR WITH CLOUDY NECK
- * INJECTION BLOW MOLDED OPAQUE WIDE MOUTH JAR
- * CLEAR SOLID PHASE PRESSURE FORMED CUP
- * INJECTION MOLDED OPAQUE WIDE MOUTH DOUBLE SEAM CAN
- * OPAQUE SOLID PHASE PRESSURE FORMED CUP
- * DUAL OVENABLE BARRIER TRAY
- * MICROWAVE ONLY BARRIER TRAY
- * INJECTION MOLDED JAR

FIGURE 1

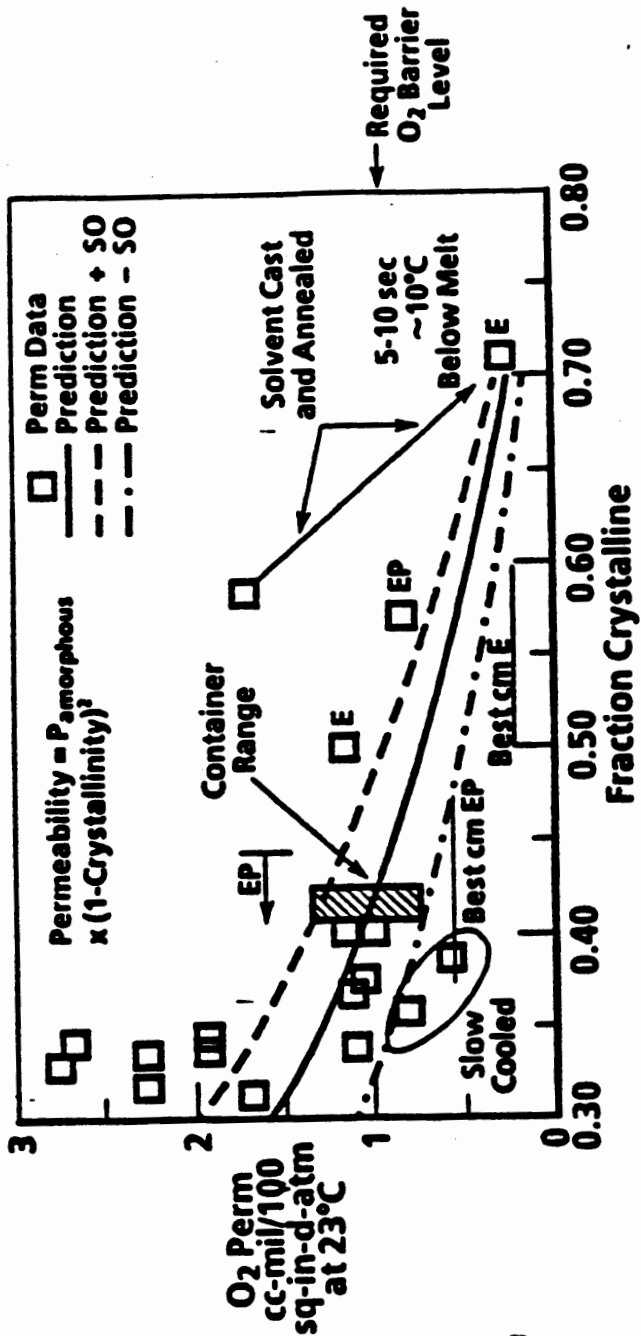
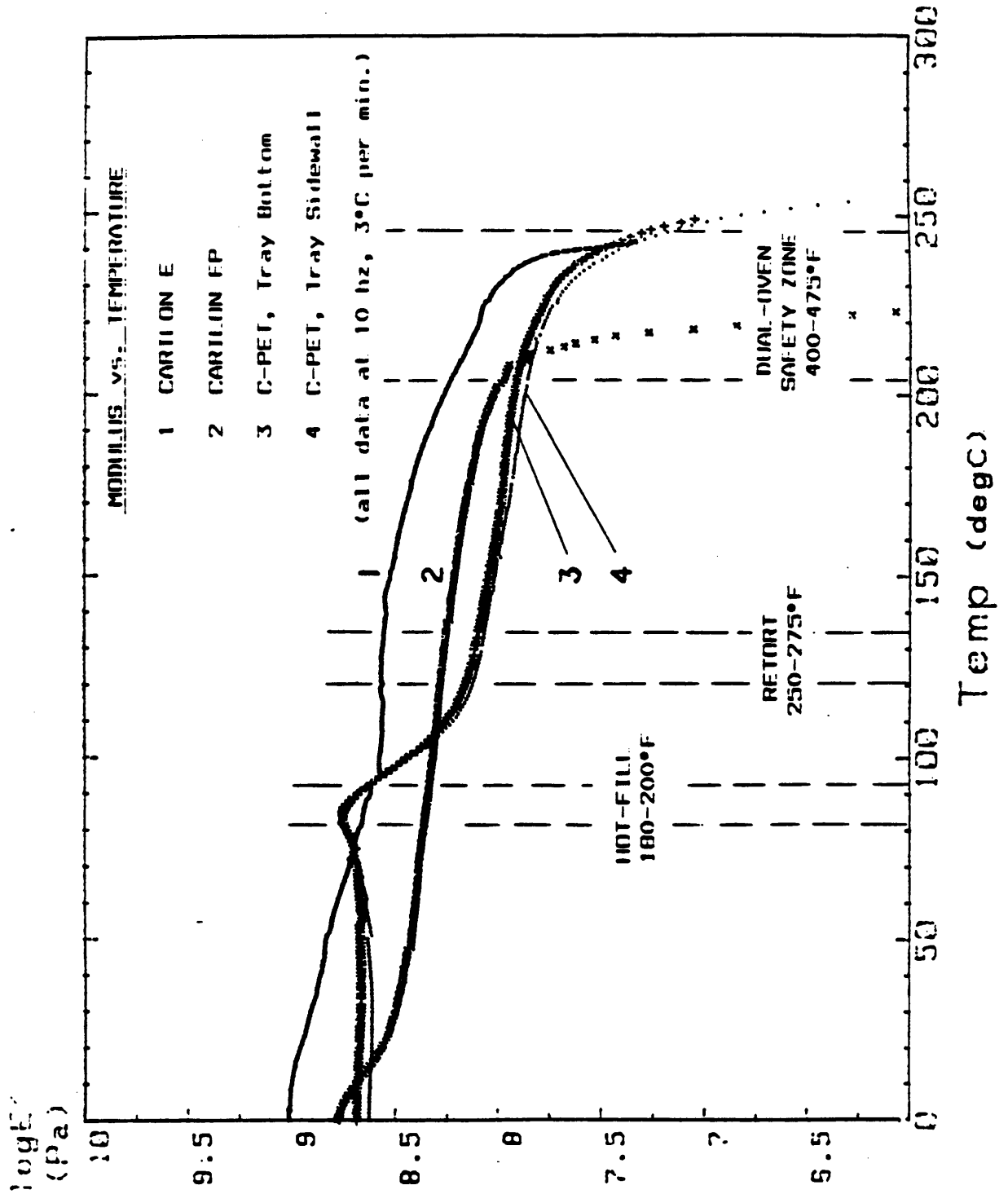


FIGURE 2



**POLYMER BLENDS WITH
CARILONTM THERMOPLASTIC POLYMERS**

W. P. GERGEN

IV. POLYMER BLENDS WITH CARILON™ THERMOPLASTIC POLYMERS

MOTIVATION

As with other polymer systems, and as the proliferation of blends in the engineering resin marketplace shows, polymer blends or blends with non-polymeric fillers and reinforcements are often more efficient in improving property deficits than changes in the basic polymer structure. The specific desired improvements in CARILON™ Thermoplastic Polymers according to desirability are:

1. Improved processing stability and continuous use temperature. This problem is usually solvable by small-molecule stabilizers and anti-oxidants. Although that approach is on-going, a more dramatic level of improvement appears to demand a rather non-conventional approach.
 2. Higher stiffness (modulus) at room temperature.
 3. Higher load bearing capability at temperatures approaching the melt temperature.
 4. Reduced creep rate (related to items 2-4).
 5. Lower thermal expansion coefficient.
- These four related problems are usually addressed with blends containing short glass fibers at significant volume fractions at the expense of greatly reduced impact strength.

6. Better low-temperature toughness and impact.
 7. Better room-temperature toughness and impact.
- Rubber modifiers usually must be used at such high concentrations that they substantially reduce the stiffness. CARILON™ Thermoplastic Polymers, however, are a unique case.

8. Amelioration of the effects of room temperature Tg including reduced effect of absorbed water.

The pursuit of a combinatorial system to provide solutions to all of these problems simultaneously or without losing the critical or unique advantages of CARILON™ Thermoplastic Polymers is the subject of on-going blends research.

BLENDS

A wide range of polymer components have been blended with CARILON™ Thermoplastic Polymers to achieve these property goals and the resulting structure and properties have been analyzed, Table 1. The CARILON™ EP Thermoplastic Polymer grade was chosen to accommodate critical temperatures of the blended polymers e.g. in the cases of polyacetal and the nitrile barrier resins. The most important blend combinations at this time appear to be:

- Blends with acid-containing polymers which improve the melt processing stability. These are more in the line of small molecule additives since they are used at low levels and may provide lubrication, passivation, and sequestering functions.
- Blends with polycarbonate which can achieve morphologies that have

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effects on stability and tend to remove the effects of the room-temperature Tg.

- Blends with functional elastomeric polymers which increase the impact strength of CARILON™ Thermoplastic Polymers.
- Blends with nylon which appear to be unusually superior in ultimate strength and toughness-related physical properties.

Significant blends have also been made in a variety of ways with short glass fibers, glass flake, mica, calcium carbonate and a variety of hydrated fillers useful in obtained self-extinguishing flammability characteristics.

MELT STABILITY AND THE USE OF BLEND MORPHOLOGY FOR THIS OBJECTIVE

There are diverse morphological forms that polymer blends or blends with fillers or reinforcements can take, determined very often by the energy of interactions between the components and the physics of the dispersing techniques. Polymer blends with CARILON™ EP Thermoplastic polymer have been shown to follow one of three distinct morphological forms:

- The blended polymer is a disperse phase in a continuous CARILON™ Thermoplastic Polymers matrix.
- The CARILON™ Thermoplastic Polymer is a disperse phase in the blended polymer matrix.
- Both polymers are continuous phases, interpenetrating and interlocked.

Since CARILON™ Thermoplastic Polymers degrade by crosslinking at high temperature, their viscosity increases as a function of time while polycarbonate is stable at high temperatures and therefore its viscosity remains constant with time.

In blends where CARILON™ Thermoplastic Polymer is the continuous phase and polycarbonate the dispersed phase, the strong interaction between these polymers accelerates the viscosity rise in the continuous CARILON™ Thermoplastic Polymer phase, Figure 1. In the opposite case, where polycarbonate is the continuous phase, changes in the structure of the dispersed CARILON™ phase is undetected since the viscosity is that of the continuous PC phase. The IPN structure which so far has only been achieved in the compositional range of 40-60% shows very little viscosity rise probably because the PC phase is accessible to all shearing planes and dominates the viscosity response.

This IPN structure offers some promise as a means of achieving long term melt processability such as in extrusion or blow molding.

BLENDS FOR IMPACT MODIFICATION

CARILON™ Thermoplastic Polymers can be toughened with a variety of rubber polymers such as thermoplastic polyurethanes, hydrogenated styrenic block copolymers, multi-segment polycondensation block copoly-

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mers such as polyamide-polyether and polyester-polyether, and maleated hydrogenated block copolymers. Of all these, the last polymer, KRATON GX-1901X, is the most efficient in terms of the level of toughening at minimum rubber volume fraction.

Recall that the transition in toughness with increasing LVNs in CARILON™ E and EP Thermoplastic Polymer was associated with a transition to shear-banding impact failure mode in the polymer, Figure 2. The effect of a discrete rubber particle toughener is to assist in the nucleation of shear banding and to add a crazing mechanism. If this is done with polymers which lie in the vicinity of the toughness LVN transition, the result is that a very small amount of toughener can raise the impact substantially, in fact a maximum is seen in one case at about 7.5% rubber, Figure 3. At LVN's considerably lower than those in this transition region, the amount of toughener needed to produce the same impact level is about 20%.

There is a substantial amount of evidence that indicates that the blends with maleated hydrogenated block polymers may be forming chemical grafts leading to increases in modulus as well as impact. That is also the case with the final blends example, CARILON™ EP Thermoplastic Polymer and nylon 6 and nylon 6-6.

When CARILON™ Thermoplastic Polymer and nylon 6 or 6-6 are blended at the appropriate nylon temperature, the viscosity rise is severe and generally makes the collection of product difficult if not impossible. On the other hand a "moderator" component can be added and can provide successful fabrication of nylon blends of up to 30% nylon in CARILON™ Thermoplastic Polymer or up to 10% CARILON™ Thermoplastic Polymer in nylon.

Blends of small amounts of CARILON™ Thermoplastic Polymer in nylon have none of the adverse flow problems of neat nylon resins; they can be molded similar to polypropylene resins without sinks or without drooling. There is also a substantial improvement in the toughness of the nylon. Other property modifications are not yet determined.

On the other side of the composition, the blends of nylon in CARILON™ Thermoplastic Polymers have unusual toughness, stiffness, and strength, higher than the levels of either component, Figure 4. These blends have dispersed nylon core particles as small as 500 Angstroms. Such a small scale of dispersion cannot be achieved mechanically and probably is the pure nylon core of a grafted nylon-CARILON™ Thermoplastic Polymer particle. The DMTA transition behavior, Figure 5, supports the notion of a graft by the presence of a broad relaxation above the Beta transition which is often present in blends heavily grafted or with very energetic interaction at the interface. The effect in this CARILON™ Thermoplastic Polymer-20% nylon 6/6 blend is an increase in the modulus at room temperature accompanying the high level of notched IZOD impact (21 FT-LB/in).

Both the CARILON-rich and nylon-rich blends offer a hope of addressing many of the problem areas which we previously enumerated or of providing alloys with new property sets, provided the reaction that makes this interaction possible can be controlled.

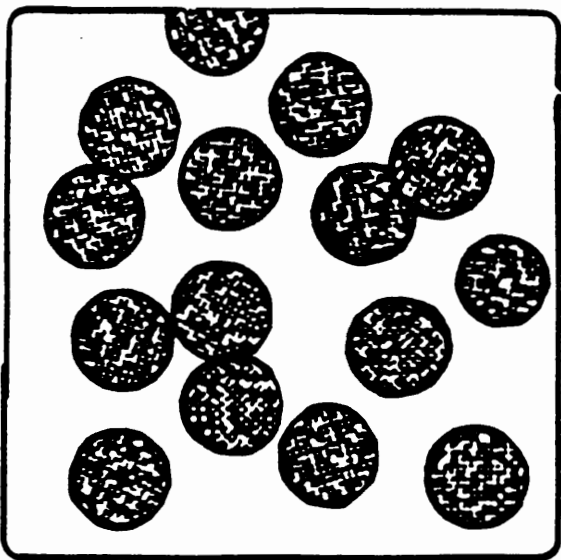
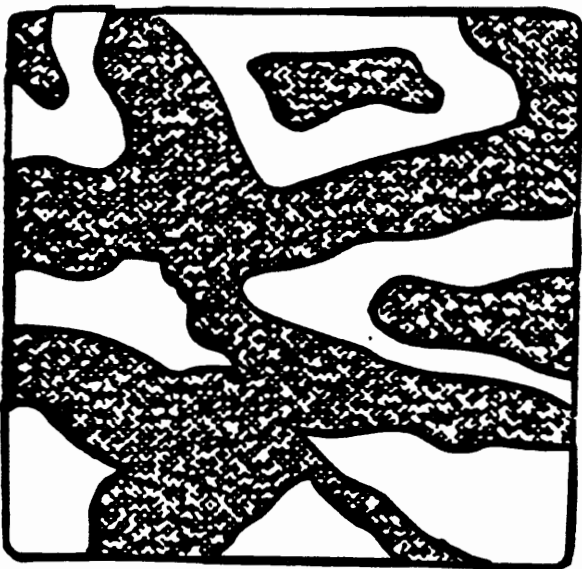
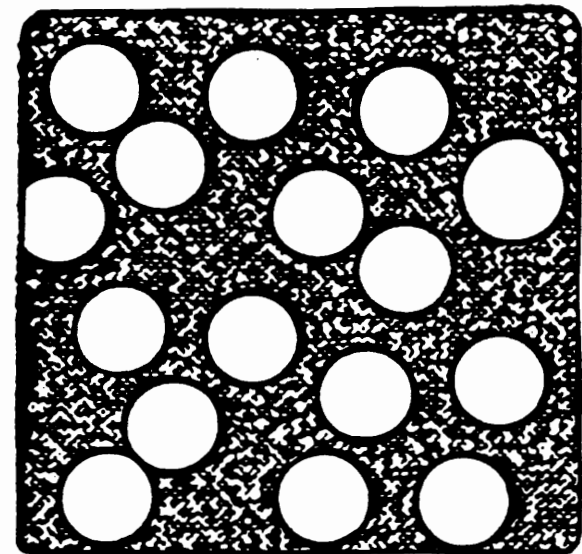
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The toughening behavior of CARILONTM Thermoplastic Polymers appears to represent a unique phenomenon among the engineering resins leading to a truly competitive or even superior impact-stiffness balance obtainable either through low-volume-fraction rubber toughening or reactive blends with polymers such as nylon 6 or nylon 6-6, Figure 6.

TABLE 1
POLYMERS BLENDED WITH CARILON™ THERMOPLASTIC POLYMERS

<u>POLYOLEFINS</u>	<u>ENGINEERING POLYMERS</u>
Polyethylene	Polyacetal Copolymer
Polybutylene	PET polyester
Polypropylene	PBT polyester
Poly 4-methyl pentene	Polycarbonate (BPA)
Polystyrene	Polysulfone (BPA)
Hydrogenated S-B block copolymer (S-EB-S)	Nylon 6 Nylon 6/6
	Nylon 11 Nylon 6-10
	Amorphous nylon
	Polyphenylene ether
	Modified PPE
	ABS SAN
	Nitrile barrier resins
	Polyester urethane
	Polyether urethane
	Polyester-ether block copolymer
	Polyamide-ether block copolymer
	Liquid-crystal polymer
<u>MODIFIED POLYOLEFINS</u>	
Ethylene acrylic acid copolymer	
Ethylene methacrylic acid copolymer	
Zn ionomers	
Maleated polybutylene	
Maleated polypropylene	
Maleated S-EB-S	
Styrene maleic anhydride copolymer	
Polyethylene glycol	
Polyethyloxazolene	
Polyethylene co-vinylalcohol	
CARILON™ EP THERMOPLASTIC POLYMERS WITH VARIOUS T _m RANGING FROM 195°C TO 230°C	

FIGU. 1



PC DISPERSED IN CARILON

CO-CONTINUOUS PC/CARILON

CARILON DISPERSED IN PC

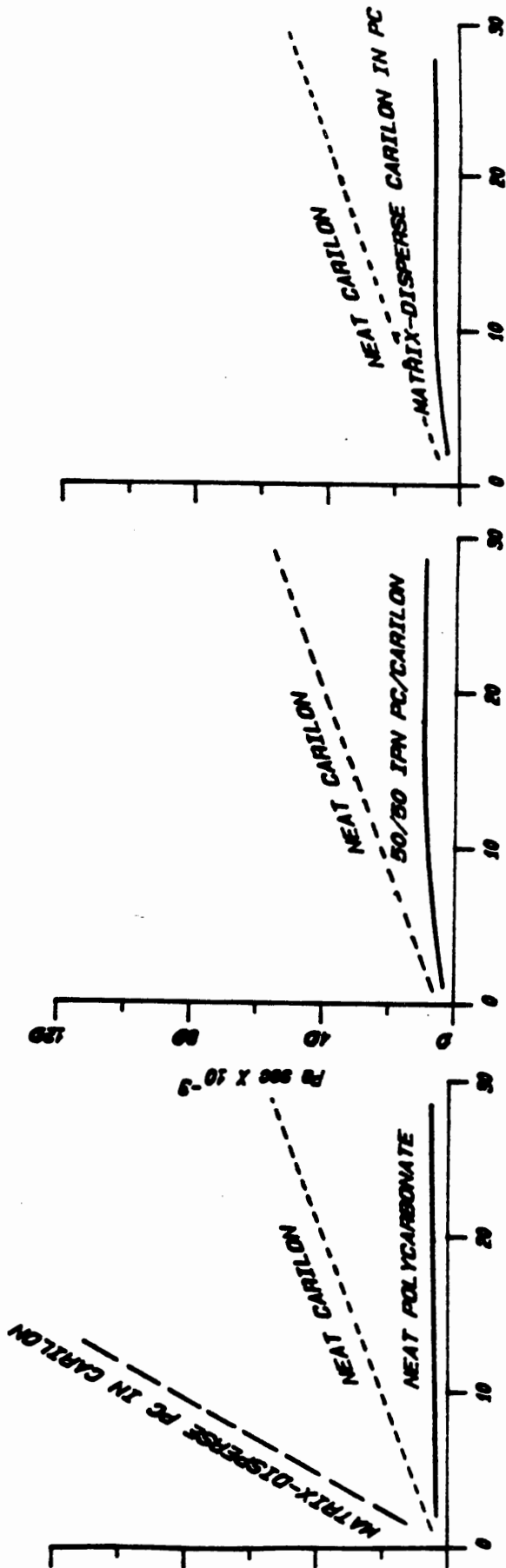
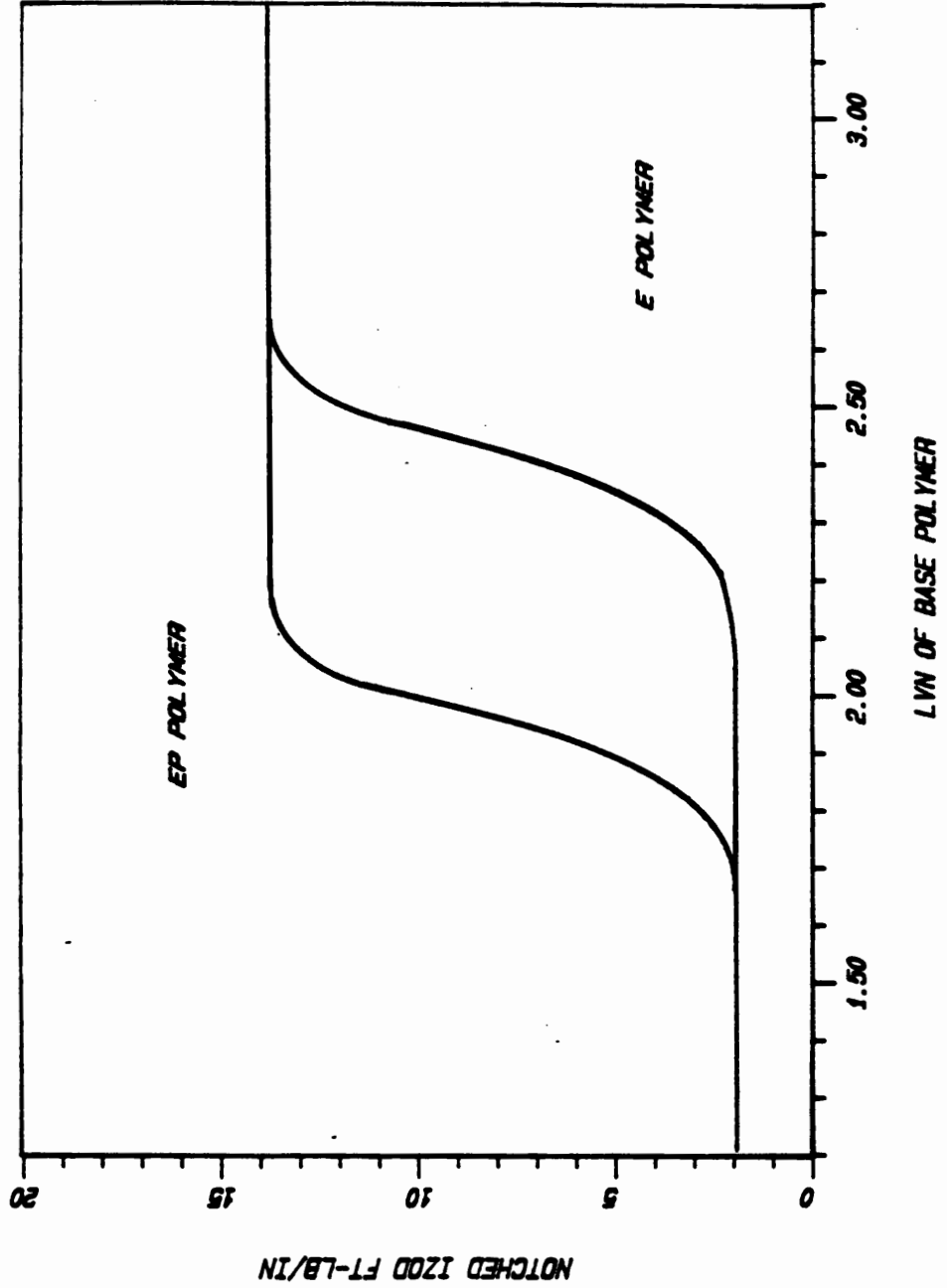


FIGURE 2
MOLECULAR WEIGHT TOUGHNESS TRANSITION



LWIZ00.2

FIGURE 3

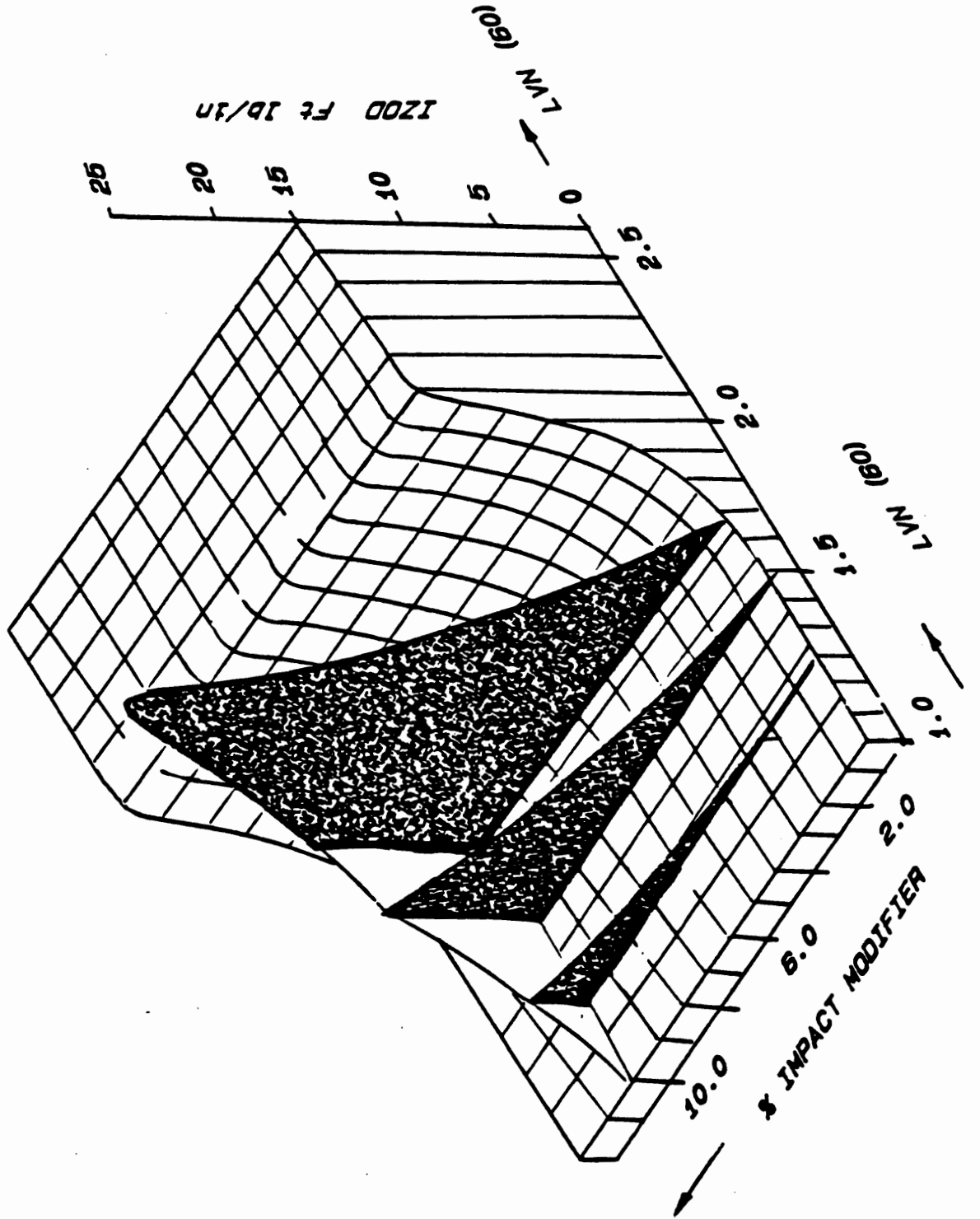
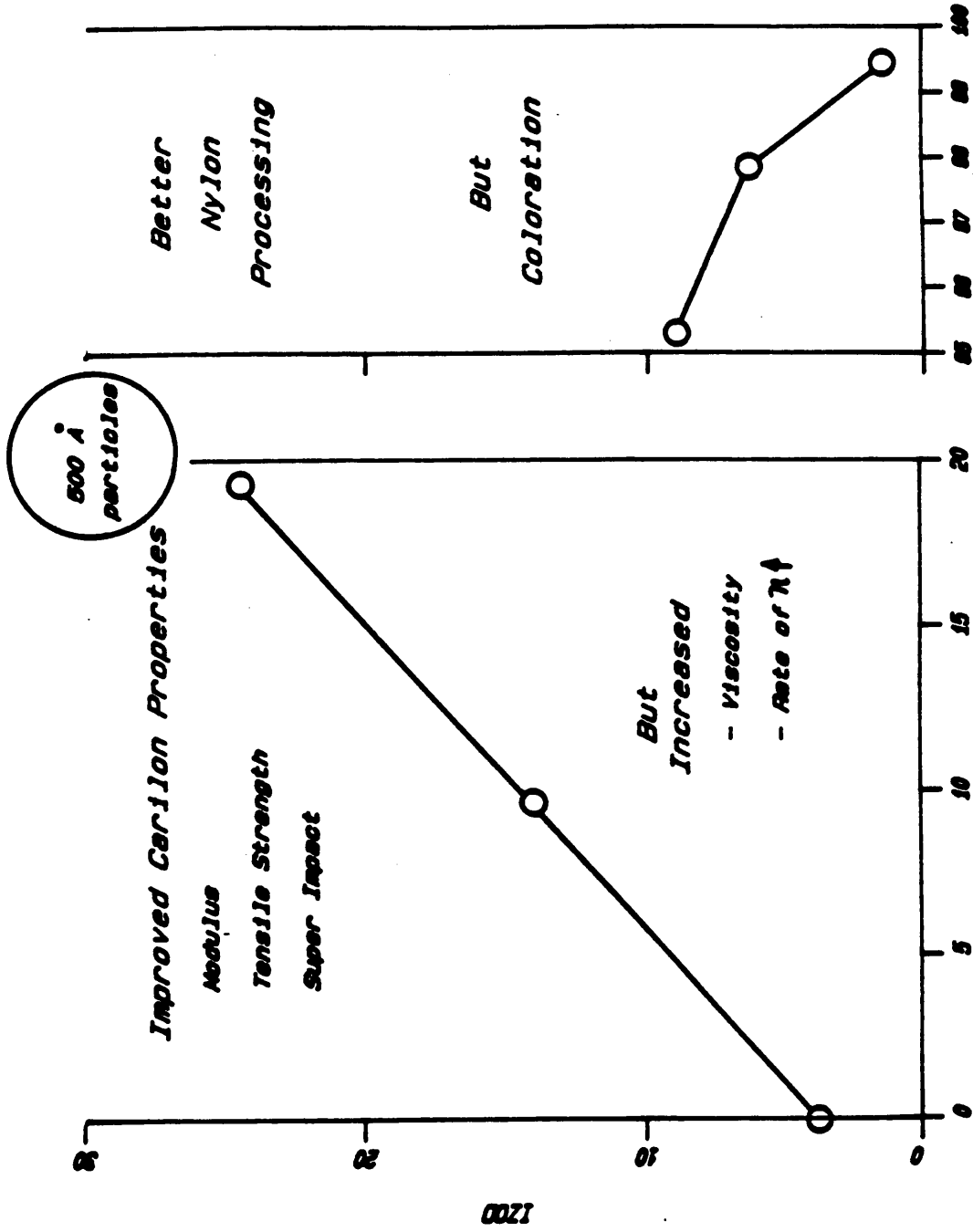


FIGURE 4

CARILON + NYLON 6 or 6-6



SW NYLON 6, 6-6 with 1% Moderator

FIGURE 5

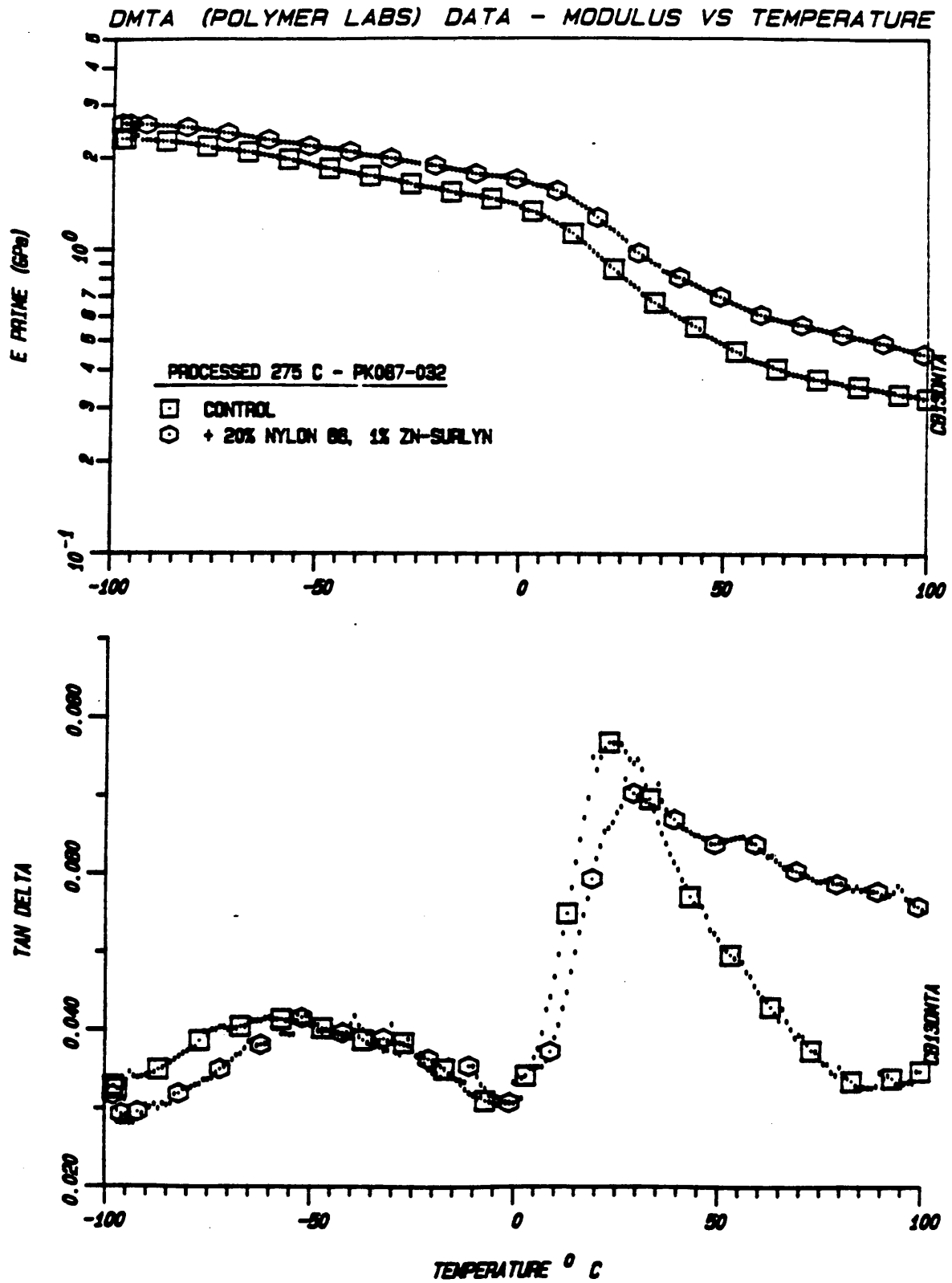
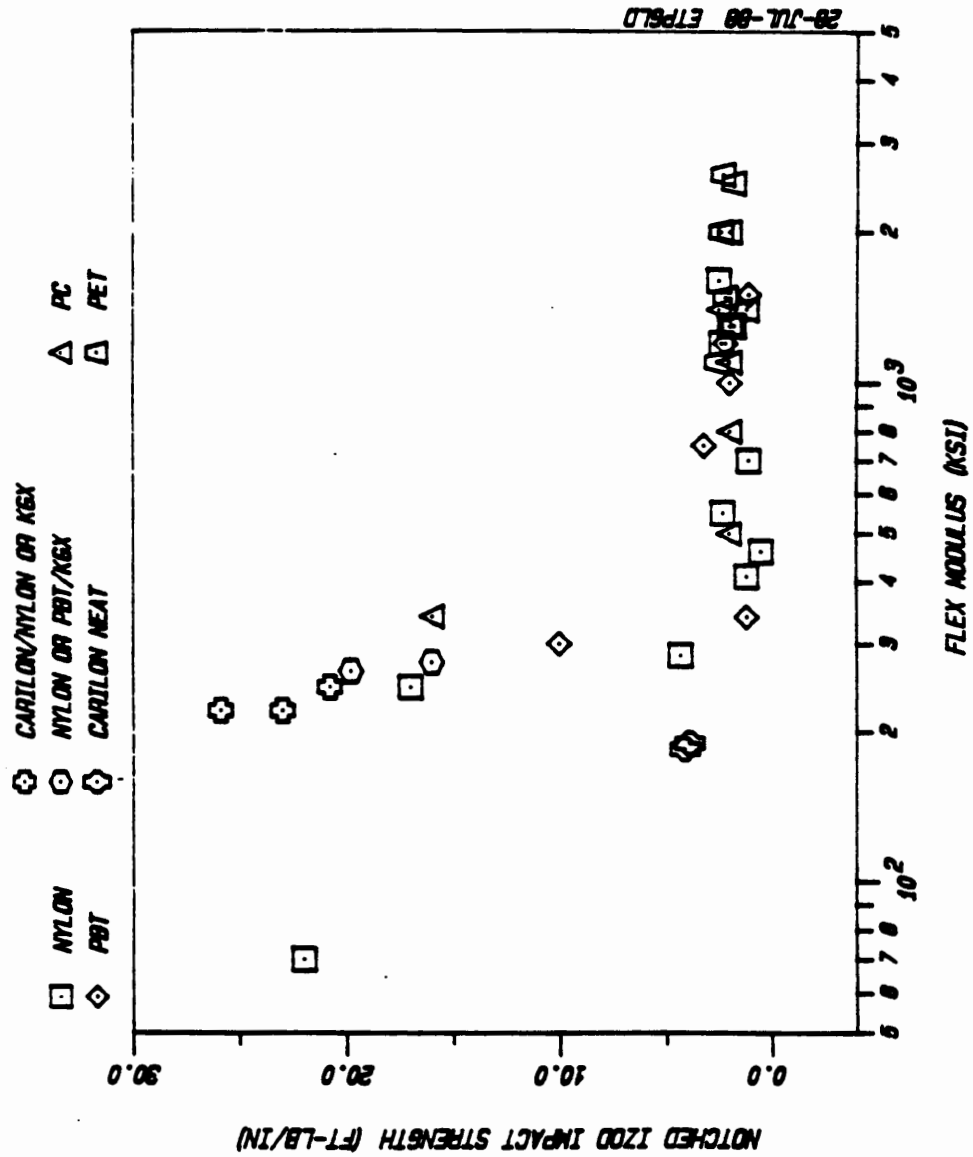


FIGURE 6
NEAT AND GLASS-FILLED ENGINEERING RESINS



**CARILON™ THERMOPLASTIC POLYMERS
IN
FIBER AND MONOFILAMENT APPLICATIONS**

A. A. BROEKHUIS

V. CARILON™ THERMOPLASTICS POLYMERS IN FIBER AND MONOFILAMENT APPLICATIONSSUMMARY

CARILON™ E and EP Thermoplastic Polymers of low to medium molecular weight have been meltspun using laboratory and commercial scale spinning equipment. The processing conditions for the spinning process were identical to normal extrusion conditions with the exception that filter packs had to be used to prevent problems in the stretching and annealing steps. With the improvements made in melt stabilization and in batch-to-batch quality, contamination problems are and will continue to be reduced.

After preliminary studies on the effect of draw down ratio and stretching conditions, the property assessment on the obtained monofilaments indicated that the maximum tenacity and modulus levels were above the levels found for filaments based on Nylon and Polyester (PET). Further optimization of the spinning process is regarded necessary in order to improve loop and knot strength.

Dyeing studies indicated that CARILON™ Thermoplastic Polymers based fine fibers are dyeable with the standard dispersed dye systems used for polyester fiber.

Application development will be concentrated on the exploitation of the merits of CARILON™ Thermoplastic Polymers based monofilament in industrial applications with the filament yarn being evaluated in rubber reinforcement.

PROCESSING

CARILON™ E and EP Thermoplastic Polymers with limiting viscosity numbers in the range of 1.0 to 1.7 dl/g have been meltspun on a Brabender single screw extruder using a one-hole die with separate draw-down and stretching units. As expected, the highest draw-down ratios were obtained with low LVN materials (Figure 1) which resulted in the best strength/modulus balance (Figure 2).

Tests on commercial and semi-commercial spinning units with multi-hole dies (i.e., standard set-up for Nylon monofilament and polypropylene yarn production, respectively) produced monofilament and yarn during two to three-hour continuous runs. The use of filter screens was found necessary in particular for the production of fine fiber. Problems encountered during these runs were related to black specks and gel particles present in the polymer. Currently, this contamination problem is gradually being reduced by a continuing improvement in batch-to-batch quality of the polymers produced in the market development unit. Because of meltstability restrictions, this demonstration on commercial equipment has been limited to the meltspinning of CARILON™ EP Thermoplastic Polymer.

Data on monofilament produced on the commercial unit are attached.

PERFORMANCE PROPERTIES

Optimization studies carried out on the Brabender unit have so far been directed at the effects of polymer composition (E vs EP), molecular weight, extrusion conditions and fiber finishing steps (i.e., stretching and annealing).

The results obviously depend on all mentioned factors. In summary, the outcome of the study is that monofilament with tenacities up to 14-15 g/den and moduli (at 4% strain) up to 220 g/den are achievable with CARILONTM EP Thermoplastic Polymers of low molecular weight.

The maximum tenacity and modulus levels obtained from CARILONTM EP Thermoplastic Polymers monofilament are shown in Figures 3 and 4 in a comparison with monofilaments based on other engineering polymers.

Loop and knot strength of CARILONTM EP Thermoplastic Polymers monofilament are in the order of 20-30% retention of the original tenacity (Table 1).

Because of the preliminary character of the data generated on laboratory equipment, the studies need to be repeated on semi-commercial and commercial meltspinning equipment. Programs are in place (Table 2).

DYEABILITY

Dyeability studies have been carried out on CARILONTM Thermoplastic Polymers based fine fiber showing a clear similarity to polyester fiber. Dispersed dye systems appeared the best in both direct experiments and in competitive experiments with Nylon-based fiber.

APPLICATION DEVELOPMENT

Application development has now been initiated aiming at the exploitation of the observed tenacity/modulus balance. Application areas under study are cords for rubber reinforcement and monofilament for technical usage.

FIGURE 1
CARILON™ THERMOPLASTIC POLYMER FIBRES

EFFECT OF LVN ON MAXIMUM DRAW-DOWN

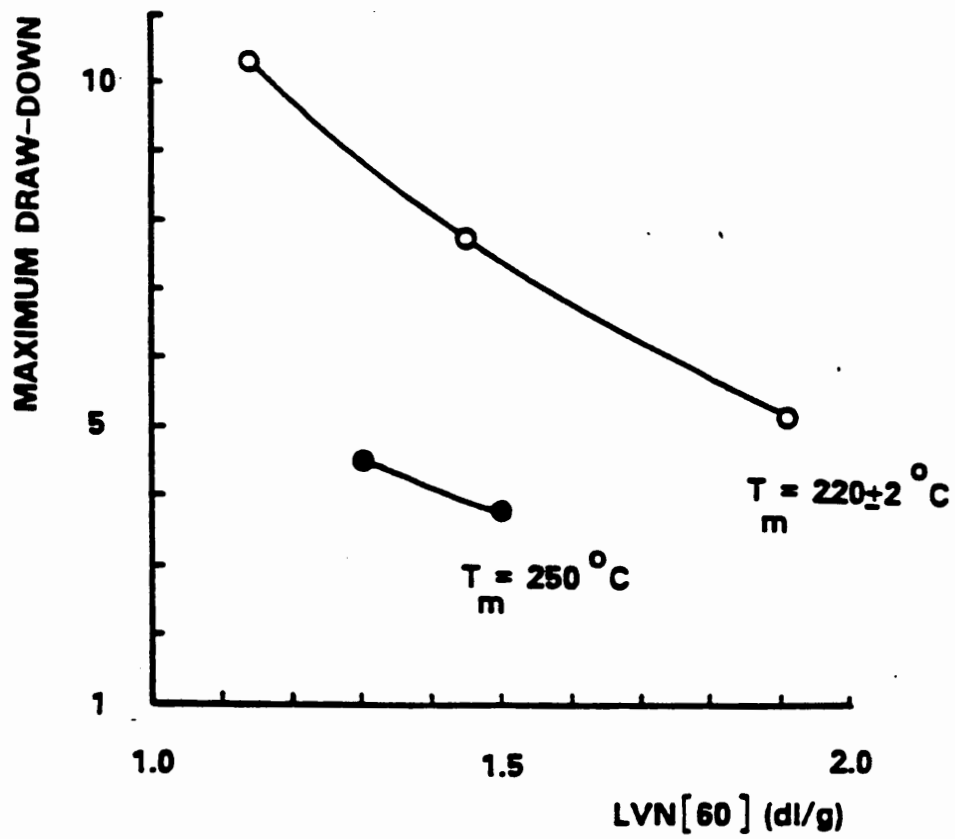
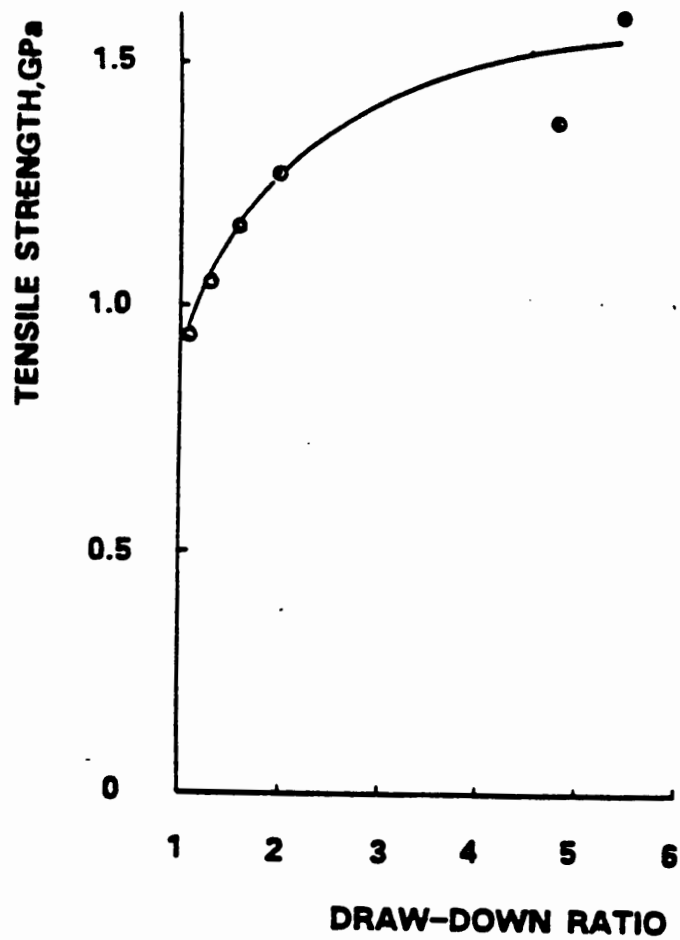


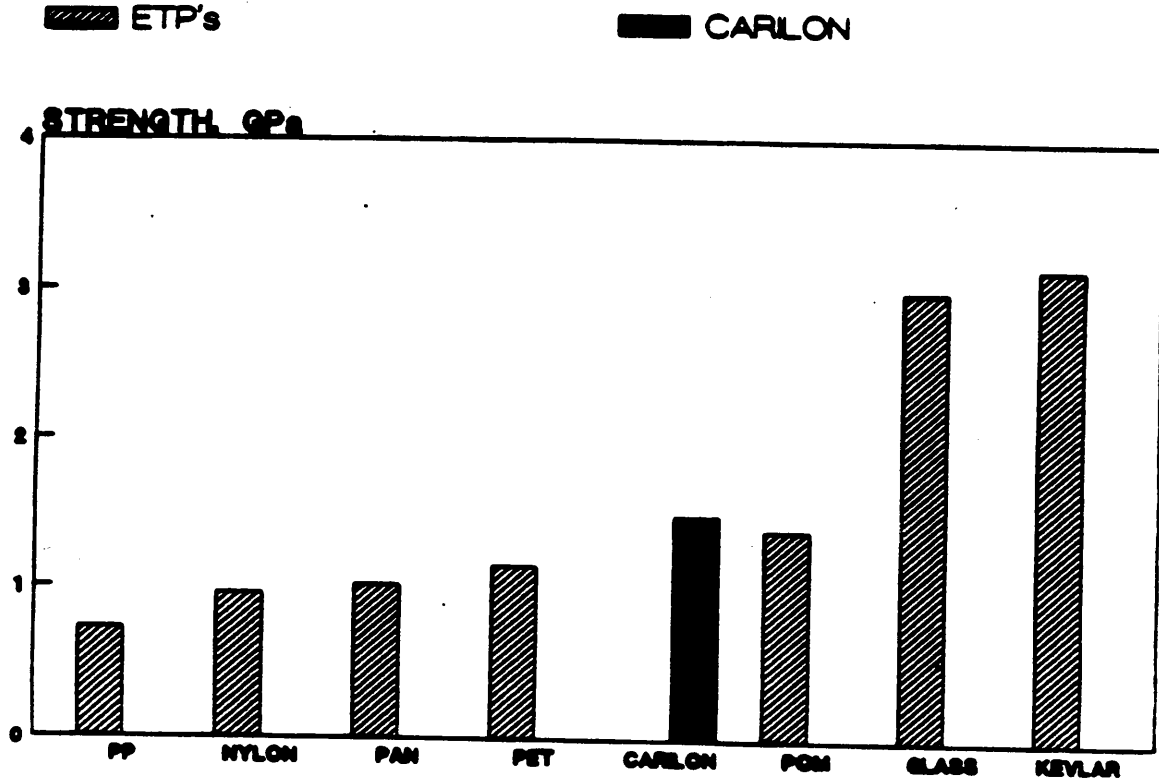
FIGURE 2
CARILON™ THERMOPLASTIC POLYMER FIBRES

RELATIONSHIP TENSILE STRENGTH VS DRAW-DOWN



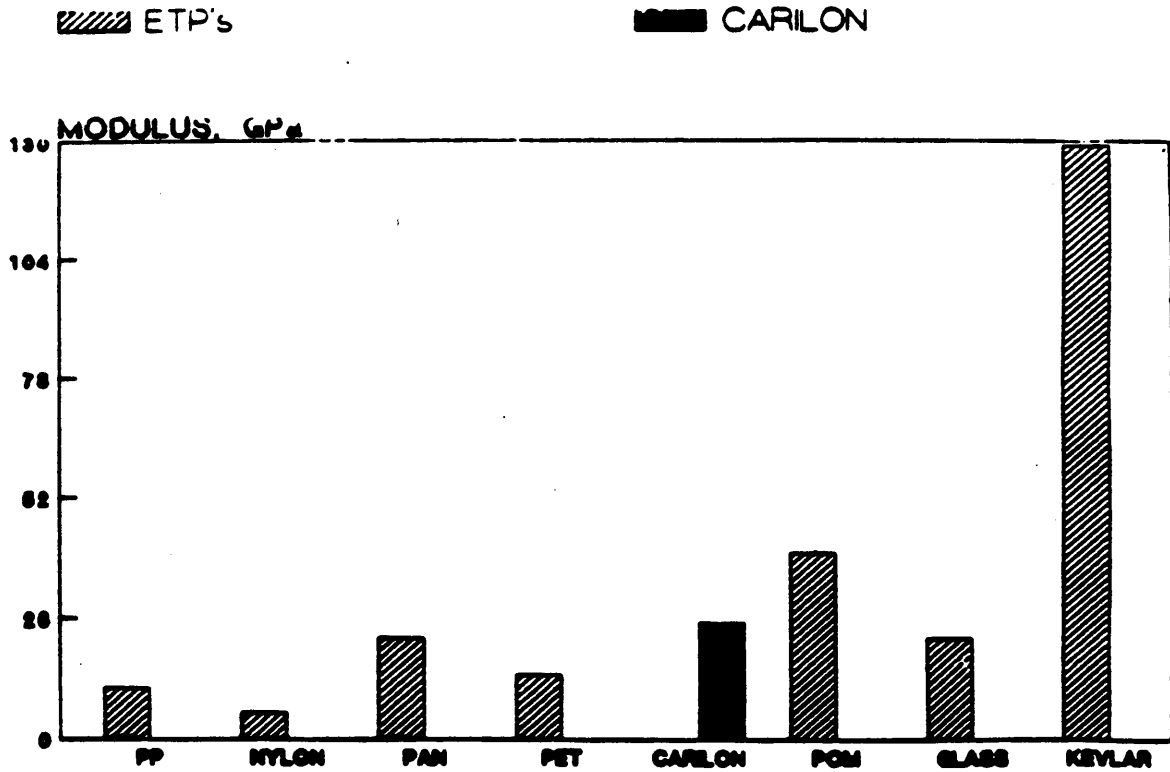
CARILON EP; $T = 218^{\circ}\text{C}$; $\text{LVN}(60) = 1.14 \text{ dl/g}$
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FIGURE 3
MONOFILAMENT PROPERTIES I.
CARILON™ THERMOPLASTIC POLYMER VS OTHER ETP'S



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FIGURE 4
MONOFILAMENT PROPERTIES II.
CARILON™ THERMOPLASTIC POLYMER VS OTHER ETP'S



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TABLE 1
MONOFILAMENT MELTSPINNING OF CARILON™ THERMOPLASTIC
EP POLYMER AT LUXILON

MELTSPINNING CONDITIONS AND TESTING DATA				
BATCH	TEMPERATURE	STRECH	STRECH	TENACITY
#	<u>PROFILE (1)</u>	<u>RATIO</u>	<u>CYCLES (2)</u>	<u>9/DEN</u>
RUN 1				
1	0	4.8	3	7.0
RUN 2				
1	1	7	3	-
2	2	7	3	5.3
3	2	10	3	-
4	2	8	3	7.3
5	2*	8	2	8.7

NOTES:**1. TEMPERATURE PROFILE FOR STRECH OVENS.**

TEMP. IN °C.

130 (OVEN 1)	150 (OVEN 2)	130 (OVEN 3)	PROFILE 0
105	150	155	1
140	180	165	2
140	180	165	2
140	180	165	2*

PROFILE 2*: STRETCHED IN OVEN 1&2 AND IN OVEN 3

2. NUMBER OF STRETCH UNITS IN USE.

TABLE 2
 LOOP AND KNOT STRENGTH OF SOME ENGINEERING FIBRES

fibre type	loop strength		knot strength	
	GPa	% original	GPa	% original
Kevlar	1.3 -2.2	40-75	1.6 -2.5	30-40
Polyester	0.8 -1.0	70-75	0.55-0.7	50-60
Nylon-6	0.7 -0.8	70-75	0.6 -0.7	60-65
Polyprop.	0.55-0.65	85-95	0.35-0.55	60-70
CARILON	0.25	23	0.3	27

TABLE 3
CARILON™ THERMOPLASTIC POLYMER FIBRES

VARIABLE PARAMETERS:

1. PRODUCT PARAMETERS:

- VISCOSITY (LVN)
- MELTING TEMPERATURE
- ADDITIVES

2. PROCESS PARAMETERS:

A. EXTRUSION:

- TEMPERATURE
- SPEED
- DIE GEOMETRY
- DESIGN

B. COOLING:

- AIR
- WATER

C. DRAW-DOWN:

- TAKE-UP SPEED

D. STRETCHING:

- TEMPERATURE
- INLET SPEED OVEN TUBE
- STRETCH RATIO
- ATMOSPHERE

○ INVESTIGATED

○ TO BE INVESTIGATED

**CARILON™ THERMOPLASTIC POLYMER
STABILIZATION**

W. P. ROTHWELL

VI. CARILON™ THERMOPLASTIC POLYMER STABILIZATION

The discovery at KSLA in 1983 of highly efficient catalysts for copolymerization of carbon monoxide and olefins provided, for the first time, a practical synthesis of high molecular weight, highly crystalline aliphatic polyketones. Since that time, a joint program between WRC and KSLA was brought about to develop the process and the family of products called CARILON™ Thermoplastic Polymers. An important component of this program has been stabilization; the aliphatic ketone functionality subjects CARILON™ Thermoplastic Polymers to a broad spectrum of chemistry. Consequently, the prevention of deterioration and change during the manufacture, handling, and use of CARILON™ Thermoplastic Polymers presented an array of problems that has been addressed through Shell's stabilization technology.

POLYMER DEGRADATION MECHANISMS

Since CARILON™ Thermoplastic Polymers represent a new class of polymers, it was judged important early in the program to elucidate the principal characteristics of degradation. The following represents some major conclusions from this work:

Physical Observations

- 1) In general, high temperature in the absence of oxygen leads to crosslinking, while moderate temperature in the presence of oxygen leads to chain scission.
- 2) At elevated temperatures, weight loss (mostly H₂O with almost no CO) occurs both in the presence and absence of oxygen. With oxygen, the weight loss is more than one hundred times faster.
- 3) The presence of alkali metals and, to a lesser extent, alkaline earth metals leads to rapid crosslinking in the melt.
- 4) CARILON™ Thermoplastic Polymers are inherently stable in the absence of oxygen at oven aging temperatures; specimens embrittle only after 6 months at 150C in vacuum. This result suggests that there is no fundamental impediment to stabilizing CARILON™ Thermoplastic Polymers to the level of heat stabilized Nylon (115UL).

Chemical Observations

- 1) Crosslinking in the polymer is most likely due to base-catalyzed aldol condensations. The species produced by chain scission have not been identified.
- 2) In the presence of strong acid, furan formation occurs. In the presence of mild base, aldol condensations occur.
- 3) Oxygen at moderate temperatures leads to furan formation by a radical process. The action of oxygen is catalytic.

The principal means used to arrive at these conclusions were reactions of the pure 3,6,9-triketo undecane model compound and pure CARILON™ Thermoplastic Polymers under various conditions and analysis of the resulting products using ¹³C NMR, IR, GC, GC-MS, LVN, and TGA.

MELT PROCESSING STABILITY

Beginning with the work of Nozaki at the Shell labs in Emeryville in the late 1960's, aliphatic polyketone polymers have been the subject of several research programs at Shell. Very poor melt processing stability resulting from high catalyst residues was a chief technical problem that prevented early commercialization of these polymers. Thus the most important factor leading to processible CARILON™ Thermoplastic Polymers was the 1983 catalyst discovery and the subsequent process improvements that reduced considerably catalyst residues. The next major improvement in processibility came with the invention of CARILON™ EP Thermoplastic Polymers. Although CARILON™ EP Thermoplastic Polymers are intrinsically no more stable than the E version, the introduction of a few percent propylene in place of ethylene along the polymer backbone lowers the melting point and thus increases the processing window of the polymer. The practical processing characteristics of native CARILON™ Thermoplastic Polymers are summarized in Figure 1.

Further improvements in the stability and processibility of both CARILON™ E and EP Thermoplastic Polymers have been made by using: (1) melt lubricants, (2) polymeric melt stabilizers, (3) novel small molecule stabilizers, and (4) conventional antioxidants.

A. Status

Kaiser Bayerite is an effective nonpolymeric additive for stabilizing the CARILON™ Thermoplastic Polymer melt. Rheometrics measurements for Bayerite, Figure 2, indicate that the rate of crosslinking is reduced by a factor of 3 (equivalent to 15C in processing temperature) over the neat polymer; Figure 3 gives an indication of the expected improvement. Bayerite is now being tested on commercial size CARILON™ Thermoplastic Polymer batches. Other small molecule additives in assessment showing positive effects on stability and processing include cellulose, glycerol monostearate, and carbon dioxide gas.

Polymeric additives are also effective melt stabilizers, especially copolymers of ethylene and methacrylic acid. Under mild processing conditions, modest benefit is seen; under severe processing conditions or in the presence of prodegradant impurities (e.g. air or Na⁺ from glass), the effects are substantial (see Table 1 and Figures 4 and 5). Nucrel 535 is currently the ethylene/methacrylic acid copolymer of choice. As oxygen pulsed rheology results of Figure 5 indicate, Nucrel 535 appears to also counteract oxidation of the polymer at high temperature. Preliminary oven aging results also support the notion that Nucrel acts as a thermo-oxidative stabilizer. Finally, low concentrations of the methacrylic acid copolymers counteract the deleterious effects of alkali metal ions and are key blending components in glass-containing blends. Primacor 1410, an ethylene/acrylic copolymer, is often chosen since it gives a good balance of properties and melt stabilization in glass blends.

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Much work has been put forward on identifying melt lubricants for CARILON™ Thermoplastic Polymers. Table 2 compares Brabender plasticorder results for selected melt stabilizers and lubricants. Work is now in progress to assess quantitatively the melt stability improvement that derives from combining two or more melt stabilizers and lubricants.

Conventional antioxidants, e.g. Irganox 245, Naugard 445, and Ethnox 330, have only a moderate effect on improving melt stability and thus are added primarily as antioxidants.

Ignoring degradation, the rheological characteristics of CARILON™ EP Thermoplastic Polymers of typical molecular weight are excellent--akin to those of general purpose, molding grade polycarbonate. CARILON™ Thermoplastic Polymers can be molded at clamp tonnages of 2-2.5 ton/sq-in, a range lower than many other ETP's. This indicates that very large parts such as fenders can be molded on conventional injection molding equipment.

THERMAL OXIDATIVE STABILITY

The UL index method is used to quantify thermal oxidative stability of CARILON™ Thermoplastic Polymers. Table 3 summarizes our current status. Work is in progress to assess the increased thermal oxidative stability imparted by inclusion of current melt stabilizers.

A. Stability Requirements for Automotive Applications

CARILON™ EP Thermoplastic Polymers have been tested under GM 7000-M material specifications for oxidative stability (HA-7 protocol using GM Test Method 9095-P) and heat resistance (W 4649). The polymer passed both tests except that discoloration was noted under the HA-7 protocol.

UV STABILITY

Work on UV stabilization of CARILON™ Thermoplastic Polymers was recently initiated. CARILON™ Thermoplastic Polymers are most sensitive to the lower UV wavelengths that are present in xenon arc, carbon arc, and UVB fluorescent test lamps, but are not present in natural sunlight or UVA test lamps. The selection of UVA lamps for accelerated testing (see below) was made in order to facilitate translation of data from artificial to real sunlight. In direct comparisons with unstabilized polypropylene, unstabilized CARILON™ EP Thermoplastic Polymer loses about 30% of its starting toughness in 4 hours UVA exposure while PP in the same exposure is unchanged. Initial tests indicate that CARILON™ E Thermoplastic Polymer is moderately more UV stable, in terms of time to embrittlement, than CARILON™ EP Thermoplastic Polymers; this is expected on mechanistic grounds since CARILON™ E Thermoplastic Polymers cannot degrade by the facile Norrish Type II mechanism.

In qualitative tests, CARILON™ E and EP Thermoplastic Polymers exposed to window-filtered sunlight for 18 months at ambient conditions shows no evidence of embrittlement; specimen bleaching was observed indicating some reaction to the longer wavelengths in sunlight. In contrast, the same samples subject to 10 days of outdoor Houston summer exposure showed severe embrittlement and yellowing in 10 days.

CONFIDENTIALA. Status

Limited screening of UV stabilizers on tenacity retention of CARILON™ EP Thermoplastic Polymer monofilament indicates that Tinuvin P is the best single additive tested to date. Current status is summarized in Figure 6. Relative toughness as measured by high speed tensile testing of thin films is used to screen light stabilizers for non-fiber applications. The best systems to date are combinations of Printex 140, Irganox MD 1024, Irganox 245, and Naugard 445 or Printex 140 and Santanox R. Preliminary results suggest that these systems increase the relative lifetime to failure by toughness loss by a factor of up to about fifty in time over the control when the sample is irradiated at diurnal eight hour intervals. Continuous irradiation under UVA results in earlier failure for this system. This phenomenon is under study and the results are to be confirmed by other standard property tests.

B. UV Stability of Painted CARILON™ EP Polymer Parts

Headlight bezzels, Ford Econoline, and Taurus fenders molded from CARILON™ EP Thermoplastic Polymer compounds painted with standard automotive exterior paint systems are being subjected to standard Florida outdoor exposure testing. As of July 1 1988, 9 months exposure data is available on the bezzels and Econoline fenders and 7 months data is available on the Taurus fenders. These systems score 10 points out of 10 (i.e. no change) in ASTM-measured gloss, film continuity, color, and delamination and 7-8 points out of 10 on mildew formation and dirt retention.

TESTS FOR STABILITYA. Melt Stability1. Differential Scanning Calorimetry

In the DSC of CARILON™ Thermoplastic Polymers the following temperature program is used: The sample is heated from room temperature to 285C and cooled immediately back to room temperature. The sample is then heated again to 285C and held at 285C for ten minutes. Finally, the sample is cooled to room temperature. All temperature ramps are at 20C/min. In this protocol, the two heats of melting, H1 and H2, and two heats of crystallization, C1 and C2, are measured. The ratio C2/C1 is a measure of the crystallizability retained after ten minutes at severe processing temperature and is used to quantify melt stability.

2. Melt Rheology

A Rheometrics Dynamic Spectrometer 7700 in the parallel plate geometry applies a sinusoidal strain of 25% at 1 radian/second at 275C. The torque and normal force are measured over a half-hour period and the dynamic complex viscosity is calculated as a function of time. In oxygen pulsed rheology, the plates are separated and the sample exposed for thirty seconds to an oxygen atmosphere. The plates are closed and the test is resumed.

3. Thermogravimetric Analysis

Isothermal TGA at 260C under nitrogen is used as an additional test of melt stability. 1-4% weight loss is typical after 30 minutes.

4. Torque Rheometer

A Brabender torque rheometer, equipped with a W30 roller mixer, is used to assess potential melt lubricants and stabilizers. The following conditions are used: cup temperature = 240C; spindle speeds 60 and 40 rps respectively; polymer load=32grams; ram weight=5Kg; scale full range (0-50Nm).

B. Thermal Oxidative Stability

1. Oven Aging

The additives are typically incorporated by melt extruding the polymer/additive mixture in a 15mm Baker Perkins twin screw extruder. CARILON™ polymer powder is compression molded to 1-mm thick sheets in a positive mold at 250C for 5 minutes. Dumbbells cut from the sheets are oven aged at various temperatures (typically 110C, 125C, and 140C) and tested for tensile properties. In the case of brittleness testing, test specimens 30x3 mm are cut from the sheets and tested for brittleness at regular time intervals; the aging time at the appearance of cracks is the failure time.

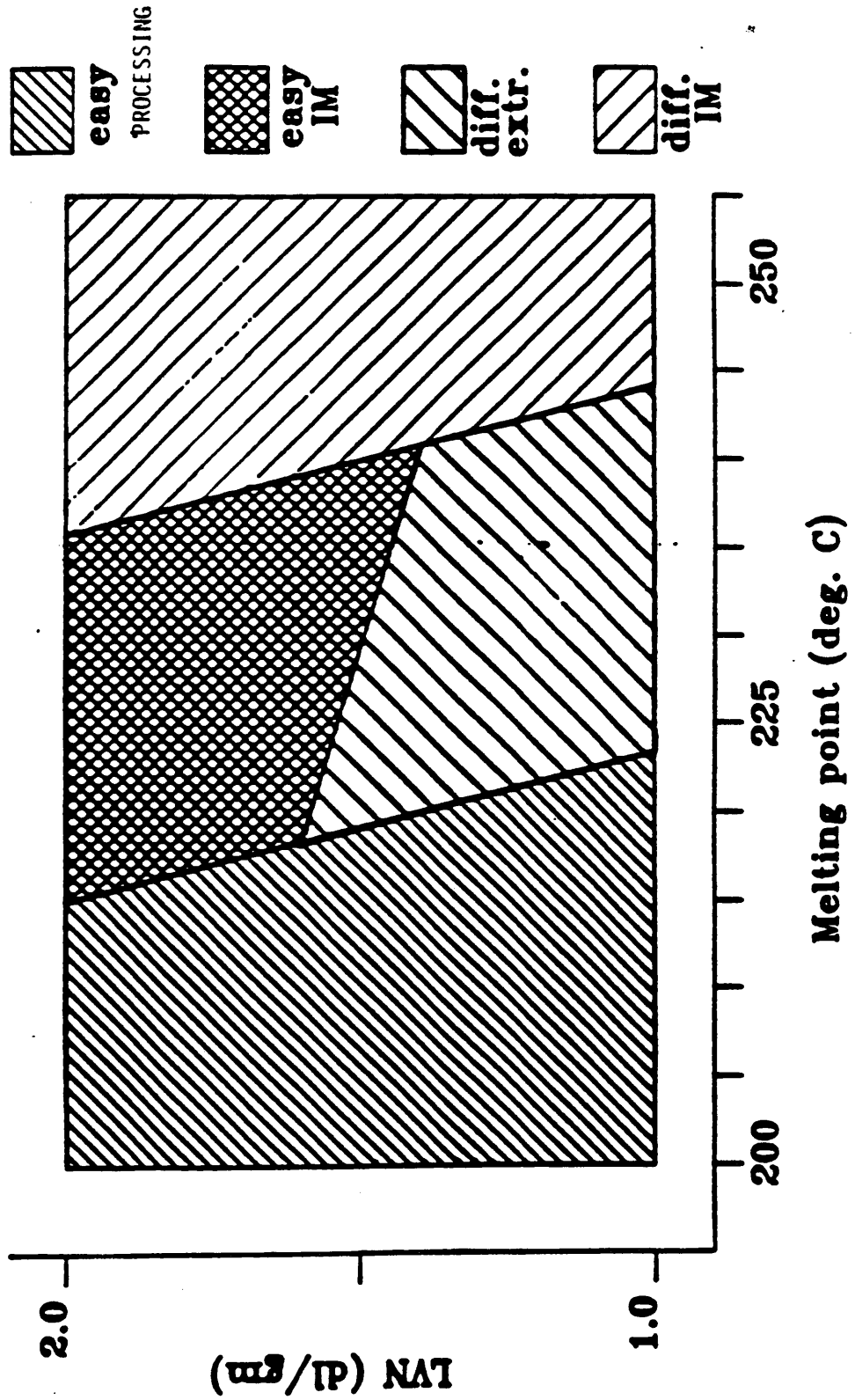
C. UV Stability

Candidate additives are incorporated by melt extrusion. Test specimens are cut from compression-molded 10 mil sheets. Accelerated exposure testing has been conducted with UVA fluorescent lamps at 40C and ambient humidity; temperature and humidity will be included as variables in later testing. Only limited outdoor exposure has been employed to date. Our key mechanical property measure is a high-speed tensile test which measures toughness.

FIGURE 1

FIGURE 1

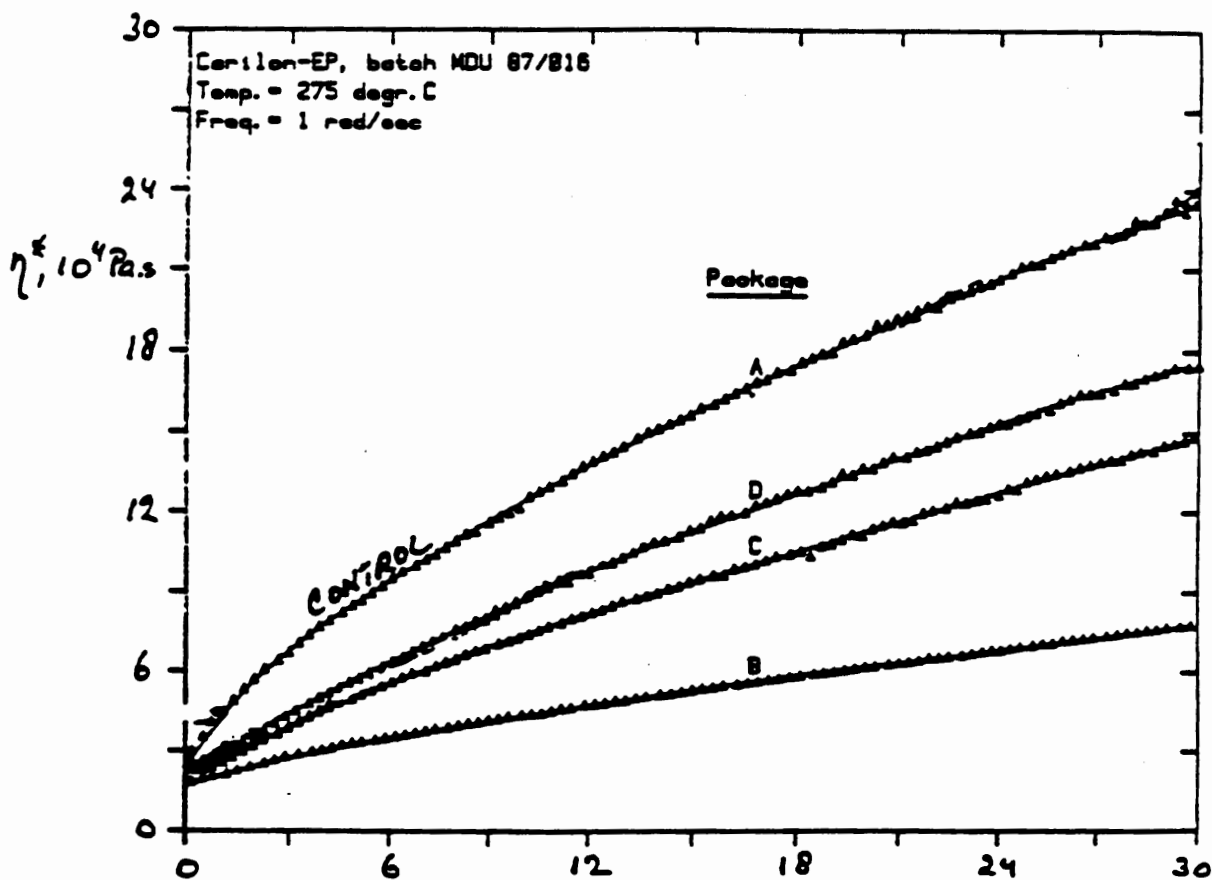
Processability of present CARILON polymers (with respect to stability - without melt stabilizer)



DM/JAS 3/66

FIGURE 2

Dynamic viscosity measurements of "CARILON" EP Polymer, with Bayerite additive. Complex Viscosity versus Time.



A: BLANK

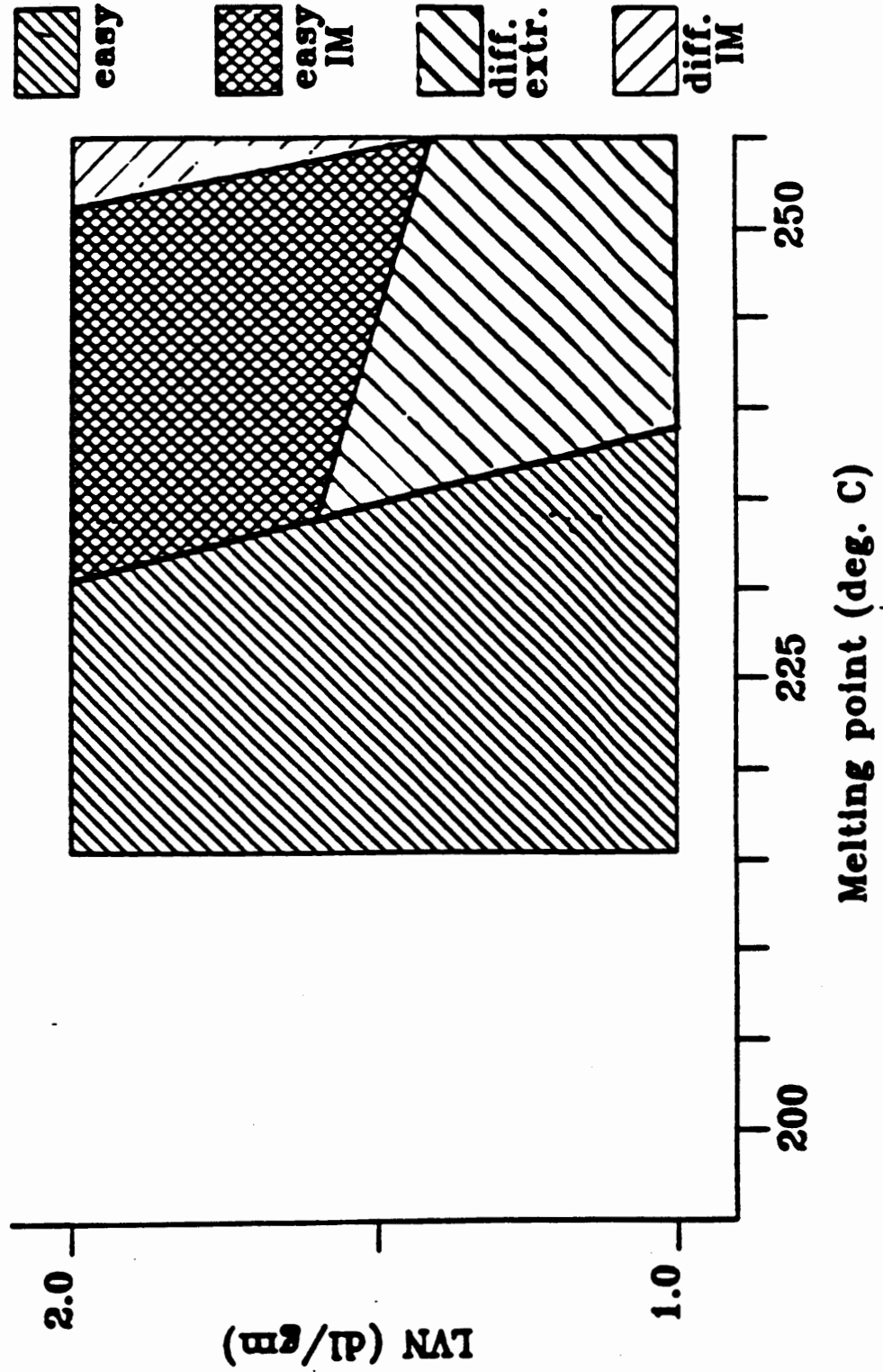
B, C, D: WITH BAYERITE. DIFFERENT CURVES ARISE FROM DIFFERENT METHODS FOR BAYERITE ADDITION

COMPRESSION MOULDED SHEETS (5', 240°C)

VISCOSITY IMPROVEMENT INDICATE 15°C INCREASE IN PROCESSING WINDOW (SEE FIGURE III)

FIGURE 3

**Processability of present CARILON polymers
(with respect to stability - with melt stabilizer)***



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* Predicted processing improvement with Bayerite Added (See Figure 2)

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TABLE 1
LVN CHANGES FOR REPROCESSED POLYMER
AS FUNCTION OF ADDITIVE

Additive	Initial LVN	Extr 1 LVN	Extr 2 LVN	Inj Mold 1 LVN	Inj Mold 2 LVN
Base Polymer	2.07	2.28	2.47	2.91	2.95
+ Bayerite/Boehmite	2.07	2.31	2.42	2.47	2.57
+ Zn-Surlyn	2.07	2.09	2.03	2.10	2.08

Extrusions 1 and 2 were at 275C with 3 minute residence times. Injection moldings were at 275C with 1.5 minute residence times. Results are for CARILONTM EP Thermoplastic Polymer 087/032. Zn-Surlyn concentration of 10% was used for this first test. Typical concentrations are now 0.1 - 2.0% for Nucrel 535.

TABLE 2
BRABENDER EVALUATION OF SELECTED ADDITIVES

Additive	Level	Torque Minimum	Torque Maximum	Td*	Rate of X-Linking
None		4.6 Nm	31.5 Nm	11.5 min	5.2 Nm/min
Stearamide	0.1%	5.5 Nm	-----	6 min	-----
	0.5%	3.2 Nm	27 Nm	25 min	1.06 Nm/min
	1.0%	2.5 Nm	16 Nm	150 min	0.11 Nm/min
Nucrel 535	0.2%	2.8 Nm	16.5 Nm	160 min	0.09 Nm/min
Kaiser Bayerite	0.2%	1.9 Nm	21.4 Nm	200 min	0.06 Nm/min
K. Bayerite Steramide	0.2% 0.2%	2.9 Nm	21.75 Nm	270 min	0.05 Nm/min

* Time to maximum torque in Brabender curve.

** Base polymer for study is 87/038; LVN=1.4dl/g, T_m=220C.

FIGURE 4

PK 087/048 AND PK 087/005

EFFECT OF NUCREL

(ETHYLENE/METHACRYLLIC ACID POLYMER)

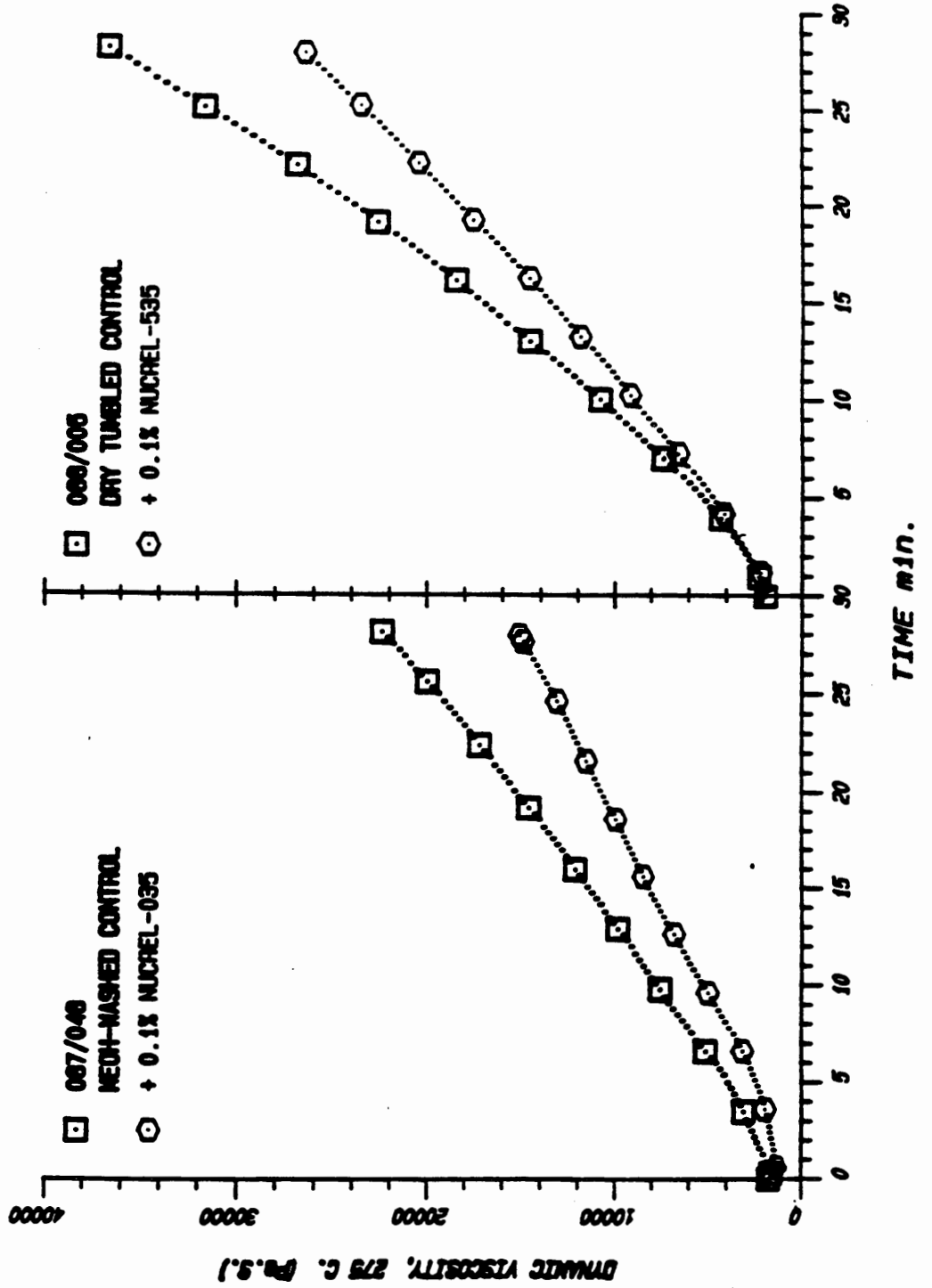


FIGURE 5

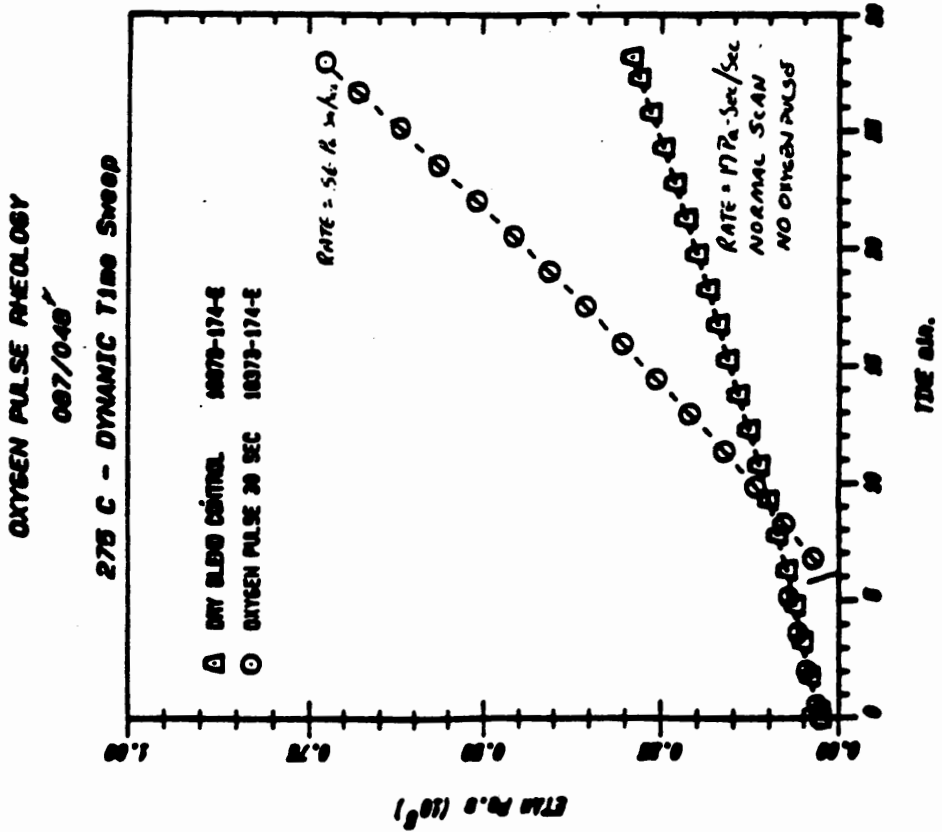
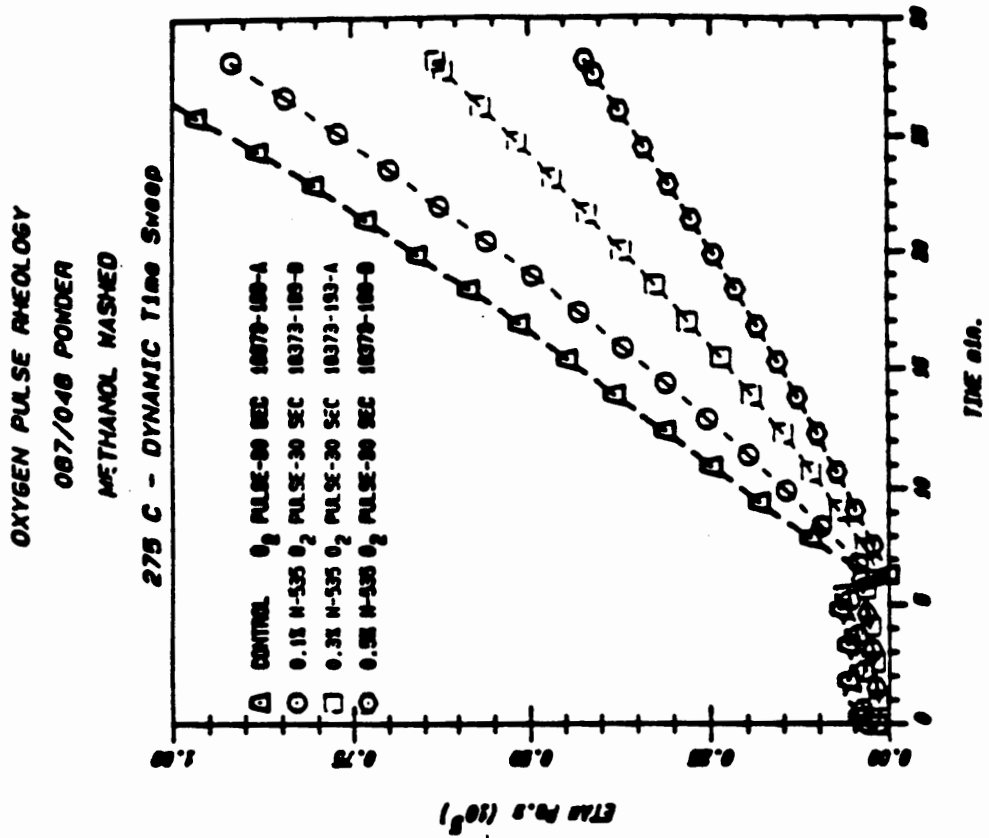


TABLE 3
THERMAL OXIDATIVE STABILITY*

Property	CARILON TM EP Thermoplastic Polymers ABS (Cyclac, GSE)	
	UL Continuous Use Temp**	UL Continuous Use Temp**
Brittleness	85C	~70C
Tensile EB	73C	<65C
Tensile Strength	88C	80-95C

* Results are from direct comparison on 1-mm thick samples. Literature indicates 70C continuous use temperature for properties with or without impact for 1.5mm ABS samples. CARILONTM EP Thermoplastic Polymers was stabilized with combination of Irganox MD 1024, Irganox 245, and Naugard 445.

** Failure is based on extrapolation to 11,000 hours.

FIGURE 6
UV RESISTANCE CARILON EP MONOFILAMENT
Weatherometer Conditions

