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Aspects of Processing and Properties of CARILON™ Polymer Thermoplastic Alloys

J. M. Machado, R. P. Gingrich, W. P. Gergen

Technical Progress Report WRC 82–89
Project No. 62177, 62182

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Aspects of Processing and Properties of CARILON™ Polymer Thermoplastic Alloys

Technical Progress Report **WRC 82–89**

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CARILON Performance Blends

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AUTHORS: J. M. Machado, R. P. Gingrich, W. P. Gergen
REVIEWER: W. P. Rothwell
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ABSTRACT

The reactive compounding of CARILON™ polymer with Nylon 6,6 can result in materials which possess an outstanding combination of stiffness and toughness. Four factors have been identified which determine the performance of a given blend. These are: blend composition, matrix molecular weight, thermal/processing history, and reaction "modifier" content. The chemically reactive nature of this polymer alloy in the melt state introduces significant processing limitations and a pronounced sensitivity of final properties to processing conditions, however, it also enhances and stabilizes the blend dispersion and improves interphase adhesion, leading to the unique property set.

The title blends exhibit synergistic behavior with respect to both stiffness and toughness. Blends have been prepared containing both CARILON E and EP polymer as the matrix phase with notched Izod exceeding 20 ft.lb/in at room temperature. This account will address how the properties and melt processing characteristics of these materials depend upon the key compositional and compounding parameters.

Technical Progress Report WRC 89-89

ASPECTS OF PROCESSING AND PROPERTIES OF CARILON™ POLYMER THERMOPLASTICS ALLOYS

by

J. M. Machado, R. P. Gingrich, W. P. Gergen

I. INTRODUCTION

In the continuing development of polyketone materials, the strategy of polymer blending has been used to overcome deficiencies or to make property improvements in diverse areas such as melt processing, impact behavior, barrier/transport properties, and thermal expansion characteristics. During these investigations, CARILON-containing materials possessing a wide variety of morphological structures have been encountered. Miscible, homogeneous blend systems have been identified (polyketone-polyvinyl phenol) [1]. Heterogeneous blends have been prepared which are either grossly phase separated or micro-phase separated (and hence compatible) [2,3]. Morphologies in which polyketone is the matrix phase, the dispersed phase, or one of the co-continuous phases (IPN structure) have been described. Accomplishments thus far have demonstrated that blending is a useful way to further expand the unique property set of CARILON™ polymers.

The present contribution focuses on blends containing CARILON polymer and Nylon 66, which exhibit an outstanding and unexpected degree of impact toughness [3,4]. It appears that the performance of these blends arises from interphase chemical grafting in the melt state, improving both dispersion and adhesion. This report addresses the relationships between blend properties and the important compounding variables, and stresses the strong interdependence between properties and processing in this chemically reactive blend system. In a subsequent report, the mechanistic aspects of toughening in this system will be addressed.

II. BACKGROUND

The ability to toughen polymeric materials by preparing heterogeneous mixtures of controlled morphology is a well understood technology of vital importance to the plastics industry. A wealth of literature has been accumulated on this subject, of which the most frequently cited is probably a monograph by Bucknall [5-8].

Most often, toughening is achieved by the incorporation of an elastomeric phase within a thermoplastic or thermoset matrix material. The manner in which this component is dispersed into the matrix is an essential consideration towards obtaining maximum toughness. Quite generally, the role of the rubbery phase is to produce a localized stress state in the matrix material which is conducive to the initiation of energy absorbing deformation processes such as localized crazing and shear yielding in preferance to brittle crack propagation [5]. The character of the local state of stress in the vicinity of a dispersed particle has been related, theoretically and experimentally, to the properties of the particle, the matrix, and the interface, to the size and shape of the dispersed phase and, of course, to the nature of the macroscopic applied stress [9].

The preparation of toughened polymers by solution or emulsion polymerization of the matrix monomer in the presence of rubber particles, such as in the commercial manufacture of HIPS and ABS, has been a long-standing industrial practice. These processes involve the chemical grafting, in solution, of matrix chains onto the rubber particles. Grafting provides the interphase adhesion necessary for efficient stress transfer between the phases [5,10].

Some toughened polymers, such as Dupont's "supertough" Nylon, are prepared by a rubber-matrix grafting process which takes place in the melt state, during compounding in an extruder [11]. Recently a great renewal of interest, both in industry and in academics, has occurred towards fully utilizing the chemical reactivity of polymers in the melt state. It is felt that reactive compounding provides an enormous potential for developing new materials exhibiting unique and specialized properties [12-15].

Studies have shown that polymer "alloys" in which the separate phases are chemically coupled, exhibit superior properties to physically mixed blends [15,16]. A number of workers have shown, for instance, that chemically functionalized rubbers are better able to toughen thermoplastics, such as Nylon, both as a result of the enhanced interphase adhesion and the improved dispersion provided by the in situ generation of graft species [17,18].

In the present case of CARILON polymer/Nylon blends, the levels of toughness which are obtained are very surprising in light of the fact that no elastomeric phase is externally added. However, it is felt that chemical reactivity between the components during compounding is a key contributory factor towards attaining these properties.

Very few examples can be found in which a relatively rigid thermoplastic is used as an impact modifier for a polymeric material. One such example is the use of polyetherimide to toughen epoxy [19]. In this case, however, the blend toughness is approximately additive with respect to the unblended components. We feel, therefore, that the synergistic toughening observed in the title blends is unique, and may be one member of an emerging class of thermoplastic alloys containing CARILON polymers [3,20]. CARILON thermoplastic polymers possess a known and often troublesome degree of chemical reactivity in the melt state which, nevertheless, may be ideally suited for alloying with other reactive polymers.

III. BLEND COMPOSITION

Effects on Blend Rheology

CARILON polymer/Nylon blends were prepared in the composition range 0-30 wt% Nylon 66. Blends with higher Nylon contents could not be compounded as a result of excessive crosslinking of the extrudate. Within the range studied, however, the blend composition exerted a profound influence over melt processing behavior.

The melt processing limitations of polyketone are well known. It is agreed that processing difficulties arise from aldol condensation between ketones (and possibly other defect structures) which give rise to crosslinks and eventual gelation. An aggressive search for polyketone melt stabilizers has led to a number of additives which reduce the rate of rise of melt viscosity in polyketone and forestall gelation [21,22]. In this respect, Nucrel, an ethylene-methacrylic acid copolymer, has been very effective.

Whereas Nucrel, in the composition range of several tenths to several percent, is helpful for melt processing CARILON polymers, it is virtually a requirement for processing CARILON polymer/Nylon blends. The addition of Nylon appears to accelerate the crosslinking processes intrinsic to polyketone itself and thus limits processibility. Thus all of the blends to be discussed in this section contain one part Nucrel per hundred parts total formulation. Specific formulations can be found in Appendix 1. Blends were compounded on a Haake 30mm corotating twin screw extruder with L/D equal to thirteen. The compounding conditions are also described in Appendix 1. The blends in this section contain CARILON EP polymer 88/023 (1.84 LVN) and Zytel 101 Nylon 66.

The rheological behavior of the blends was measured by oscillatory parallel plate experiments on compression molded films, in accordance to the protocol developed for CARILON polymers. The increase in dynamic melt viscosity with time is shown in Figure 1 for blends of various composition. The destabilizing effect of Nylon with respect to both the initial melt viscosity and its temporal rate of rise is evident in this figure. The magnitude of this effect is proportional to the Nylon content.

The composition dependence of melt viscosity is shown in Figure 2. Here the initial melt viscosity is plotted against composition for the blends in Figure 1 and also for a series of blends from the Nylon-rich composition regime. It is clear that melt viscosity increase very significantly either as Nylon is added to polyketone or as polyketone is added to Nylon, making blend compositions in the range of about 25-60% CARILON polymer completely intractable due to excessive melt viscosity. We believe these results strongly suggest an interfacial grafting process where viscosity becomes asymptotic at compositions where co-continuity of phases is developed. In a practical sense, it is clear from Fig.2 that melt processing behavior will be strongly composition dependant.

It may be considered straightforward to claim that strong positive deviations from additivity in the melt viscosity of a polymer blend provides compelling evidence for melt reaction. Nevertheless, a brief examination of the rheological behavior of other reactive and non-reactive blend systems may also prove instructive. The rheological behavior of a miscible blend (PPO/PPS) has been examined both theoretically and experimentally by Prest and Porter [23]. In general, the melt viscosity of the blend is intermediate between the pure components following a monotonic function of composition.

For two phase melts, the analysis is frequently more complex [24]. In the absence of chemical reactions the viscosity versus composition curves tend to be S-shaped (one can apply the Einstein relationship adapted for liquid-liquid dispersions except in the vicinity of phase inversion). As an example, Figure 3 shows data for the immiscible, non-reacting polystyrene/polyethylene blend system [25]. Again, the melt viscosity of the blend is a simple monotonic function of composition. In no case does the viscosity of the blend exceed that of the more viscous component.

In contrast to non-reacting systems, reactive blend systems are often characterized by relative maxima in their viscosity-composition relationships. Examples of this are cited from the literature [12,26,27]. Baker, in Banbury mixing studies of reactive blends, has suggested that an increased torque upon melt mixing relative to those required by the pure components is diagnostic of melt reaction.

Thus the rheological behavior of the current blend system, represented by Figure 2, would strongly suggest a melt grafting process. More direct characterization of the melt chemistry will be discussed in a forthcoming study.

Accompanying melt viscosity, melt elasticity also increases substantially as a result of melt reaction. In Figure 4, tan delta, equal to the ratio of energy dissipated by viscous effects to that stored elastically during deformation, is plotted as a function of time for blends of different composition. Here, it is clear that tan delta decreases more rapidly as Nylon is added to the system. Consequently, the time to reach gelation (tan delta = 1.0) [28] is reduced by the presence of Nylon. This effect further contributes to processing limitations.

It may also be noted in Figure 4 that, although tan delta initially decreases more rapidly with the addition of Nylon, the tan delta of the blends eventually crosses over that of the control and approaches a higher limiting value at long times. This may indicate that a significant fraction of the Nylon component is not participating in grafting or crosslinking reactions and continues to exhibit dissipative behavior long after gelation occurs (again suggesting interfacial reaction).

Effects on Processing

It is obvious that the reduced melt stability of the above blends leads to processing difficulties. In fact, the compounding of CARILON* polymer/Nylon 66 blends requires strict control of processing conditions. An interruption or fluctuation in the process which results in an overheating or hold-up of material in the extruder barrel can result in rapid degradation and gelation of the extrudate, a condition from which it is difficult to recover without purging the extruder barrel. One reason for the difficulties observed in processing these blends arises from the high viscosities and unusual viscosity-temperature relationship which they exhibit.

Gergen has shown that the activation energy for crosslinking reactions in CARILON polymers exceeds the activation energy for viscous flow (22 and 8 kcal/mol respectively) [3]. The consequences of this are that beyond a given critical residence time in the melt, the viscosity of CARILON polymers will actually increase with temperature, a prediction which has been verified by experiments [29]. Such behavior can lead to difficulties in melt processing because in practice the thermal energy required to heat and melt polymers during extrusion is supplied both by internal dissipation (or mechanical work energy) and by an external source such as electrical heaters. In general, the temperature control mechanism feeds back only to the external heat source. Thus a situation can be reached in CARILON-like materials in which, upon supplying external heat to the material, the temperature is raised and the viscosity increases so that mechanical heat production also increases which further raises the temperature and so on. In such a situation, an adiabatic condition is quickly reached in which heat is supplied solely by the work of deformation and temperature control through an external loop is impossible.

Such a condition has been observed in CARILON polymer/Nylon 66 blends where the crosslinking tendencies of the CARILON component are accelerated by Nylon. In Figure 5 for example, the measured melt temperature is plotted as a function of the barrel set temperature during extrusion at constant shear rate and throughput. For a low viscosity resin such as Nylon 66 the actual melt temperature is linearly related and reasonably close to the setting temperature. For the neat CARILON* polymer control (88/023) the melt temperature at a given set temperature is higher than for Nylon due to viscous dissipation, however, the relationship is still well-behaved permitting good temperature control. The situation with the 75/25 CARILON polymer/Nylon blend is quite different. As Figure 5 demonstrates, the melt temperature of the blend is independent of the setting temperature over a wide range of settings indicating adiabatic behavior. In this case, the melt temperature is determined solely by the properties of the melt (viscosity, heat capacity, thermal conductivity, etc.), the flow kinematics, and the flow geometry. The temperature could not be controlled by means of electrical heaters. Beyond the adiabatic region in Figure 5, a catastrophic temperature runaway situation is encountered which is accompanied by gelation and degradation of the extrudate.

In practice, the melt temperature can be controlled at the desired level for the blend in Figure 5 by suitable control of the shear rate. In Figure 6 the melt temperature of this blend at constant set temperature and throughput rate is shown as a function of the screw speed. The melt temperature in this case is stable and nearly linearly dependent on the screw speed, giving further evidence of adiabatic behavior.

In polymer processing the adiabatic region is most often considered undesirable because of the control limitations which are introduced. In the present case of CARILON polymer/Nylon blends the region of adiabatic behavior is greatly reduced by decreasing the Nylon content and by decreasing the shear rate (as well as by decreasing the molecular weight of either component). Thus, compounding is greatly facilitated by using less Nylon (<20 wt%) and lower screw speeds (<200 rpm).

Effects on Properties

Blends of CARILON polymer with Nylon 66 exhibit an unusual degree of synergism with respect to a number of aspects of mechanical performance. In this section the relationships between composition and properties will be discussed.

Figure 7 demonstrates the composition dependance of toughness in this system. Notched Izod values at room temperature are shown versus composition for blends prepared from CARILON polymers 88/022 and 88/023. It is apparent that small amounts of Nylon have no toughening effect in the blend. Rather, a critical level of modifier is required resulting in an abrupt improvement. Such behavior is typical of toughened polymers [5,30] and has been studied in detail by Wu, concerning the rubber toughening of Nylons. For example, Wu related the critical rubber content for toughening to a "critical ligament thickness" in the Nylon matrix [7,31-33]. In the present system, the critical modifier level appears to be around 20 wt% which can be reduced to 15 wt% by extended thermal treatment (the effect of thermal history is discussed in a later section). The emergence of tough behavior, shown in Figure 7, is accompanied by a change in the fracture mode in the Izod test from a semi-brittle fracture, to a ductile, hinged failure with a dense, stress-whitened plastic zone surrounding the crack.

An unusual characteristic of the present system is that once the critical Nylon level is reached, further addition of the modifier results in a decrease in impact performance. This result is associated with the processing behavior discussed above. Excessive amounts of Nylon result in high melt temperatures during compounding and increased degradation of the matrix polyketone, thus impairing final blend performance. It is clear that a minimum effective content of Nylon is desirable for optimum properties.

At lower temperatures, the notched Izod values exhibited a similar composition dependance with a maximum value at 20 wt% Nylon. The blends share with CARILON materials the disadvantage of reduced toughness below room temperature. This has been attributed to CARILON polymer's beta-transition at approximately $20^{\circ}C$.

The tensile moduli of the blend series containing 88/023 are given in Figure 8. Also shown is the maximum predicted modulus for a two-phase material with individual component moduli of 225 ksi and 390 ksi corresponding to the measured values of dry CARILON EP polymer and Nylon 66 respectively. This line represents a true upper bound since it assumes that the component moduli are additive in the blend. It is interesting to note that the measured values of all of the blends fall significantly above this line with maximum deviation at 15-20 wt% Nylon. This would suggest that the system is not behaving purely as a composite, but that the Nylon has modified the CARILON polymer matrix. A very similar modulus-composition relationship was reported by George in CARILON* polymer/KRATON 1901X blends [20].

Figure 9 gives the yield stress of these blends as a function of composition. Yield stress increases monotonically and nearly additively with Nylon content reaching a value of 10,600 psi at 30 wt% Nylon. The ultimate tensile strength also increases with the addition of Nylon reaching a value of 13,900 psi for a 30% Nylon blend. The ultimate elongation data is considerably scattered. However, some samples of all compositions exhibited tensile elongations in the range of 200-300%, thus no loss in ductility upon the addition of Nylon 66 was observed.

The Gardner (falling dart) impact test was also performed on these materials. This test gave puzzling results in light of the notched Izod data. As Figure 10 demonstrates, the Gardner impact values at both room temperature and at -30^{o}C decrease substantially as Nylon is added to the blend. The reason for this is not clear. However, it is well understood that unnotched tests of this type are extremely sensitive to surface morphology and topology and may not be indicative of bulk material properties. No attempt will be made to interpret the results at this time. However, a future report will address this issue directly.

IV. MOLECULAR WEIGHT

Effects on Properties

The failure characteristics of polymeric materials, along with associated properties such as elongation, strength, and impact toughness, frequently have a strong dependance upon molecular weight [34]. This dependence has been described in a theoretical framework by Kausch [35]. Essentially, ductile failure, associated with plastic deformation, can be related to a multiple disentanglement phenomenon which, of course, depends strongly upon chain length.

Handlin found that the impact behavior of polyketone also depends strongly upon molecular weight [1]. He related an abrupt increase in Izod impact to a failure mode transition (from brittle fracture to shear band formation), which occurs at LVN's greater than 1.8-2.0 dl/g for CARILON EP polymer at room temperature.

The properties of CARILON polymer/Nylon blends showed a similar dependence upon the molecular weight of the CARILON polymer which was used to make the blend. A series of blends was prepared containing 20 wt% Nylon 66 (and 1% Nucrel) with a series of CARILON polymers of differing LVN. The detailed formulations are tabulated in the Appendix 1. Figure 11 gives notched Izod impact values at room temperature versus the LVN of the base polymer (as measured in m-cresol at 60^{o}C). It is apparent that impact strength increases abruptly from about 5 ft.lb/in to as high as 20 ft.lb/in in the narrow LVN range of about 1.7 to 1.8 dl/g. Below this "critical LVN" the blends exhibit approximately equivalent toughness to the matrix polyketone from which they were made. Above this transition, however, toughening by the Nylon may take place. As Figure 11 demonstrates, the degree of toughening which is realized in the blends is quite variable. It is determined by other compounding factors, such as those to be discussed in the following sections (Note for example in Figure 11 that blends above the critical LVN reached a higher toughness when prepared with a long molding cycle rather than a short one).

The rheological behavior of CARILON polymers is sufficiently well known that it is possible to calculate the expected LVN of a given batch of polyketone based upon melt viscosity measurements. This "calculated LVN" is often more predictive of material behavior than the measured LVN because it is a composite property which takes into account not only the "as made" molecular weight but aspects of chemical stability in the melt [3,29]. When some of the data from Figure 11 were plotted against calculated LVN (where available), as in Figure 12, a slightly less abrupt transition in toughness was observed, which probably better describes the phenomenon.

The low temperature (OC) Izod values of the same blends are given in Figure 13. They show the same transition in toughness at around 1.8 LVN. It may be noted that at this temperature even the best material had a value of 2.75 ft.lb/in, which is much lower than its room temperature value (21 ft.lb/in). Thus, brittleness below Tg is a shortcoming of the blends as well as the unblended polyketone.

The tensile properties of this blend series were examined and are shown in Table 1. These results, particularly elongation, exhibit no correlation with the Izod measurements. Handlin did find the expected correspondence between molecular weight and elongation in unblended CARILON polymer [1]. This is not apparent, however, in the present series of blends.

Low temperature (-30^{o}C) Gardner impact testing was performed on this blend series. Again this test gave results in direct conflict to Izod measurements. Figure 14 shows that Gardner impact decreases substantially with increasing LVN of the polyketone. No satisfactory explanation has yet been found for this behavior.

Effects on Melt Behavior

A polymer's chain length is a key determinant of its behavior in the melt. The relationships between melt rheology and molecular weight in polyketone have been described by Gergen [3,29]. Both melt viscosity and its rate-of-rise scale to high powers of the LVN. Blends with Nylon appear to behave in a similar manner. Figure 15 demonstrates this point. Here, dynamic melt viscosity versus time is shown for three 80/20 CAR/N66 blends which differ only in the LVN of the base polyketone. Blends with low LVN polyketone show reasonable melt stability and process without difficulty. However, blends with very high LVN PK's yield extremely high viscosity blends. It may be noted that the blend corresponding to the upper curve in Figure 15 (from 87/029;LVN=2.25) could be compounded only by removing the extruder die head and could not be injection molded successfully.

Thus with respect to both processing and properties an optimzed blend would possess a minimum LVN while still retaining "toughenability". Current work is focused on reducing the required LVN for toughening.

V. THERMAL/PROCESSING HISTORY

Residence Time

The mechanical properties of polymer blends are determined to a great extent by the multiphase morphologies which they possess [36]. The morphological structure is created and subsequently affected by any melt processing operations to which the material is subjected during the fabrication of a finished part. Thus, the method by which a polymer blend is prepared is an essential consideration towards achieving the desired properties. However, in cases where melt compounding involves chemical reaction between the two blend components, leading to the creation of new macromolecular species which can modify the thermodynamics and kinetics of phase behavior, melt processing protocol may exert an especially strong influence over the final material properties. The current blends represent such a system where the details of melt fabrication can profoundly affect properties.

Experiments were performed on a series of blends which differed only in the total melt history of the compound. The two most straightforward ways to vary thermal history during processing are to vary the residence time in the extruder barrel by controlling the throughput, or to vary the residence time in the injection molding machine barrel by controlling the cycle time. In this experiment the latter method was chosen because of limitations over which the extruder residence time can be varied without affecting other mixing variables and because of experimental economy.

The molding conditions used in this experiment and the relationship between cycle time and total residence time are discussed in Appendix 2. The base blend used was an 80/20 CAR/N66 made from 88/022 (1.78 LVN). This blend, which is of optimum composition and critical LVN, is expected to have maximum sensitivity to processing conditions.

The notched Izod results, shown as a function of cycle time and of total residence time, can be found in Figure 16. The impact strength of the unblended CARILON polymer control does not change significantly in these experiments, maintaining a value of about 5 ftlb/in regardless of cycle time. However in the case of Nylon blends, the notched Izod values increase dramatically as the residence time is increased, spanning between about 8 ftlb/in at a cycle time of 25 seconds to about 24 ftlb/in for a three minute cycle. The initial drop in impact strength on going from a 16 sec to a 25 sec cycle is surprising. This may result from a morphological change caused by holding the material quiescently in the melt before injection. Electron microscopy studies do not support this explanation however. Nevertheless, beyond this point impact strength increases steadily as residence time increases and intermolecular reactions are allowed to advance.

In fact, the increase in impact strength as residence time increases is not as gradual as Figure 16 would suggest. The values in Figure 16 represent averages of multiple samples. For the blends exhibiting "intermediate" average impact strength in Figure 16 (10-15 ft.lb/in), there is actually a bimodal distribution of values in the sample population, as shown in Figure 17 for a number of samples prepared under identical conditions. For this material there are clearly two populations, those with Izods around 7 ft.lb/in, which fractured in a brittle manner, and those with Izods in the vicinity of 15 ft.lb/in which exhibited hinged, ductile failure and stress whitening surrounding the crack. As thermal history increases the effect is actually to change the relative proportions of these two populations. Relatively few individual samples had Izod values in the range of 8-12 ft.lb/in. Thus the transition in fracture mode is an abrupt one, and may depend upon subtle morphological features in the blend. The distribution of material behavior at intermediate residence times may reflect the distribution of residence times of material elements in the barrel (see Appendix 2).

One of the important aspects of this experiment is that it provides us with a series of materials of identical composition which nevertheless vary in impact performance over a wide range. Careful analysis of these samples may provide clues about the dominant structural and morphological requirements for obtaining super-toughness in this class of materials.

The tensile properties of these blends can be found in Table 2. It may be interesting to note that although the impact properties change by a factor of three as this series is traversed, the modulus changes by only 5%. Thus no loss in modulus is associated with the transition to tough behavior. Likewise, yield stress is only slightly affected by the increased residence time.

Unblended polyketone, when subjected to increasing thermal history, exhibits decreasing elongation to break, as crosslinking proceeds. However, as the data in Table 2 indicate, the blends can undergo increasing elongation as thermal history increases. This behavior is unusual and coincides with the increase in impact properties. A note of caution is required, however, because subsequent work has not shown a consistent relationship between impact properties and tensile elongation.

Molecular Weight

Earlier, the ability to impact modify CARILON polymers was shown to depend upon the molecular weight of the base material. Above, it was shown that melt history is also an important variable. Of some practical significance, is the question: to what extent are these contributing factors to impact improvement coupled? More specifically, is it possible to prepare a blend containing a low LVN CARILON material, below the level required for impact modification, and achieve a super-tough material by subjecting it to a sufficiently long melt history?

Figure 18 shows the relationship between Izod toughness and thermal history for blends of differing LVN. For a blend made from a low LVN material (88/010; 1.53 LVN) no toughening was observed for the blend relative to the matrix polymer, regardless of thermal history. Similarly for a blend made from a polyketone above the critical LVN (88/040; 1.82), toughening is achieved even at short residence times and maintained at longer times. Only blends made from polyketones near the critical value displayed an extreme dependence upon residence time.

Reprocessing

The ability to reprocess CARILON polymer/Nylon blends was investigated and will be presented in this section. A study by Danforth and Smith showed that unblended CARILON polymer could pass through a 13/1 L/D extruder five times and still withstand an injection molding cycle [37]. Whereas the Nylon blends possess considerably poorer melt stability than the neat material, the reprocessibility of these materials was open to question.

Experiments with an 80/20 CAR/N66 blend showed that it could undergo three extruder passes (although the third was very marginal) and still withstand molding. Compounding conditions, shown in Table 3, indicate that extruder throughput decreased substantially with each successive pass as a result of rapidly rising melt viscosity.

Notched Izod values of the molded specimens, shown in Figure 19, indicate that the blends forfeit all of their impact improvement upon a second extrusion. The loss in impact properties is clearly a result of excessive degradation in the matrix polyketone which renders it "untoughenable" due to crosslinking. However, the results are somewhat surprising in light of the findings discussed earlier where impact properties improved substantially upon increasing the residence time during molding. The difference, however, is attributable to excessive melt temperatures developed during (adiabatic) re-extrusion of the very high viscosity melt.

Blends were also prepared in which either 20% or 40% of an 80/20 dry blend was substituted with previously compounded 80/20 CAR/N66 material. Unlike the completely reprocessed blends, Table 3 shows that the melt processing behavior was not greatly affected by only partial incorporation of reprocessed material.

Notched Izod results for these materials are shown in Figure 20. These results demonstrate that no loss in impact properties is associated with the partial incorporation of previously processed material. The explanation for property retention in the case of partial "regrind" material follows from above. Excessive melt viscosity is not built up in these blends during re-compounding; thus thermal crosslinking of the matrix is greatly reduced.

Masterbatched Blends

The idea of "masterbatching" these blends was investigated as a possible strategy to achieve toughening at a lower Nylon content. A series of blends was made containing 10%, 15%, 20%, and 30% Nylon 66. The 20% and 30% "masterbatch" blends were again compounded in equal proportions with unblended CARILON polymer 88/022 yielding net 10% and 15% Nylon blends, respectively. In Table 4, these latter blends are compared to directly compounded blends of the same composition, with respect to impact performance. Notched Izod values at room temperature are reported for blends which were injection molded with both a short and a long molding cycle. These data show that for a 15% Nylon blend there is no difference between a masterbatched blend and a directly compounded blend; both develop good toughness with a long molding cycle. For a 10% Nylon blend, there actually is some benefit to the masterbatching procedure. However, the masterbatched 10% Nylon blend does not develop toughness equivalent to a directly compounded 15% or 20% Nylon blend.

Of course, a net 20% masterbatched Nylon blend could not be prepared by the present method because of the inability to compound the required 40% Nylon blend (due to crosslinking).

VI. MELT STABILIZING ADDITIVES

Nucrel Concentration

The ability of certain acrylic acids copolymers (and their Zinc and Aluminum salts) to exert a stabilizing influence upon polyketone thermoplastic melts has been well established [21,22]. The mechanism by which these stabilizers operate has been investigated but is still not known with certainty. In addition to their stabilizing role these additives can also impart a degree of impact modification to the materials [20].

In the study of polyketone/polyamide reactive alloys it has become apparent that the presence of one of these polymeric acids is essential in order to successfully melt compound the blend and fabricate acceptable parts. In light of the known chemical reactivity of commercial Nylons towards polymers possessing carboxylic acid and anhydride functionality [7,38], it is uncertain whether these additives are playing the same role in the blends as they do in the unblended polyketones (slowing down the intrinsic crosslinking processes in the PK phase) or whether they play an expanded role in the blends (by competing with polyketone for reaction with the polyamides) and thereby are capable of moderating the extent of polyketone/polyamide melt reaction.

Thus far, we have described three key factors affecting the development of toughness in poyketone/polyamide blends: composition, matrix molecular weight, and thermal/processing treatment. Presently, we will address the effect of concentration and type of melt stabilizing additive upon both the processibility and properties of blends containing CARILON polymer and Nylon 66.

The nature and concentration of the additive profoundly affected the melt behavior of the blend. Nucrel 535 has been one of the most successful melt stabilizing additives for polyketone. Blends were prepared containing an 80/20 ratio of polyketone/polyamide and various amounts of added Nucrel 535. The materials were compounded with identical extruder settings while the extrudate temperature and throughput were monitored. These quantities are plotted in Figure 21. As these data show, melt temperature increases and throughput decreases (residence time increases) significantly as the

Nucrel level is lowered. Both factors may lead to severe degradation of the product. Observation of the extrudate indicated that the best material was produced with 0.3% to 3.0% added Nucrel.

It has been suggested that one of the important functions of Nucrel may be chemical passivation of the metal surfaces of the compounding equipment [39]. In this study it was found that the CARILON polymer/Nylon blend could be compounded (with difficulty) in the absence of any stabilizer only when extruded in a "Nucrel-conditioned" machine. When the unstabilized blend was run in a unconditioned machine, degradation was very severe and a steady operating condition could not be reached. Thus the notion of surface passivation is supported.

Rheological analysis confirmed the findings based on extruder monitoring. Figure 22 shows that the initial melt viscosity and its temporal rate-of-rise both incease as the Nucrel level is reduced. Similarly during molding, higher injection pressures were required for blends containing less Nucrel. Thus, a stabilizing additive such as Nucrel is an essential ingredient towards making tractable blends.

The effect of Nucrel concentration on final blend properties is more complex than its effect on processibility. The level of toughness obtained arises from a balance between the favorable effects of interphase chemical bonding and the detrimental effects of matrix degradation through crosslinking. Thus, an optimum additive level is expected whose value may depend on thermal/processing history.

Such an optimum level of modifier is demonstrated in Figure 23. Notched Izod values are given versus Nucrel content for blends subject to either a short or a long thermal history. For the blends having a short thermal history, no significant toughening occurs as a result of insufficient reaction time. As demonstrated earlier the same blends subject to longer thermal histories become much tougher. The maximum toughness is observed for the blend containing 1.0 wt% Nucrel 535, which had a notched Izod of 19 ft.lb/in. At very high Nucrel levels no impact improvement is observed, either because Nucrel limits the extent of melt reaction or because it begins to interfere with blend morphology. At very low Nucrel levels, impact properties are also impaired as a result of embrittlement of the matrix phase due to crosslinking.

The tensile properties of the above materials paralleled the notched Izod results. In Figure 24, the elongation at break is shown versus Nucrel content. Maximum elongations are observed at an intermediate level of the additive, again demonstrating an optimum concentration. As expected, the yield stresses were similar for all of the blends.

It is hypothesized that the reaction modifier, Nucrel, can be used to influence the kinetics of melt reaction and thus to "tune" a given reactive compound to the thermal/processing treatment to which it will be subjected.

Other Modifiers

A number of different stabilizers were examined when added at a level of 1 wt% to the 80/20 CAR/N66 base blend. The series included: 1) the known CARILON polymer stabilizers: Nucrel, Surlyn, and Primacore; 2) two acidic additives which do not improve the melt stability of pure CARILON polymer: styrene-acrylic acid copolymer and stearic acid; and 3) one polyacid which is clearly detrimental towards polyketone stability: polyacrylic acid [22].

The compounding behavior of these formulations are described in Table 5. Essentially, the blends stabilized by Nucrel, Primacore, and Surlyn exhibited identical processing behavior characterized by higher throughput rates and lower melt temperatures than unstabilized blends or those containing the other additives. This is consistent with previous findings that these additives impart mutually similar stabilities to polyketone. The styrene-acrylic acid copolymer, polyacrylic acid, and stearic acid modified blends all behaved similarly to the unstabilized blend, with the exception that the polyacrylic acid containing blend also had an unusually poor melt strength.

Rheological studies generally supported the above findings. The Nucrel containing blend had the lowest melt viscosity of the blends studied. The blends containing polyacrylic acid and stearic acid had higher viscosities than the unstabilized control. Despite their high melt viscosity in the Rheometrics test, all the blends could be injection molded.

The different additives types were also examined with respect to their effect upon properties. In Figure 25, notched Izod results are shown for blends containing 1 wt% added stabilizer which were subjected to either a long or a short thermal history. As expected, the blends containing Nucrel, Primacore, and Surlyn all exhibited similar behavior, developing exceptional toughness with sufficient thermal history. Blends containing styrene-acrylic acid copolymer and polyacrylic acid did not develop high toughness, as a result of excessive matrix degradation.

The blend containing stearic acid was a rather exceptional case. Although this blend did not exhibit good melt processing characteristics, it developed very high impact strength at short cycle times. With longer thermal history, however, matrix degradation prevailed and toughness was lost. This unexpected result was reproduced with two separate batches of 1 wt% stearic acid stabilized CARILON polymer/Nylon blend. Although no comment can be made here about its specific role, stearic acid appears to accelerate the development of toughness in this reactive blend system.

VII. OTHER RELATED SYSTEMS

Nylon Rich Blends

CARILON polymer/Nylon blends from the Nylon-rich composition regime were investigated. These blends also exhibited synergistic toughening and interesting melt rheology [40]. These blends will be discussed in some detail, in a forthcoming report.

CARLION E Polymer/Nylon 66 Blends

Blends were made in which CARILON E polymer rather than EP polymer is compounded with Nylon 66. The ability to extend the foregoing technology of polyketone toughening to blends containing CARILON E-polymer had been in doubt based upon earlier studies of the unblended polyketones. Handlin found, for instance, that the pure E-polymer required a higher LVN than the EP-polymer to undergo the transition to shear banding (ductile) behavior at room temperature. Thus, in view of the compounded processing difficulties introduced by higher LVN polymers, by higher melting E-polymers, and by reactive compounding with Nylon, it was anticipated that the requirements for achieving a super-tough alloy with CARILON E polymer might be impractically stringent. However, this was not the case.

During compounding the E-polymer based blends behaved comparably to EP-based materials. However, an unusually large degree of screw deposit build-up was noticed at the end of each series of runs. The source of this screw deposit is known to be degradation of polyketone.

Notched Izod values of two 80/20 CAR-E/N66 alloys are given in Figure 26. Details of the formulations can be found in Appendix 1. Izod values for the E-polymer blends are given for specimens prepared with both a short and a long molding cycle (see Appendix 2). Most noteworthy is that the blend prepared from the lower LVN material (88/034; 1.68 dl/g) exhibited excellent toughness with a 16 ftlb/in Izod at short cycle times, which increased to 21 ftlb/in at long cycle times. Thus, with respect to Nylon blends, it would appear that the E-polymer has a lower "critical LVN" to achieve toughening than the EP-polymer. This finding is very encouraging in regards to developing low LVN super-tough systems.

The results of tensile testing are given in Table 6. The unblended E-polymers in this study exhibited brittle behavior, probably arising from their long melt history. Many samples fractured prior to yielding. Thus, the values of yield stress in Table 6 are calculated from only those samples that actually yielded. The ultimate strain values, however, include all samples tested.

It may be noted that blending with Nylon improved the ductility of both E batches, 88/034 and 88/035. A modest increase in yield stress was also found upon blending. Like CARILON EP polymer/Nylon blends, the modulus showed synergistic behavior. For example, one blend exhibited a tensile modulus of 435 ksi, which was higher than either blend component. It may be noted that the combination of stiffness and toughness demonstrated by this material represents a further improvement upon the outstanding performance of CARILON EP polymer/Nylon blends. Of course, higher stiffness and HDT would be anticipated for any E-polymer based blends.

CARILON Polymer/Nylon/Elastomer Ternary Systems

We have already seen that CARILON polymer/Nylon blends exhibit a remarkable balance of properties but suffer to some extent from poor low temperature toughness. Of course this is a direct result of the absence of an elastomeric toughening phase. Both polyketone and polyamide have amorphous Tg's at room temperature or above.

In his investigations, George found that CARILON polymer/ Functionalized KRATON binary blends have enhanced toughness both at room temperature and below [20]. Thus a number of three component systems were explored containing polyketone, Nylon 66, and a reactive rubber. Initial studies with a hard block carboxylated, hydrogenated SHELLVIS diblock copolymer gave a reasonable improvement in low temperature impact with a 3.4 ftlb/in OC Izod at a composition of 85/10/5 CAR/N66/SHV. However, these blends were particularly difficult to process.

Recent work, however, in which KRATON 1901X is used as the reactive rubber component has been much more promising. KRATON 1901X is a maleic anhydride, soft block functionalized, hydrogenated diblock copolymer. CAR/N66/KGX ternary systems display remarkably improved processing characteristics and a wide composition window of super-tough behavior. Table 7 lists some preliminary results for these materials. A more complete study will be forthcoming.

VIII. CONCLUSIONS

Thermoplastic alloys between CARILON polymer and Nylon 66 represent one member of an emerging class of extraordinary engineering materials based upon polyketone. The reactive nature of this compound in the melt places considerable constraints upon processibility and introduces a strong interdependence between processing and properties. This report presents an empirical study of the relationships between final blend properties and several key compounding and processing variables. An accompanying report will describe the morphological structures and deformation behavior which give rise to toughening in these materials.

Based upon this study, the following conclusions can be drawn:

- With regards to overall performance, an optimum Nylon concentration of 20 wt% can be identified.
- For blends containing CARILON EP, a critical LVN for the base polymer of about 1.8 dl/g, is required for significant toughening. For E-polymer blends this value may be lower.
- The toughness of CAR/N66 alloys increases very substantially with increasing melt history if the base polymer LVN is near the critical value.
- Melt processing becomes increasingly difficult as Nylon is added to the blend or as the LVN of the base polymer is raised.
- The melt reaction can be controlled to a limited extent by the incorporation of up to several percent of a "modifier" such as Nucrel or related copolymers.

Ongoing work in this area is aimed at identifying additional reactive blend systems with improved melt stability for engineering applications. Polyketone/polyamide/KRATON 1901X ternary alloys appear to be a very promising lead.

ACKNOWLEDGEMENTS

Many thanks are extended to R.G. Lutz and D.R. Paul for helpful discussions and invaluable assistance.

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Table 1. Tensile properties of 80/20 CAR/N66 blends having varying LVN of the CARILON polymer component.

Sample	CARILON Polymer batch - LVN	Yield Stress (psi)	Elongation (%)
MG-6B	87/053 - 1.31	9910	71
MG-6D	88/010 - 1.53	9550	121
MG-6F	88/024 - 1.73	9650	74
MG-6H	88/022 - 1.78	9650	113
MG-6J	88/005 - 1.79	9570	94
MG-6L	88/023 - 1.84	9770	81

Table 2. Tensile Properties of MG-7 Blend Series.

SAMPLE	PK 88/022 (wt%)	NYLON 66 (wt%)	CYCLE TIME (sec)	MODULUS (ksi)	YIELD STRESS (psi)	ELONGATION (%)
MG-7AI	100 [a]	0	16.5	217 [b]	8470	310
MG-7AIV	100	0	54.3	238	8350	263
MG-7AVI	100	0	124.2	228	8530	95
MG-7BI	80	20	16.5	307 [c]	9500	85
MG-7BII	80	20	25.4	309	9390	91
MG-7BIII	80	20	34.3	300	9370	127
MG-7BIV	80	20	54.3	288	9100	225
MG-7BV	80	20	84.3	303	9110	180
MG-7BVI	80	20	124.2	297	9140	177

a) All formulations contain an additonal 1 wt% Nucrel 535

b) MG-7A moduli were calculated from grip separation.

c) MG-7B moduli were determined using a strain gauge.

Table 3. Melt compounding conditions of reprocessed materials.

Sample	Description	RPM	Throughput	Melt Temp.	Comments
MG-13A	1st pass	200	108 g/min	-	smooth strands no gels
MG-13B	2nd pass	200	72 g/min	>300C	gels, very rubbery
MG-13C	3rd pass	200	66 g/min	>300C	die clogged with gels
MG-28A	20% regrind	200	88 g/min	282C	smooth strands no gels
MG-28B	40% regrind	200	90 g/min	285C	smooth strands no gels

Table 4. Notched Izod Results of Masterbatched Blends.

Sample	Composition (CAR/N66)	Method	Izod (S.C)*	Izod (L.C)** (ft lb/in)
MG-22B	10/90	direct	3.11	4.52
MG-15A	10/90	MB	6.49	8.68
MG-22B	15/85	direct	4.22	15.59
MG-29A	15/85	MB	4.36	13.79

* Short molding cycle (16.5 sec)

** Long molding cycle (2 min)

Table 5. Compounding characteristics of 80/20 CAR/N66 blends with 1 wt% of various additives.

Sample	PK (88/022)	N66 (Z-101)	Additive (1 wt%)	Melt Temp. (^{o}C)	Throughput (g/min)
MG-18F	80	20	none	317	78
MG-18C	80	20	Nucrel 535	293	99
MG-25A	80	20	Surlyn 9520	295	--
MG-25B	80	20	Primacore 1430	292	97
MG-25C	80	20	Styrene-Acrylic Acid Copolymer	>300	71
MG-25D	80	20	Polyacrylic Acid	298	81
MG-27D	80	20	Stearic Acid	308	80

Table 6. Tensile properties of CARILON E Polymer blends.

Sample	CARILON E Polymer batch-LVN-pph	Nylon 66 pph	Modulus (KSI)*	Yield Stress (PSI)	Strain at Break (%)
MG-12AI	88/034 - 1.68 - 100	0	364	11,400	16
MG-12BI	88/034 - 1.68 - 100	0	350	no yield	13
MG-12BVI**	88/034 - 1.68 - 100	0	--	9,900	80
MG-12CI	88/034 - 1.68 - 80	20	431	12,000	40
MG-12CVI	88/034 - 1.68 - 80	20	--	12,600	63
MG-23BI	88/035 - 1.86 - 100	0	--	11,800	40
MG-23CI	88/035 - 1.86 - 80	20	--	11,400	112

* Moduli were measured on separate samples with strain gauge and slow (0.2 in/min) crosshead speed.

** Samples names with suffix VI indicate those molded with long (2 min) cycle time. (see Appendix 2)

Table 7. Impact properties of CAR/N66/KGX ternary blends.

Sample	88/022	Nylon 66	Kraton 1901X	IM Cycle Time *	Notched Izod (R.T) (ft lb/in)
MG-7AI	100	0	0	16.5 sec	4.7
MG-7AVI	100	0	0	2 min	5.7
MG-7BI	80	20	0	16.5 sec	13.4
MG-7BVI	80	20	0	2 min	17.5
MG-30BI	95	0	5	16.5 sec	13.2
MG-30BVI	95	0	5	2 min	11.2
MG-30DI	85	10	5	16.5 sec	15.4
MG-30DVI	85	10	5	2 min	25.3
MG-30GI	75	20	5	16.5 sec	20.9
MG-30GVI	75	20	5	2 min	24.8
MG-30HI	70	20	10	16.5 sec	25.8
MG-30VI	70	20	10	2 min	27.1

* See Appendix 2

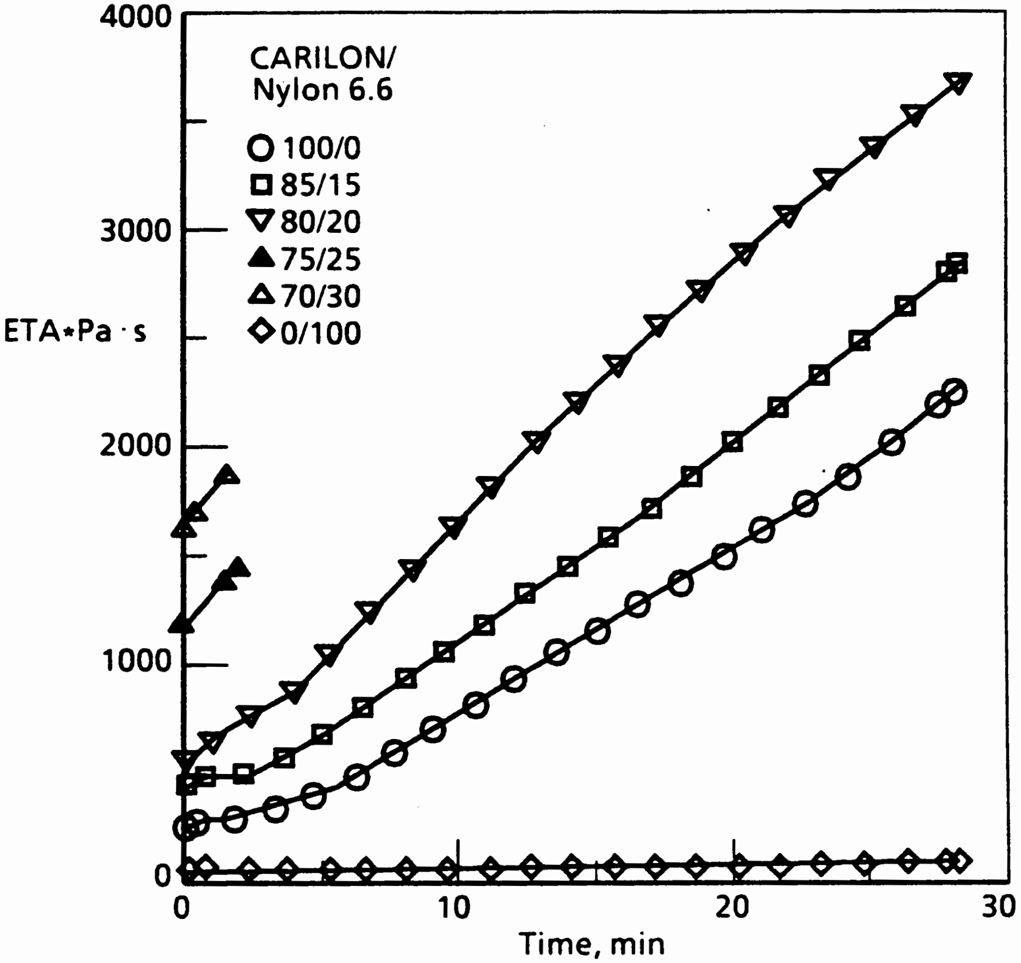

Figure 1. Dynamic Melt Viscosity (at 275°C) vs. Time for CAR/N66 Blends of Varying Nylon Content

013647-1

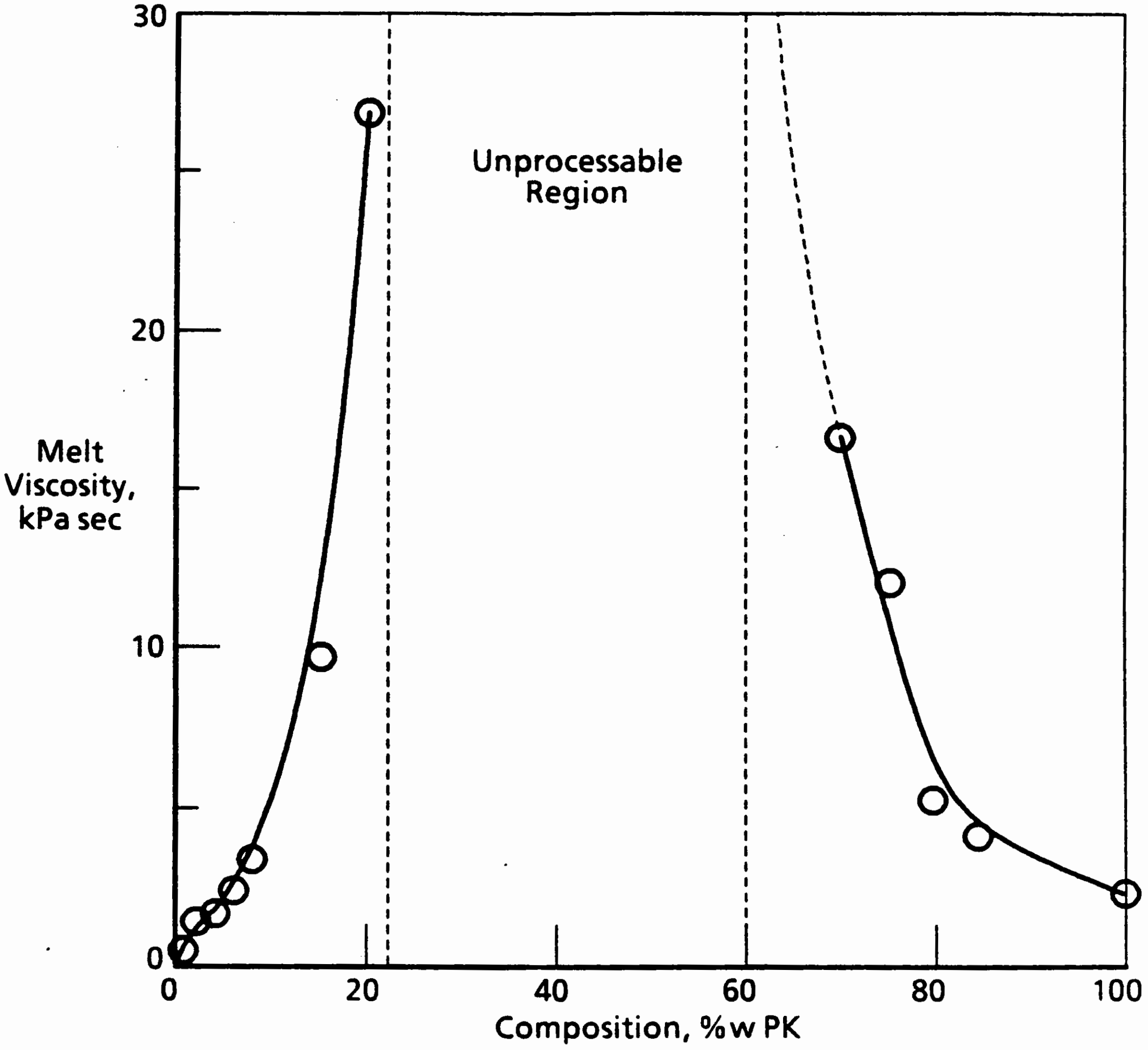

Figure 2. Initial Dynamic Melt Viscosity vs. Composition for CAR/N66 Blends Over the Full Range of Composition

013647-2

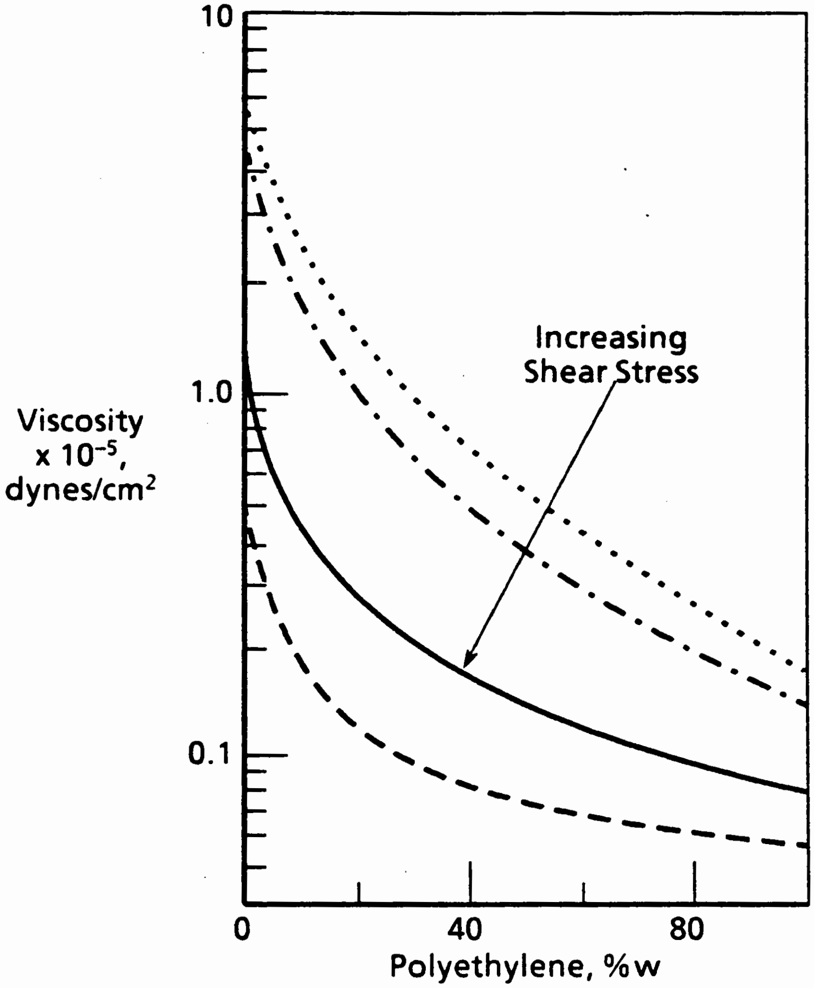

Figure 3. Composition Dependence of Melt Viscosity for the Polystyrene/Polyethylene Blend System
(From Reference 25)

013647-3

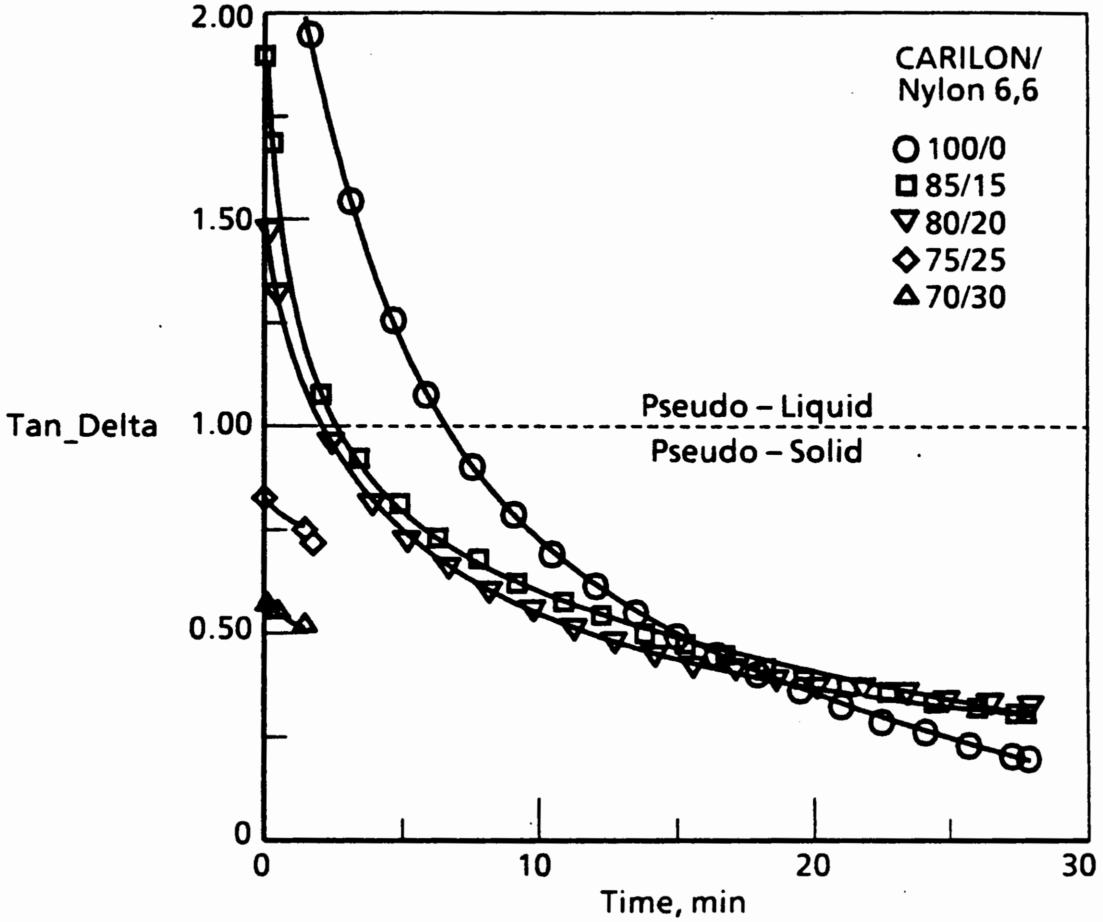

Figure 4. Tan Delta (G"/G') as a Function of Time for CAR/N66 Blends of Varying Nylon Content

013647-4

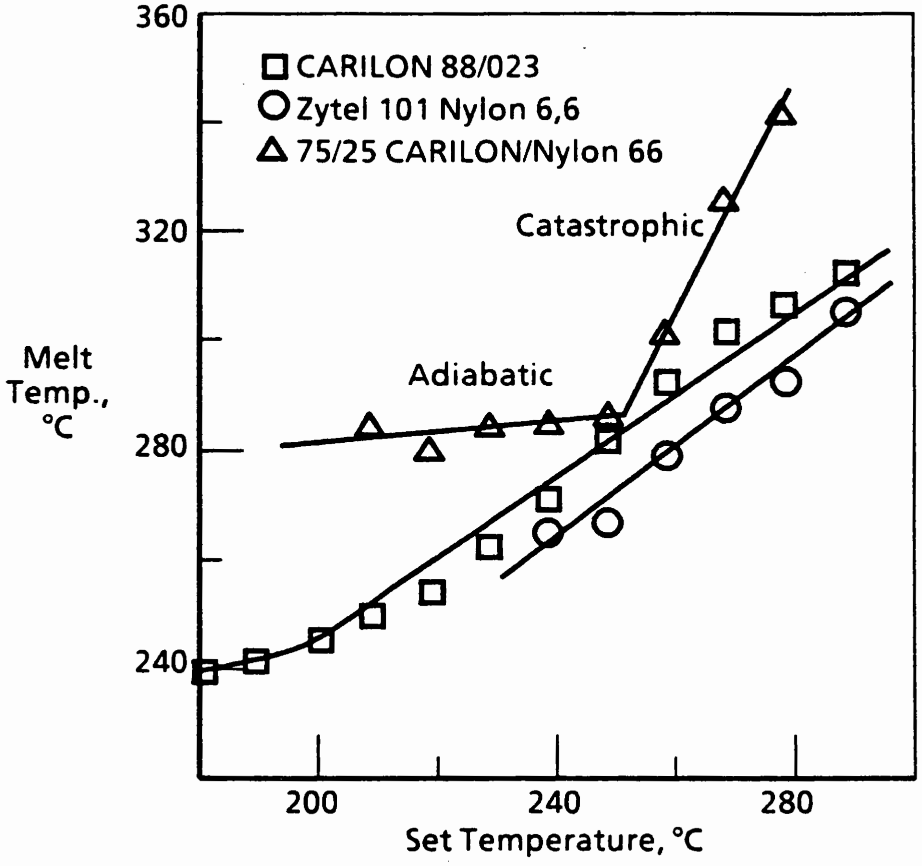

Figure 5. Melt Temperature of Extrudate Measured as it Emerges from the Die Plotted Against the Extruder Set Temperature for Neat CARILON Polymer, Neat Nylon, and a 75/25 CAR/N66 Compounded Under Identical Conditions

013647-5

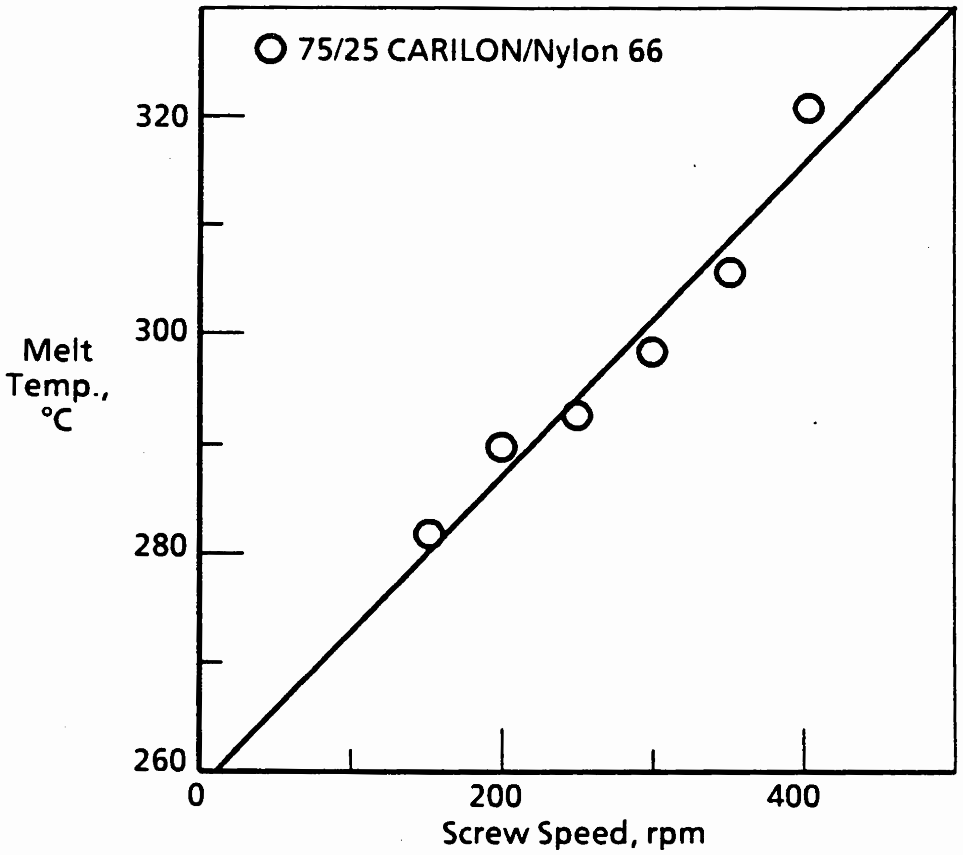

Figure 6. Measured Melt Temperature as a Function of Screw RPM for a 75/25 CAR/N66 Blend Where All Other Compounding Variables Were Held Constant

013647-6

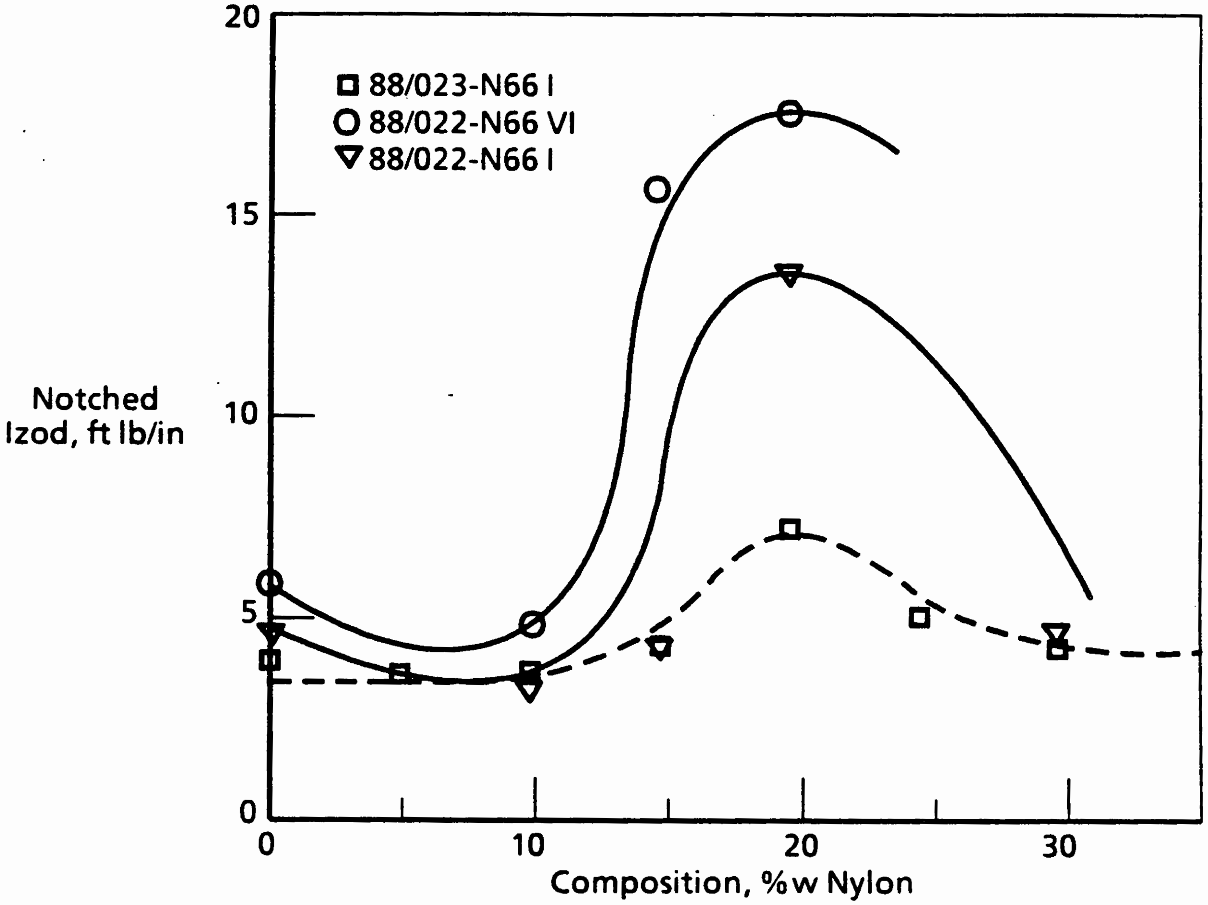

Figure 7. Notched Izod Impact Values Measured at Room Temperature Shown as a Function of Nylon Content for Blends Made from Different Base CARILON Polymers (88/022 and 88/023) and Having Different Thermal Histories (Molding Conditions I and VI; See Appendix 2)

013647-7

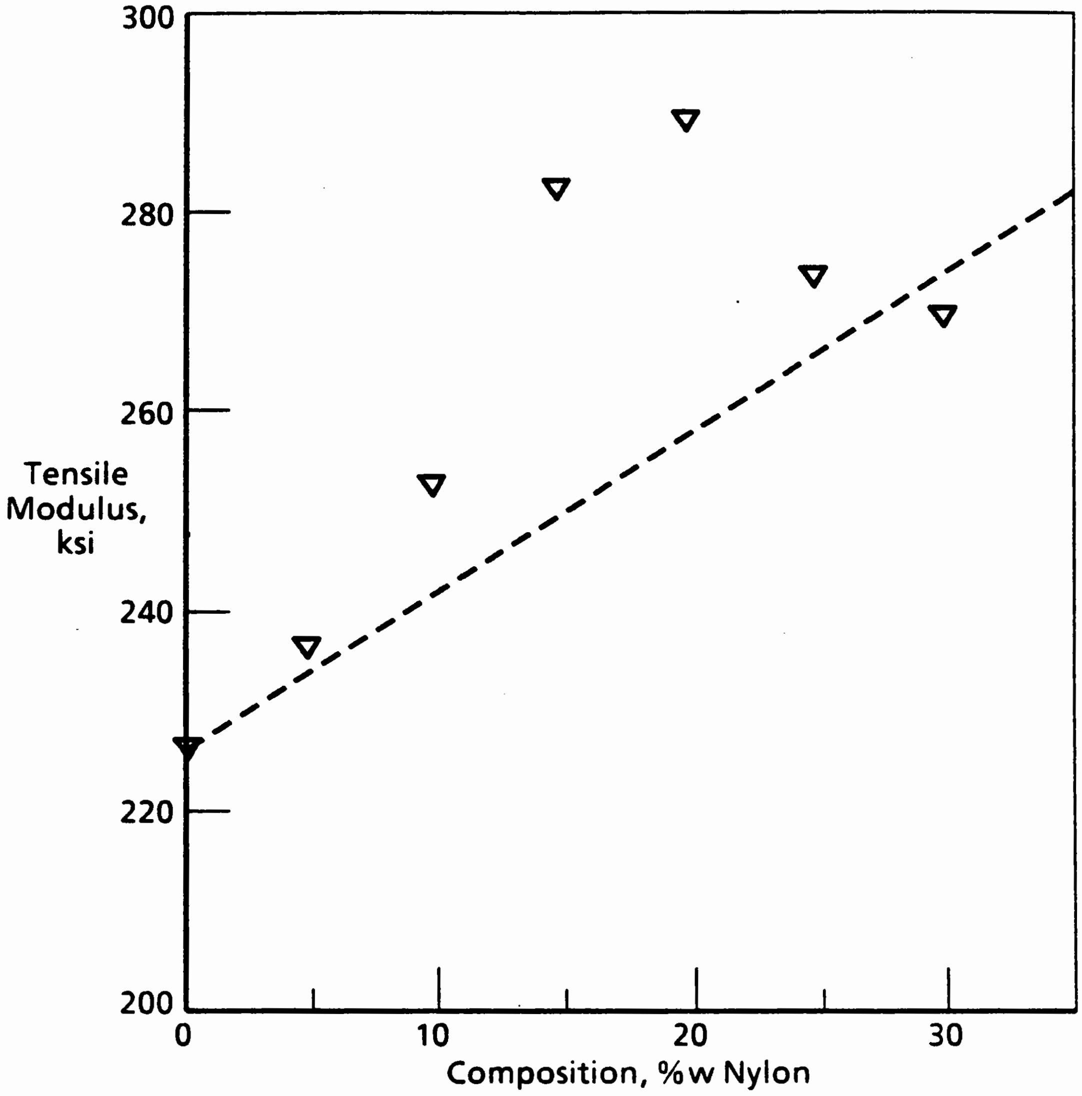

Figure 8. Tensile Modulus vs. Nylon Content in CAR/N66 Blends
The dotted line indicates additivity of modulus between those of the two pure components, which is usually considered an upper limit for this property.

013647-8

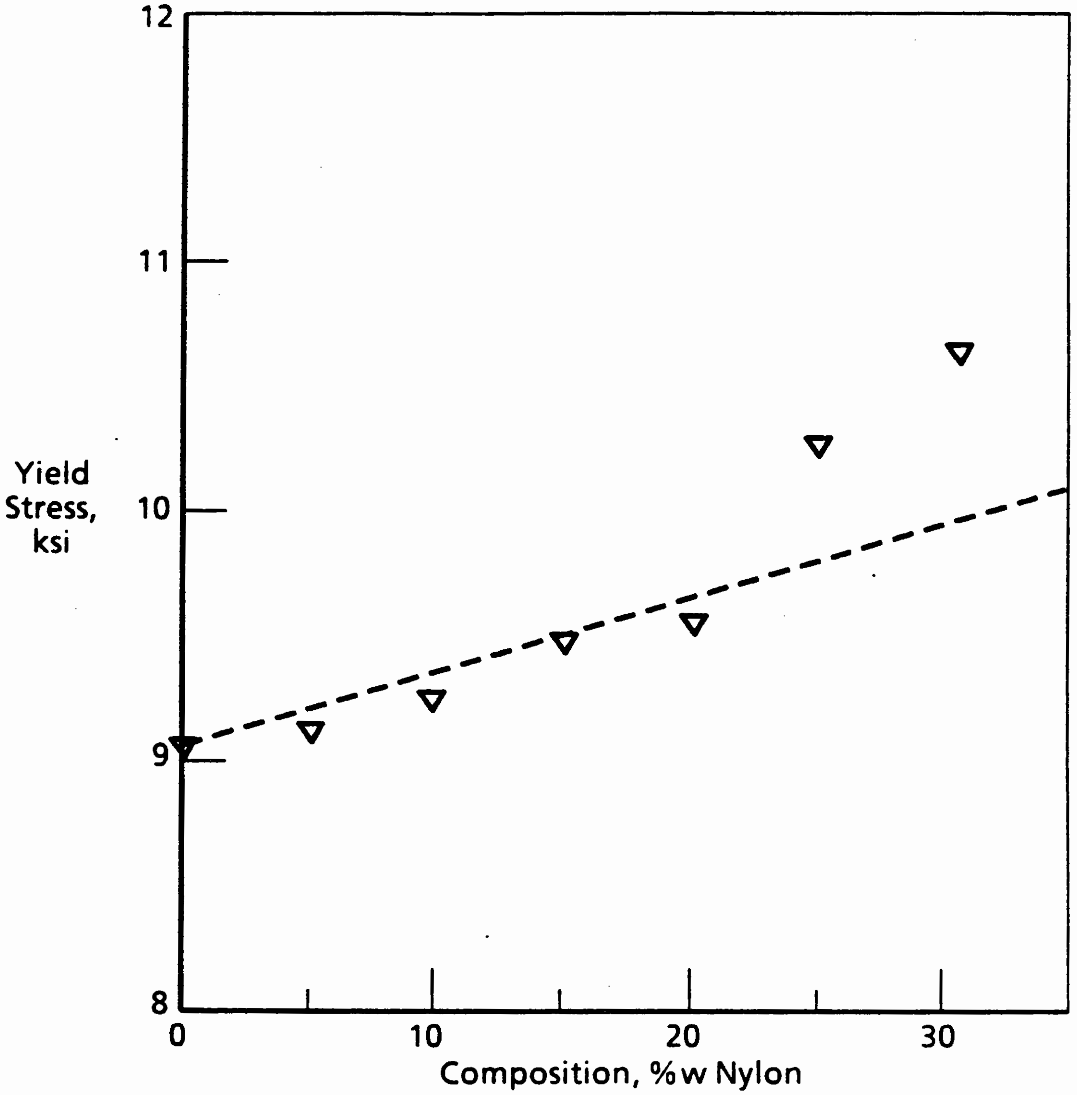

Figure 9. Tensile Yield Stress vs. Nylon Content in CAR/N66 Blends
The dotted line is the prediction for simple additivity.

013647-9

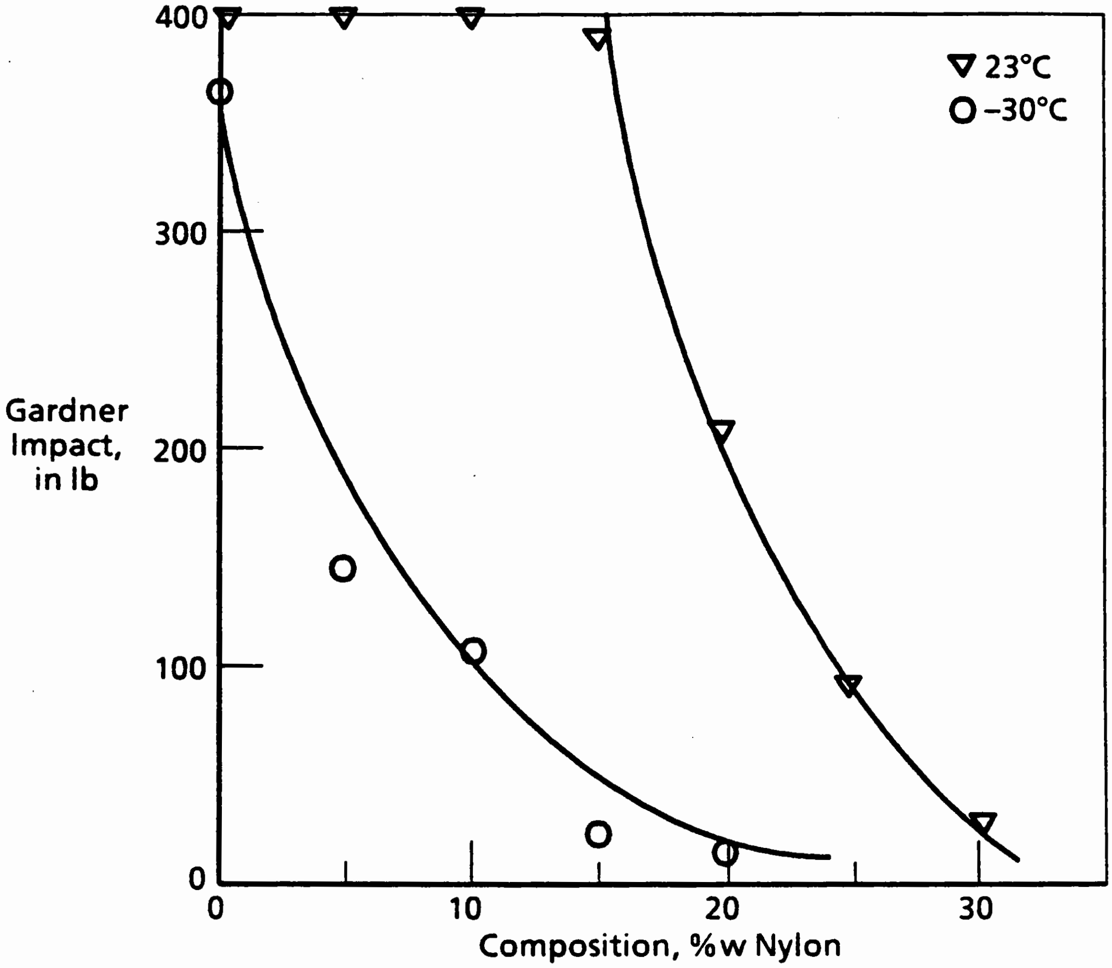

Figure 10. Gardner (Falling Dart) Impact Strength, Measured at R.T. and at −30°C, Shown vs. Nylon Content in CAR/N66 Blends

013647-10

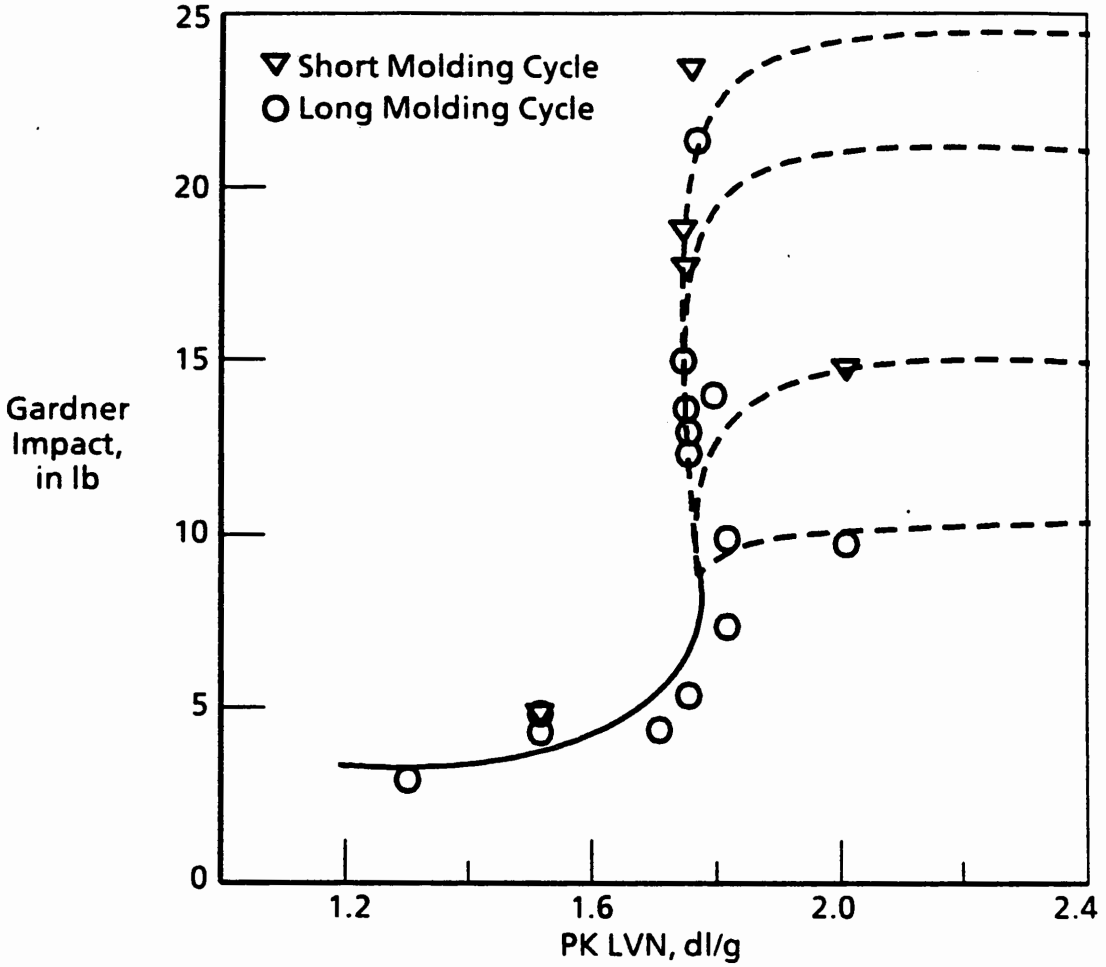

Figure 11. Notched Izod Values at Room Temperature for a Number of Differnt CAR/N66 Blends All Having a Nylon Content of 20%w, Plotted Against the Reported LVN of the Base CARILON Polymer Used to Make the Blend

013647-11

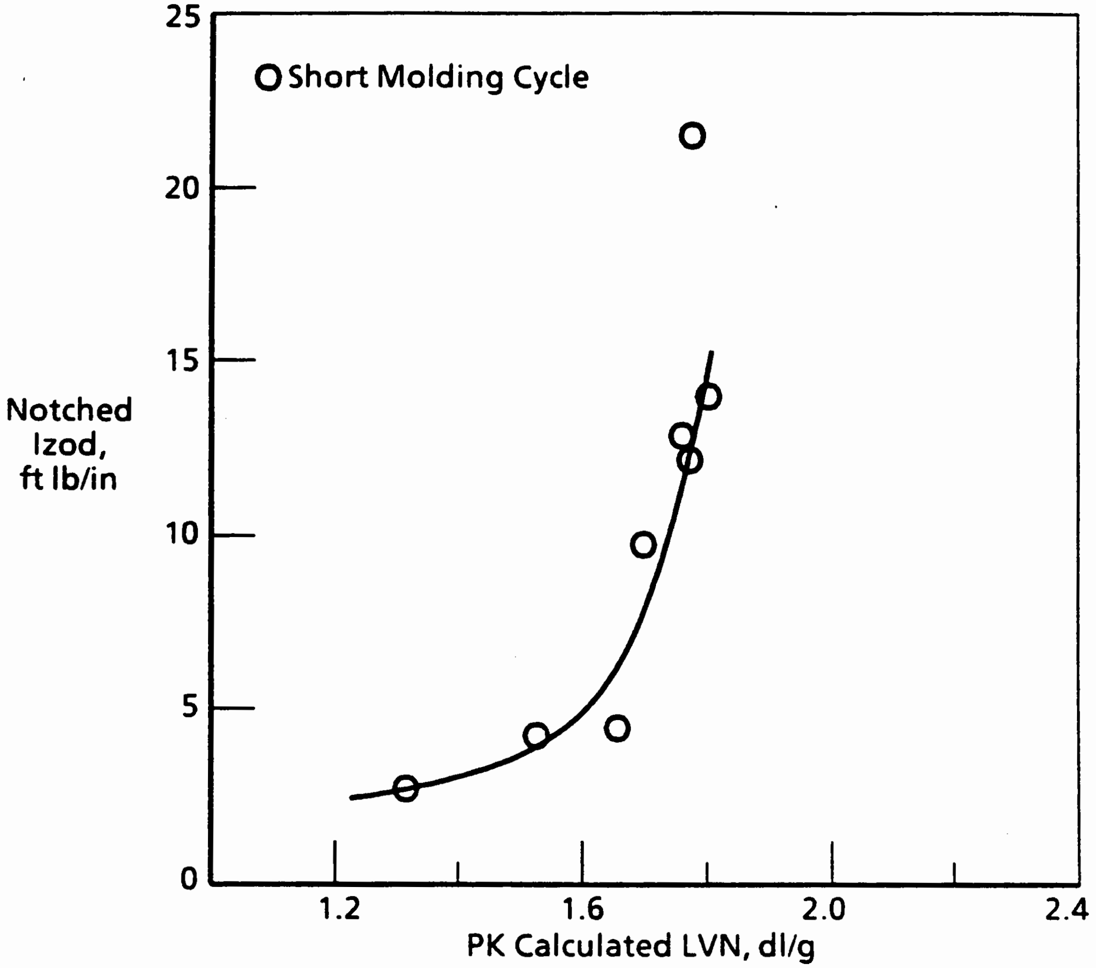

Figure 12. Some of the Data from Figure 11 Replotted Against the Calculated LVN (Determined from Rheological Behavior) Rather Than the Measured LVN

013647-12

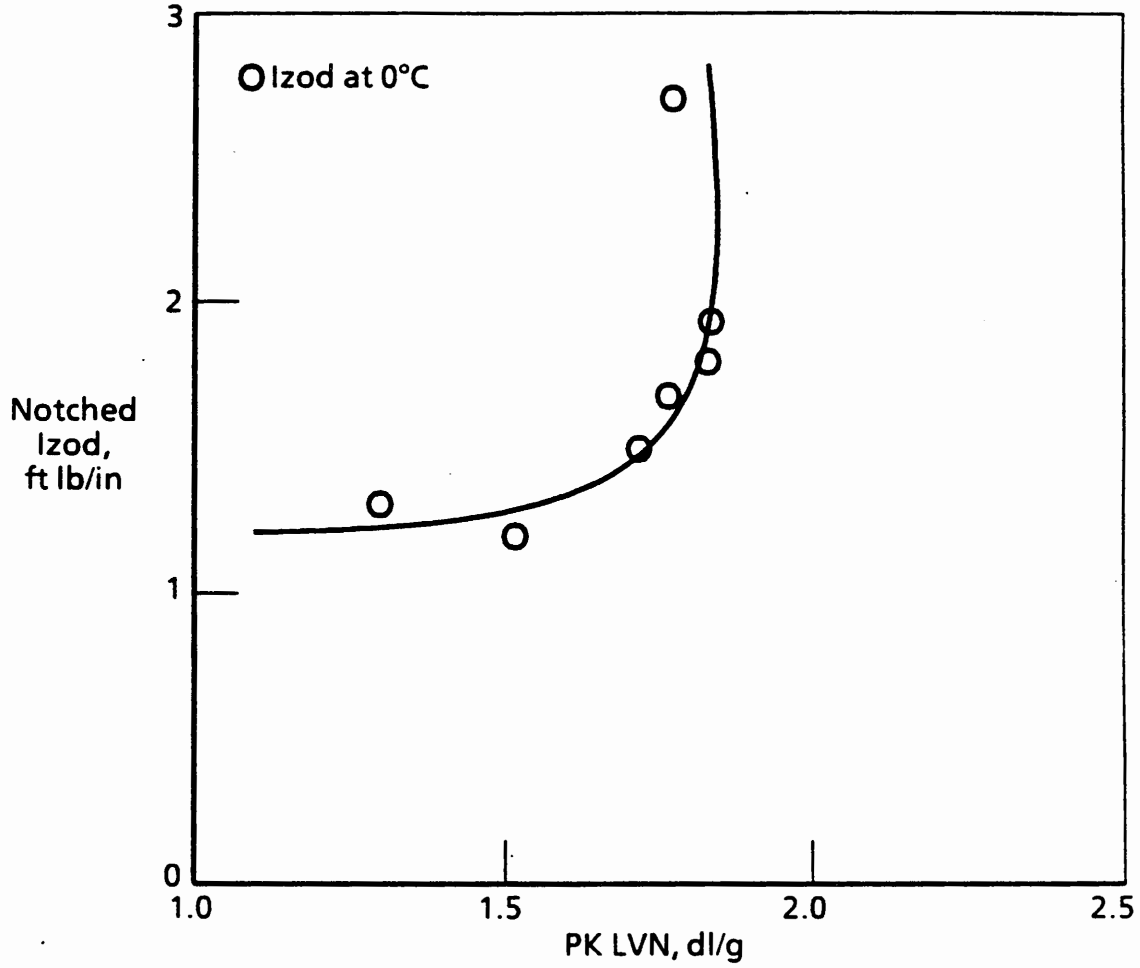

Figure 13. Notched Izod Values Measured at OC for CAR/N66 Blends Containing 20%w Nylon, Shown vs. the LVN of the Base Polyketone

013647-13

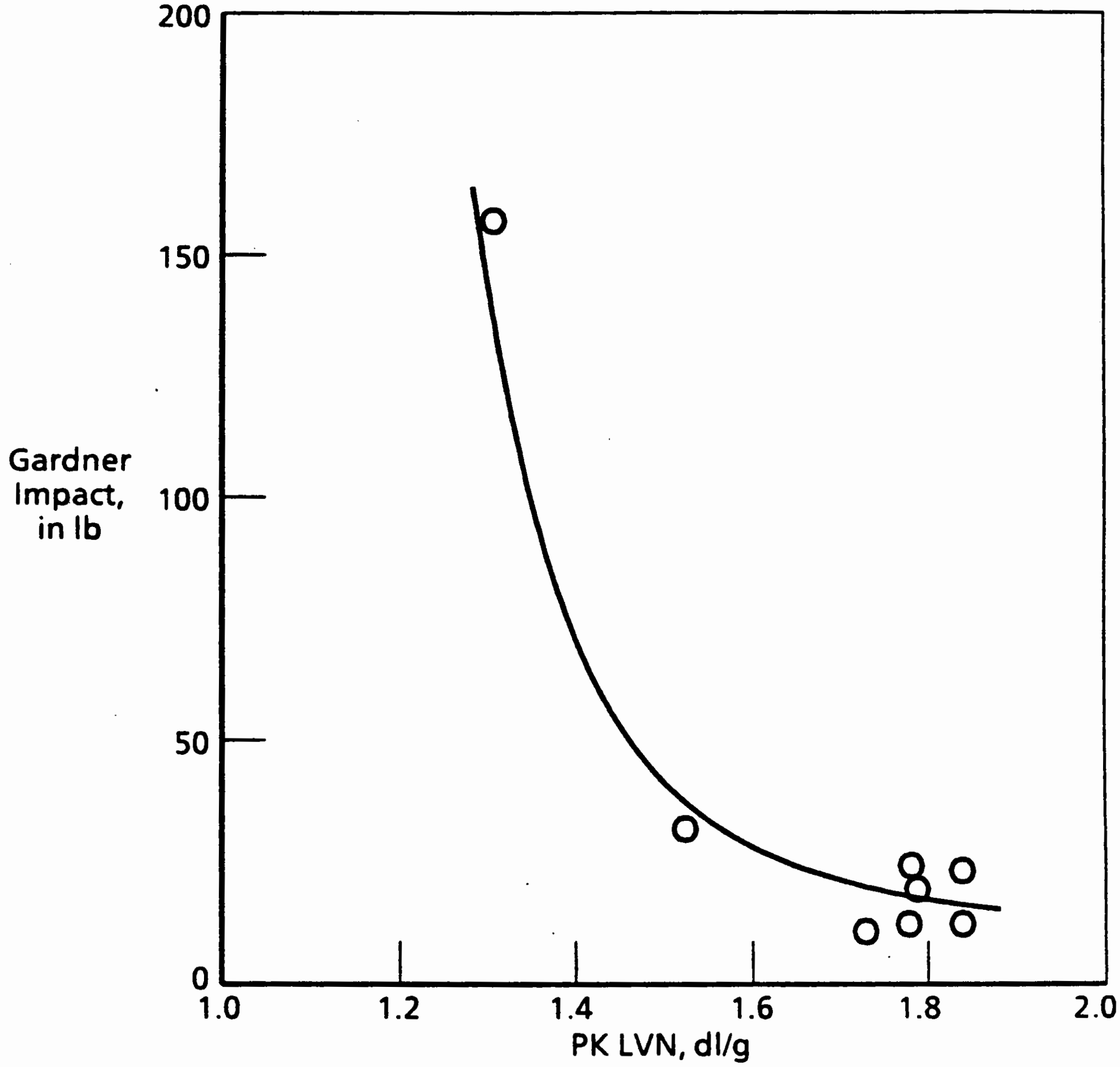

Figure 14. Gardner Impact Strength (–30°C) of 80/20 CAR/N66 Blends Shown vs. the LVN of the Base Polyketone

013647-14

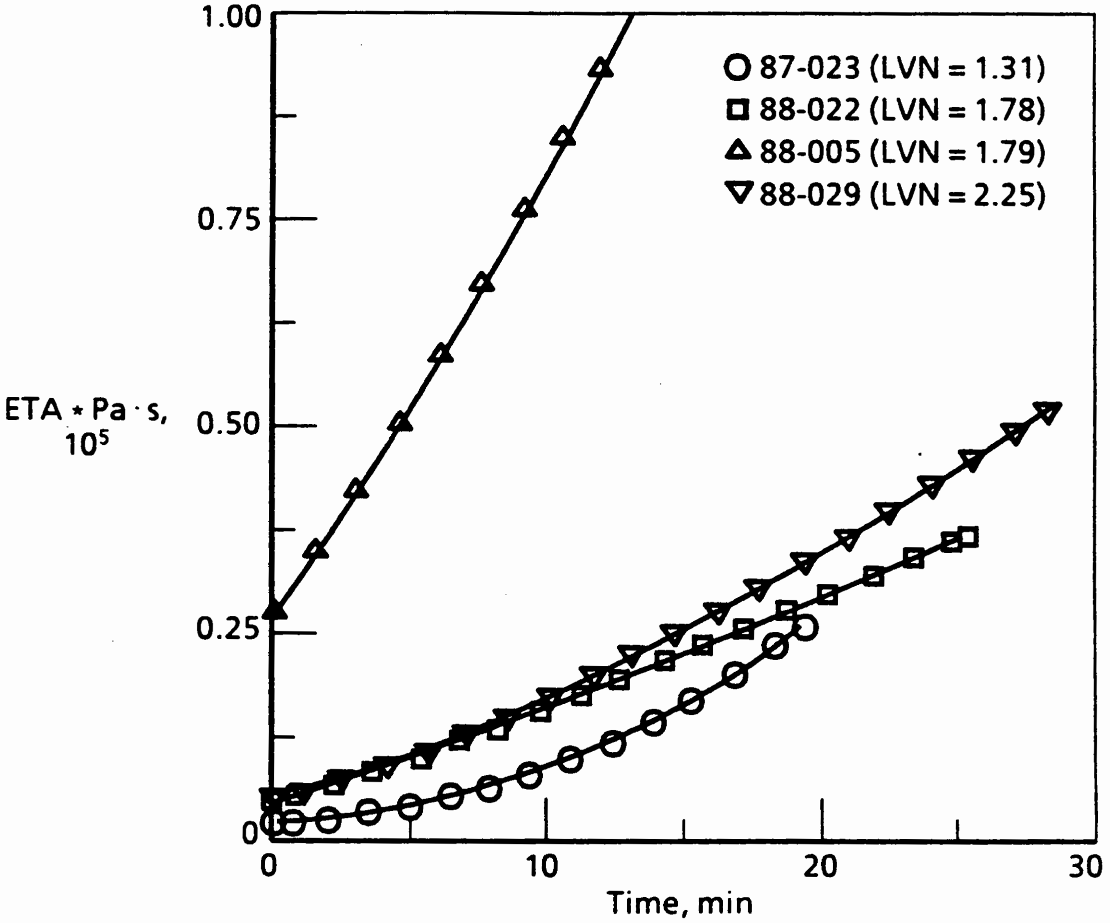

Figure 15. Dynamic Melt Viscosity at 275°C vs. Time for 80/20 CAR/N66 Blends Differing in LVN of the Base Polyketone

013647-15

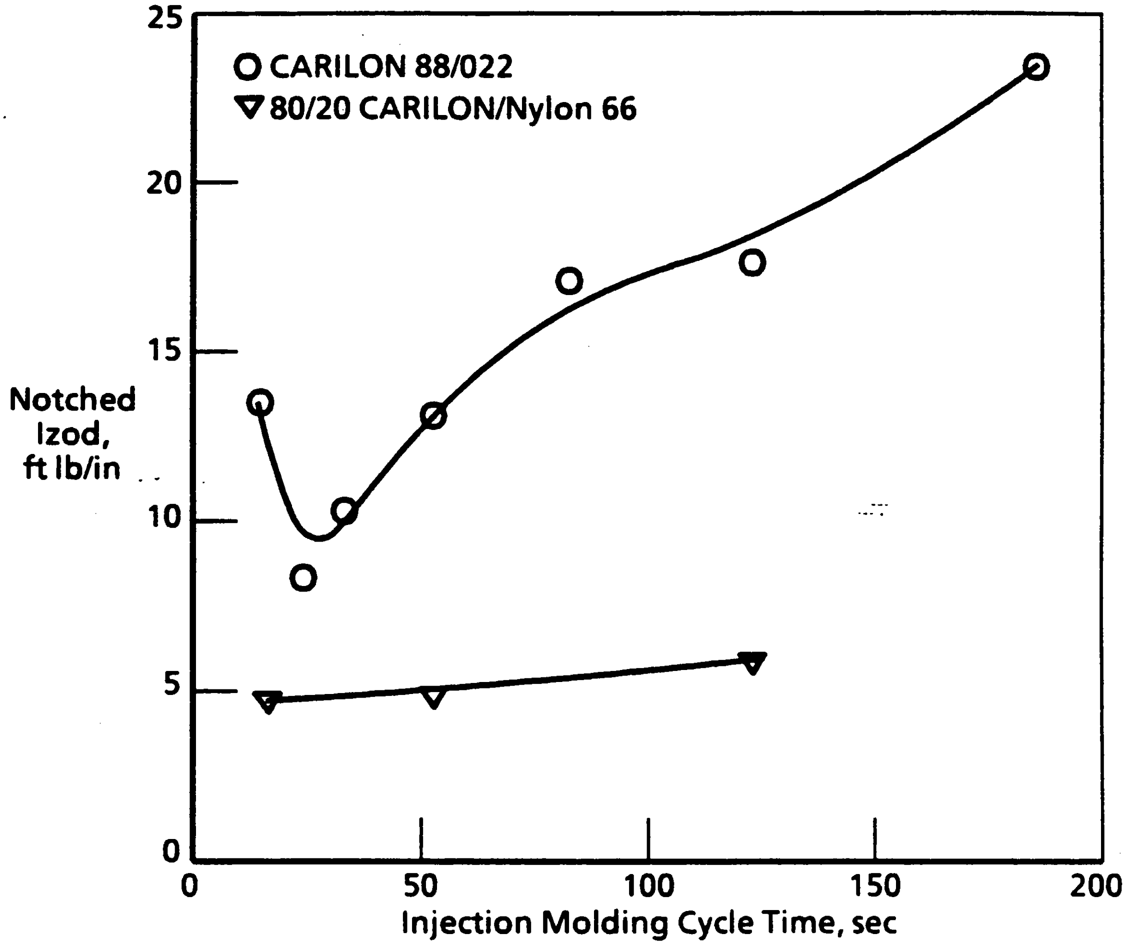

Figure 16. Notched Izod Values vs. Injection Molding Cycle Time for Unblended CARILON Polymer Control and 20%w Nylon Blend

013647-16

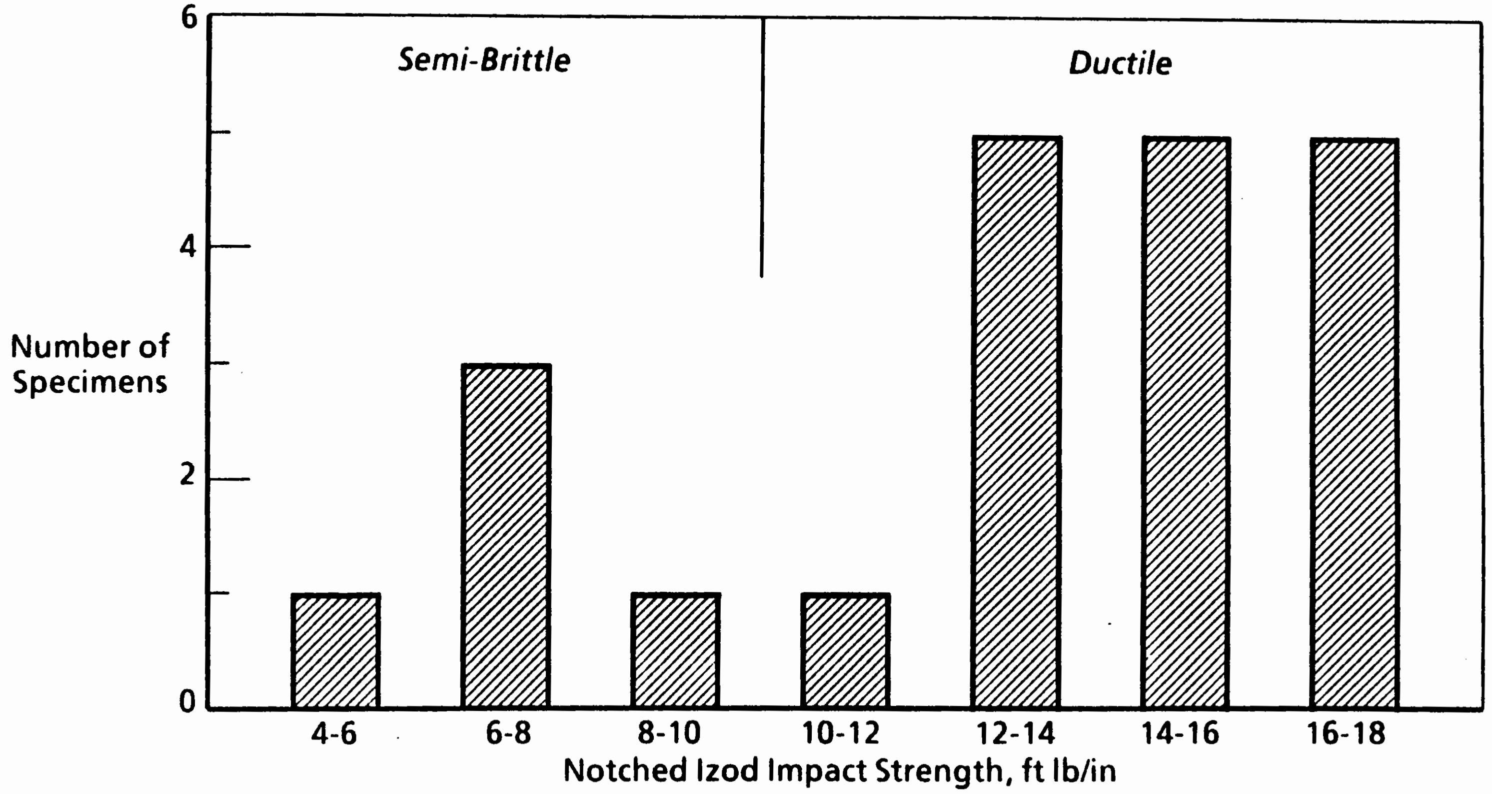

Figure 17. Distribution in Notched Izod Impact Strength in a Single Population of 80/20 CAR/N66 Blends Showing Variability in Brittle and Ductile Behavior

013647-17

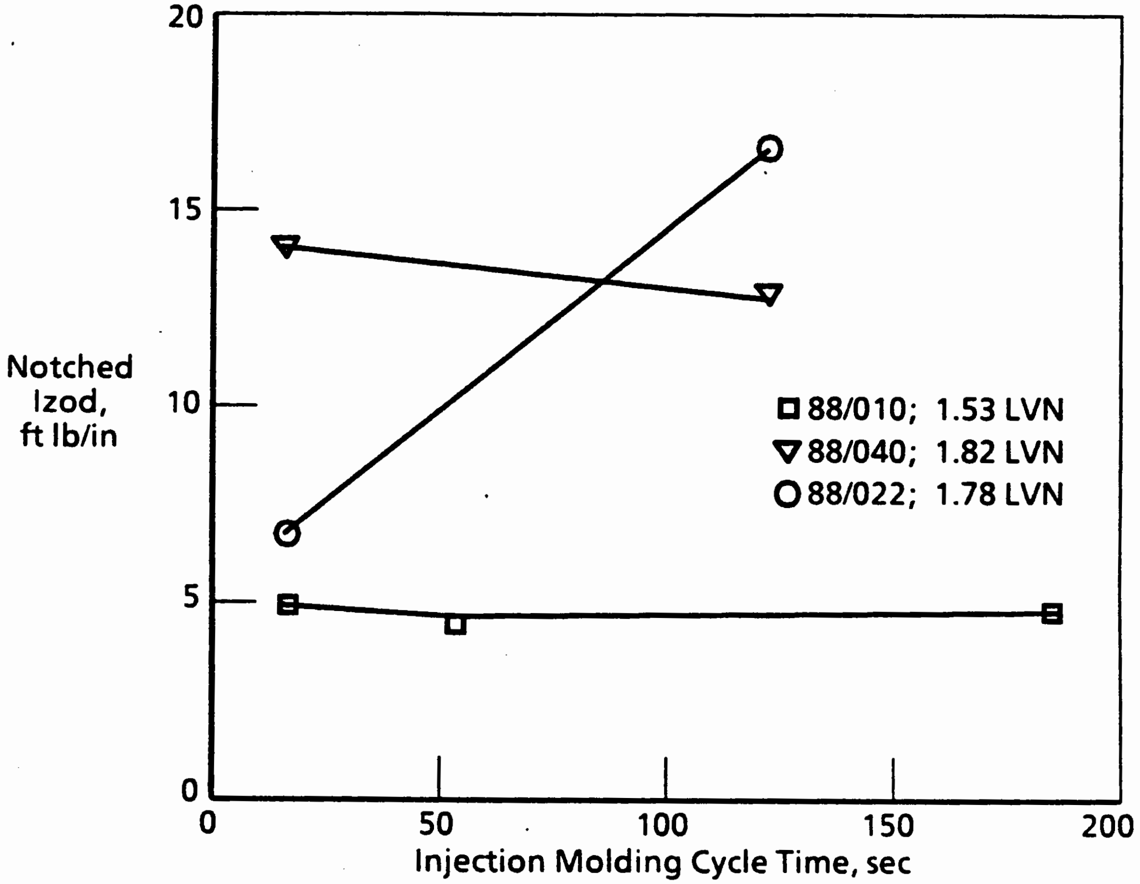

Figure 18. Notched Izod Values at Room Temperature Plotted vs. Injection Molding Cycle Time for Three 80/20 CAR/N66 Blends Made from CARILON Polymer Material Which was Either Below, Equal to, or Above the "Critical" LVN for Toughening

013647-18

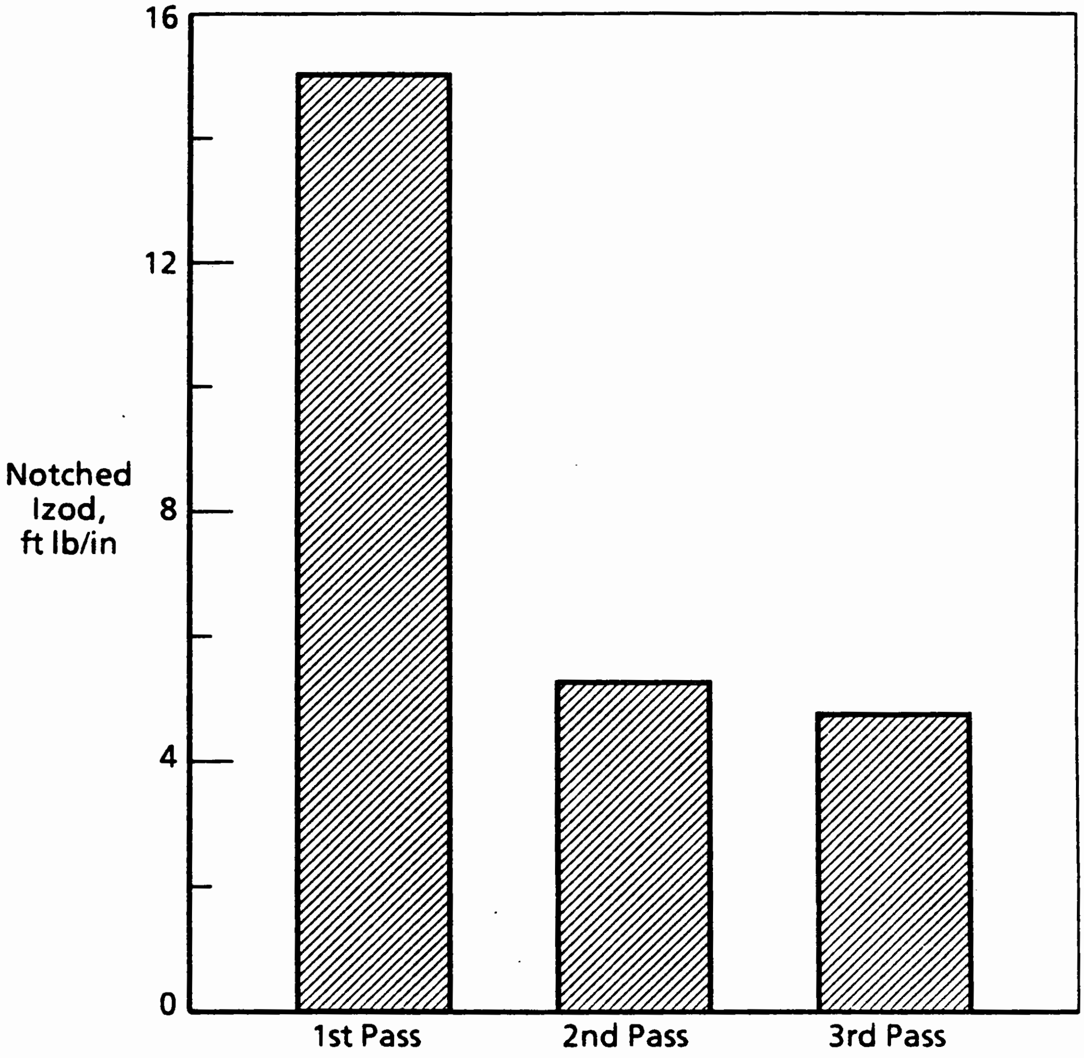

Figure 19. Notched Izod Values at R.T. for an 80/20 CAR/N66 Blend, Which was Subjected to Either One, Two, or Three Passes Through a Twin Screw Extruder

013647-19

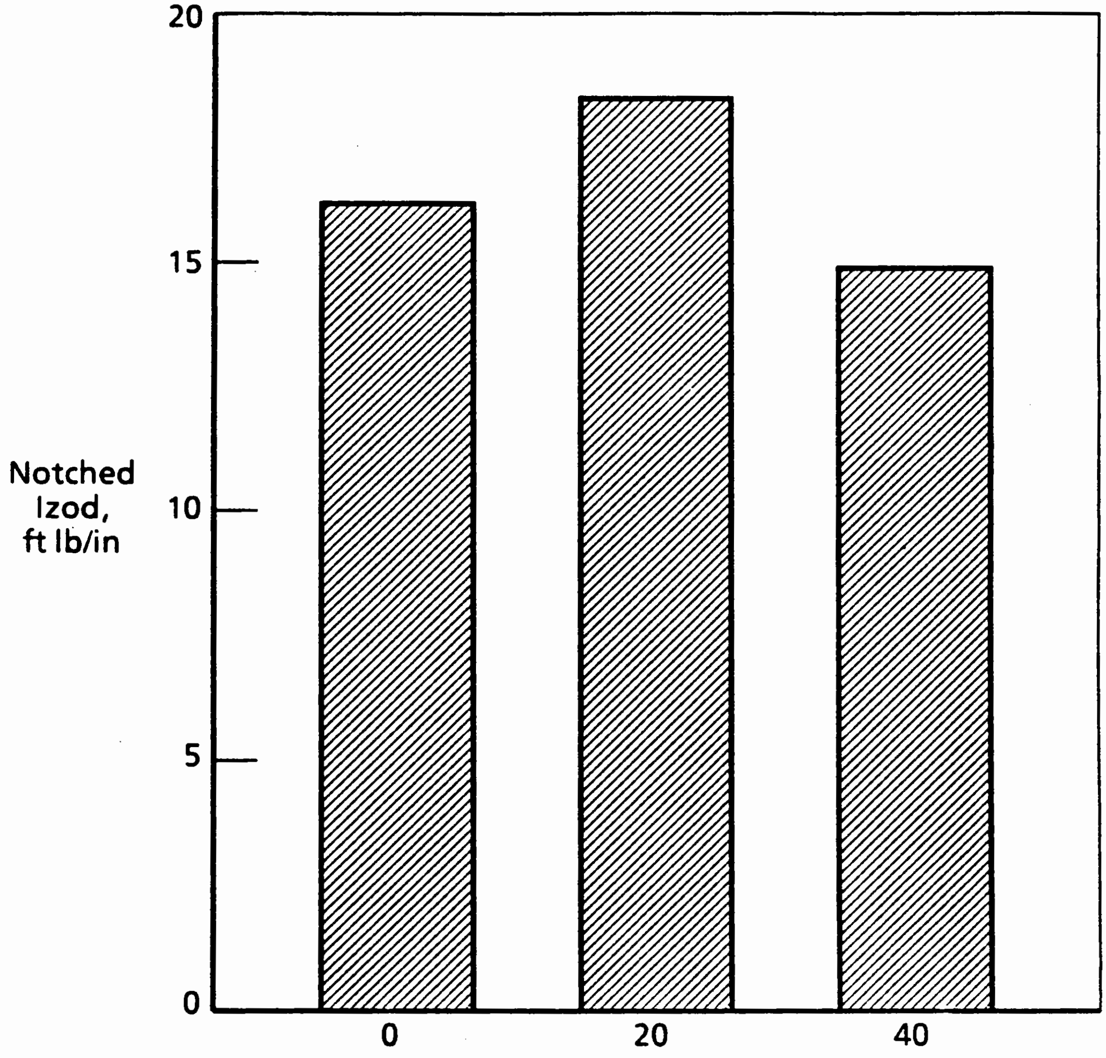

Figure 20. Notched Izod Values at R.T. for 80/20 CAR/N66 Blends Plotted vs. the Content of Previously Melt Processed Material (Regrind) of the Same Composition

013647-20

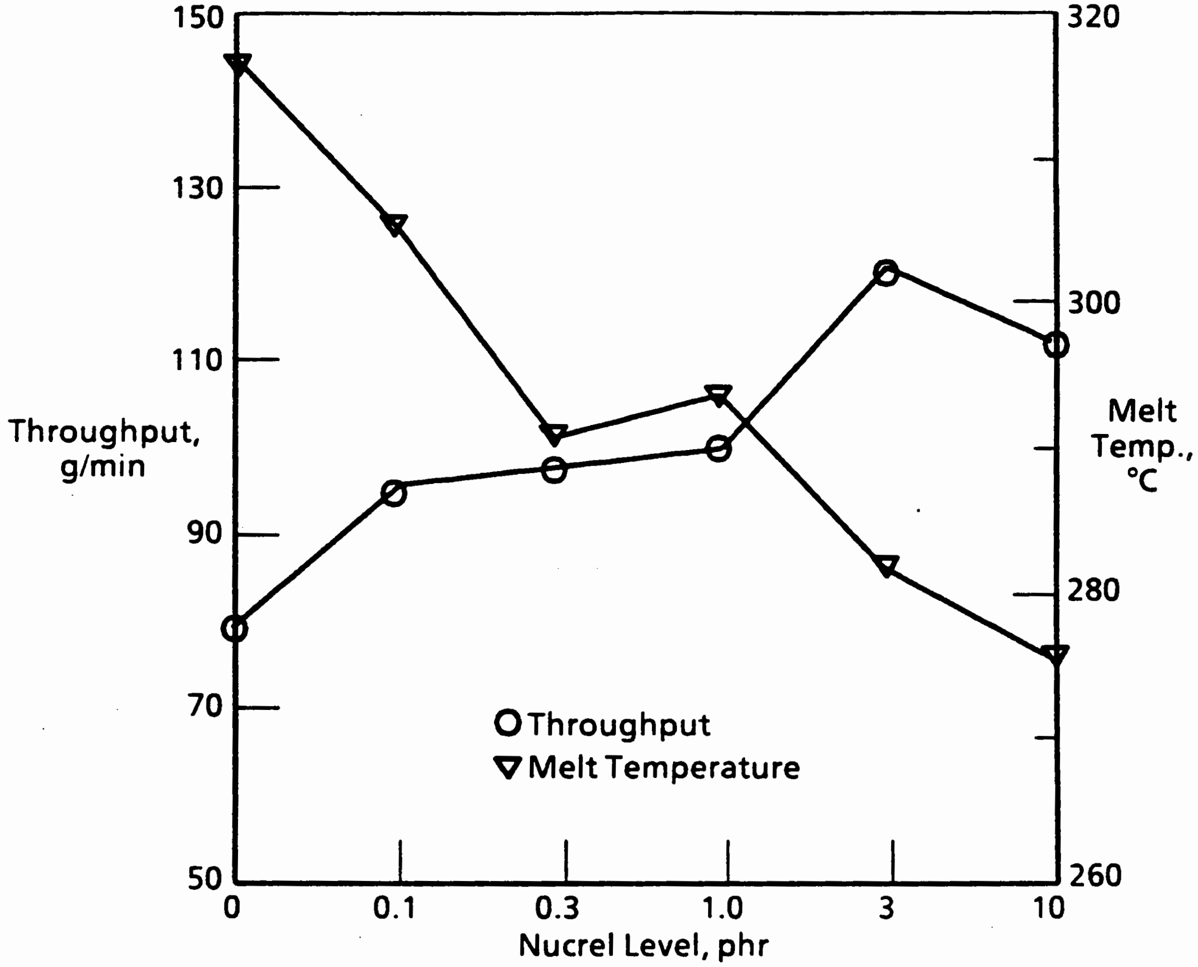

Figure 21. Extruder Throughput and Measured Melt Temperature for 80/20 CAR/N66 Blends Plotted Against the Amount of Nucrel 535 Added to the Blend to Aid in Compounding

013647-21

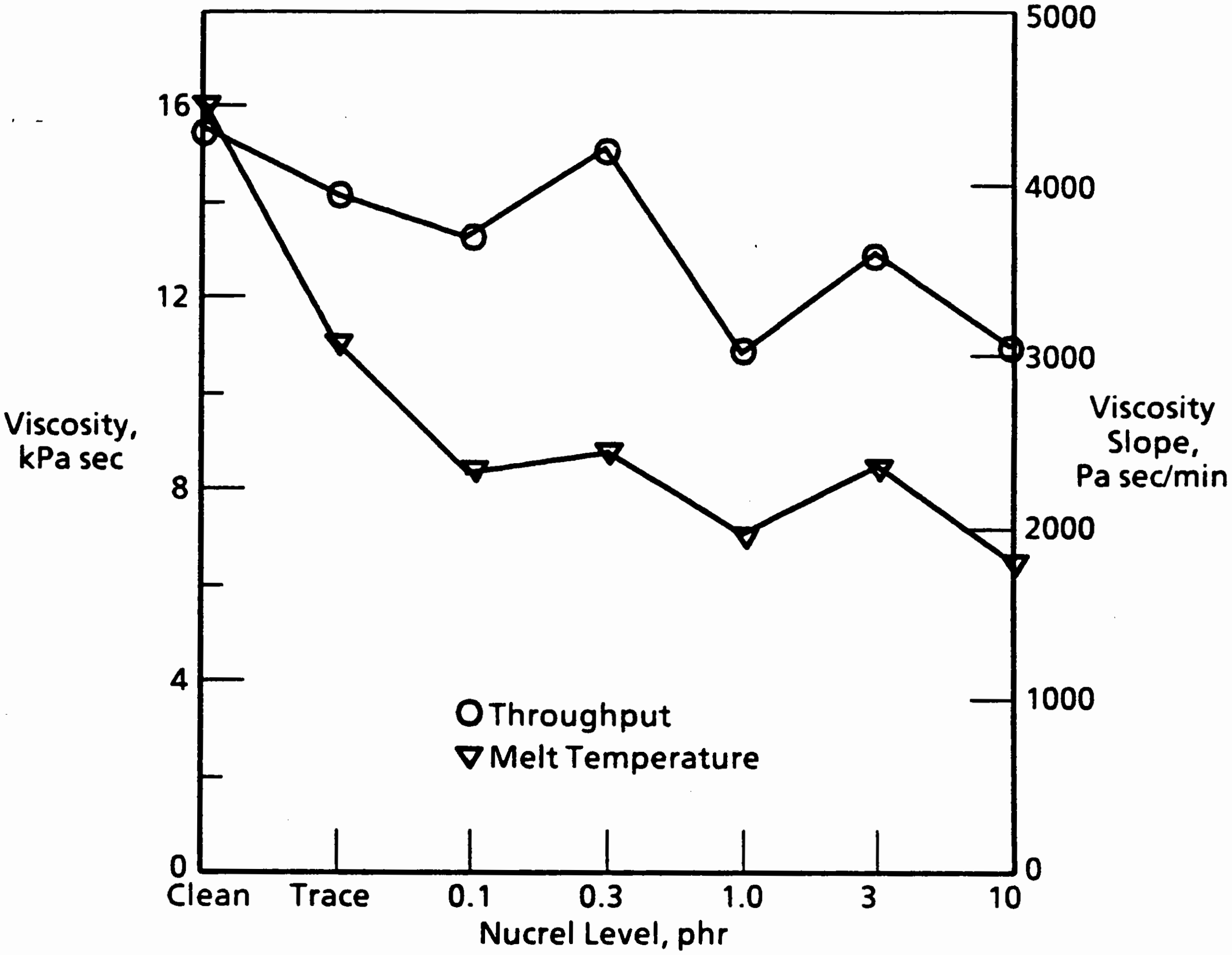

Figure 22. Initial Melt Viscosity and Viscosity Rate-of-Rise vs. the Nucrel 535 Content in a Series of 80/20 CAR/N66 Blends
Rheological testing was according to the standard CARILON protocol.

013647-22

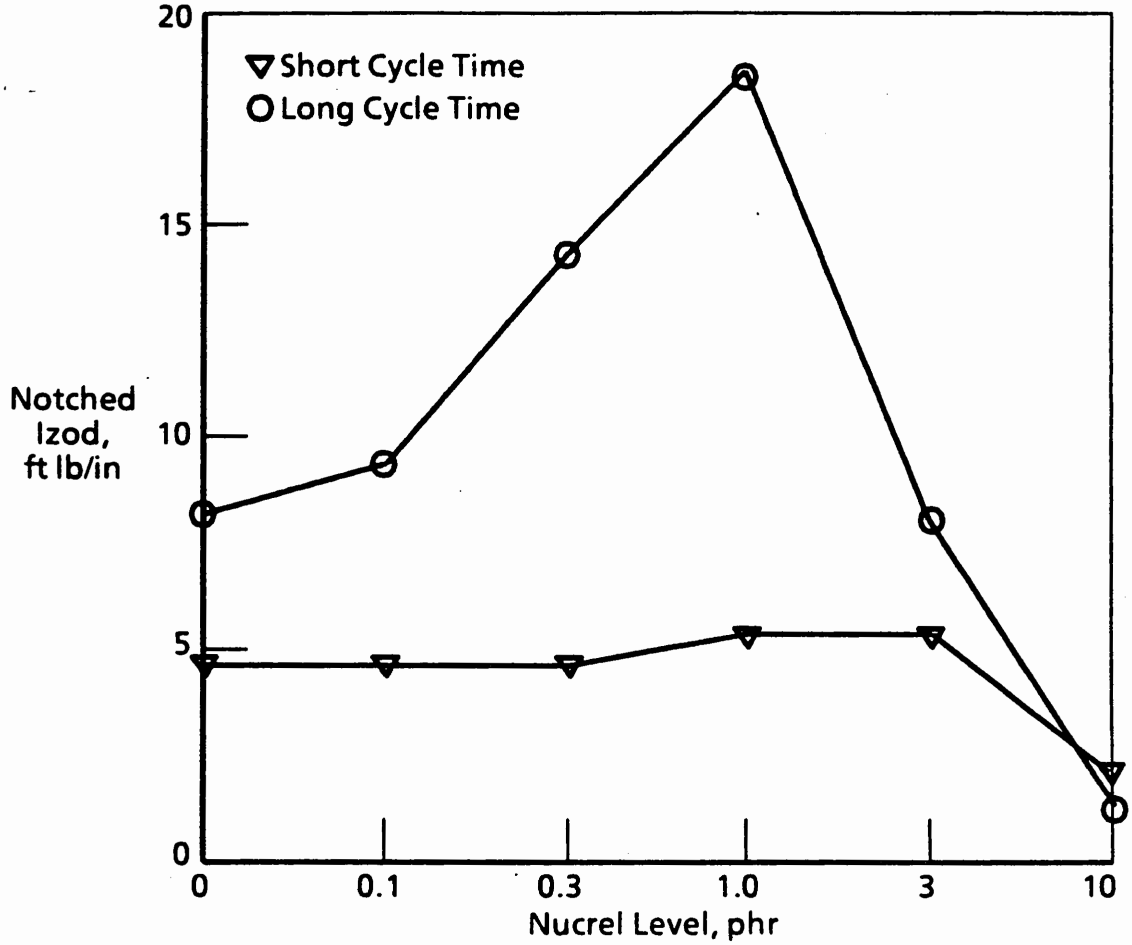

Figure 23. Notched Izod Values Measured at R.T. for a Series of 80/20 CAR/N66 Blends Plotted Against the Content of Nucrel 535 Added to the Blend
Data are shown for materials molded with either a short (cycle I) or a long (cycle VI) molding cycle (see Appendix 2).

013647-23

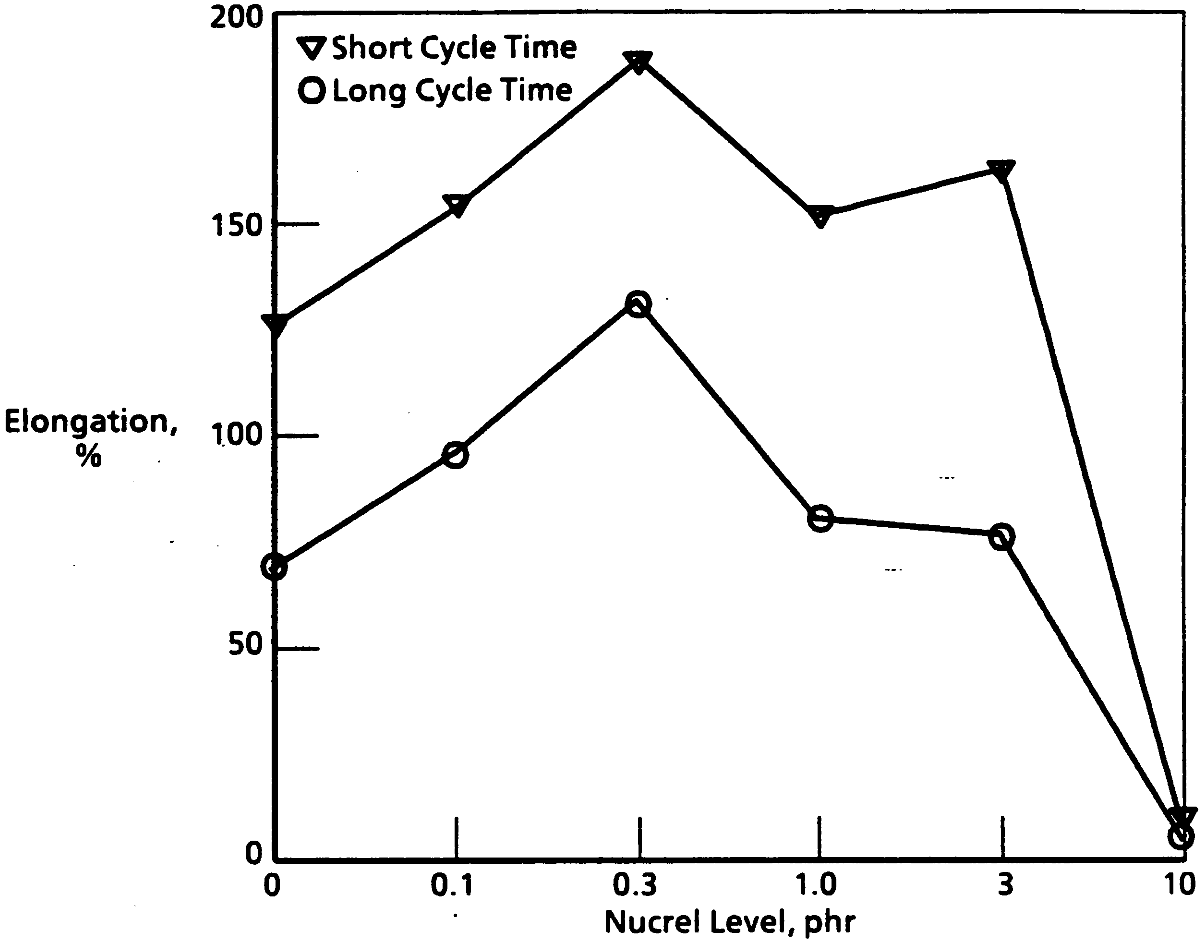

Figure 24. Tensile Elongation for a Series of 80/20 CAR/N66 Blends Plotted Against the Content of Nucrel 535 Added to the Blend

013647-24

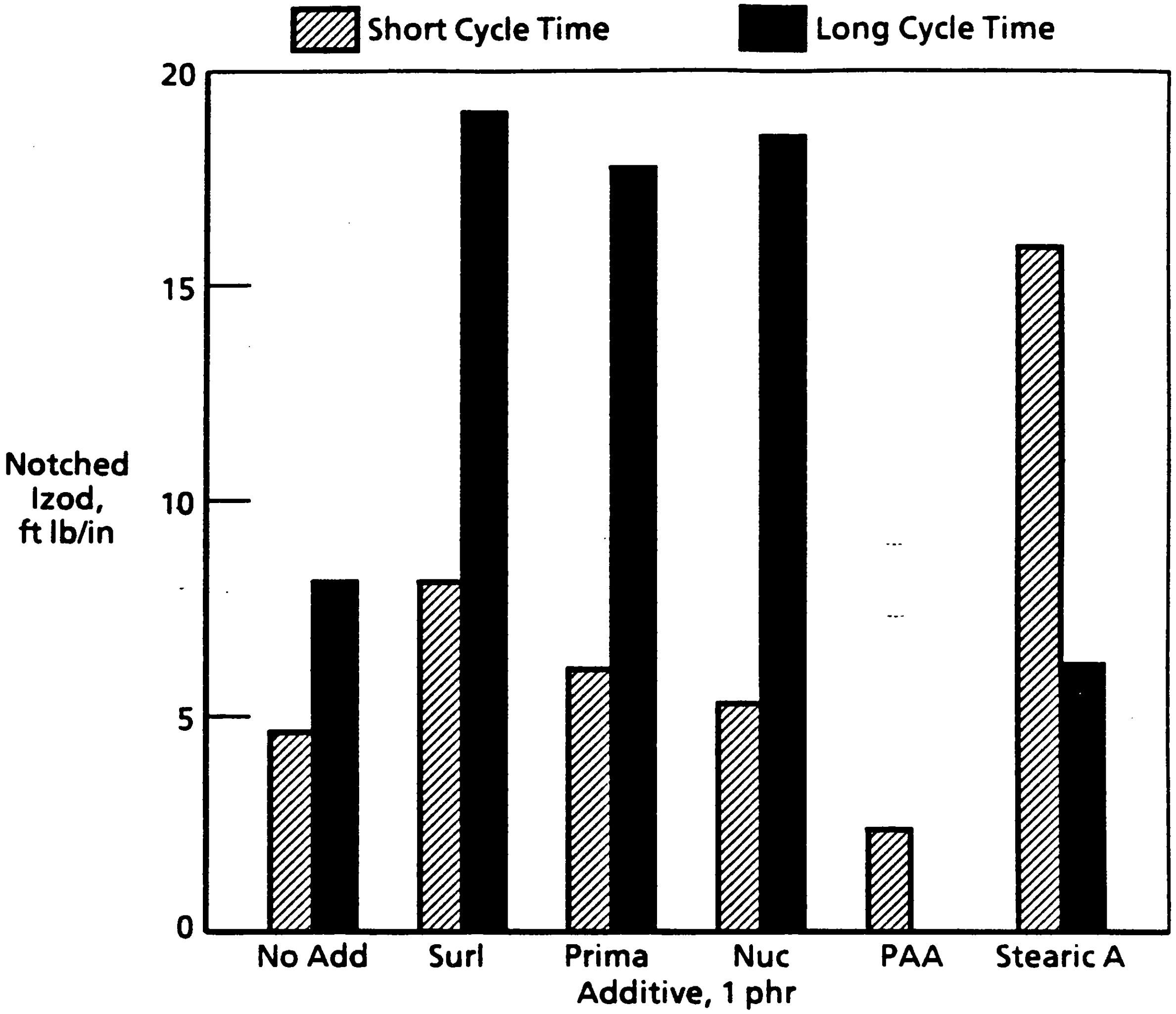

Figure 25. Notched Izod Measured at Room Temperature for a Series of 80/20 CAR/N66 Blends Containing 1 phr of Various Additives Which May Act as Reaction "Modifiers"

013647-25

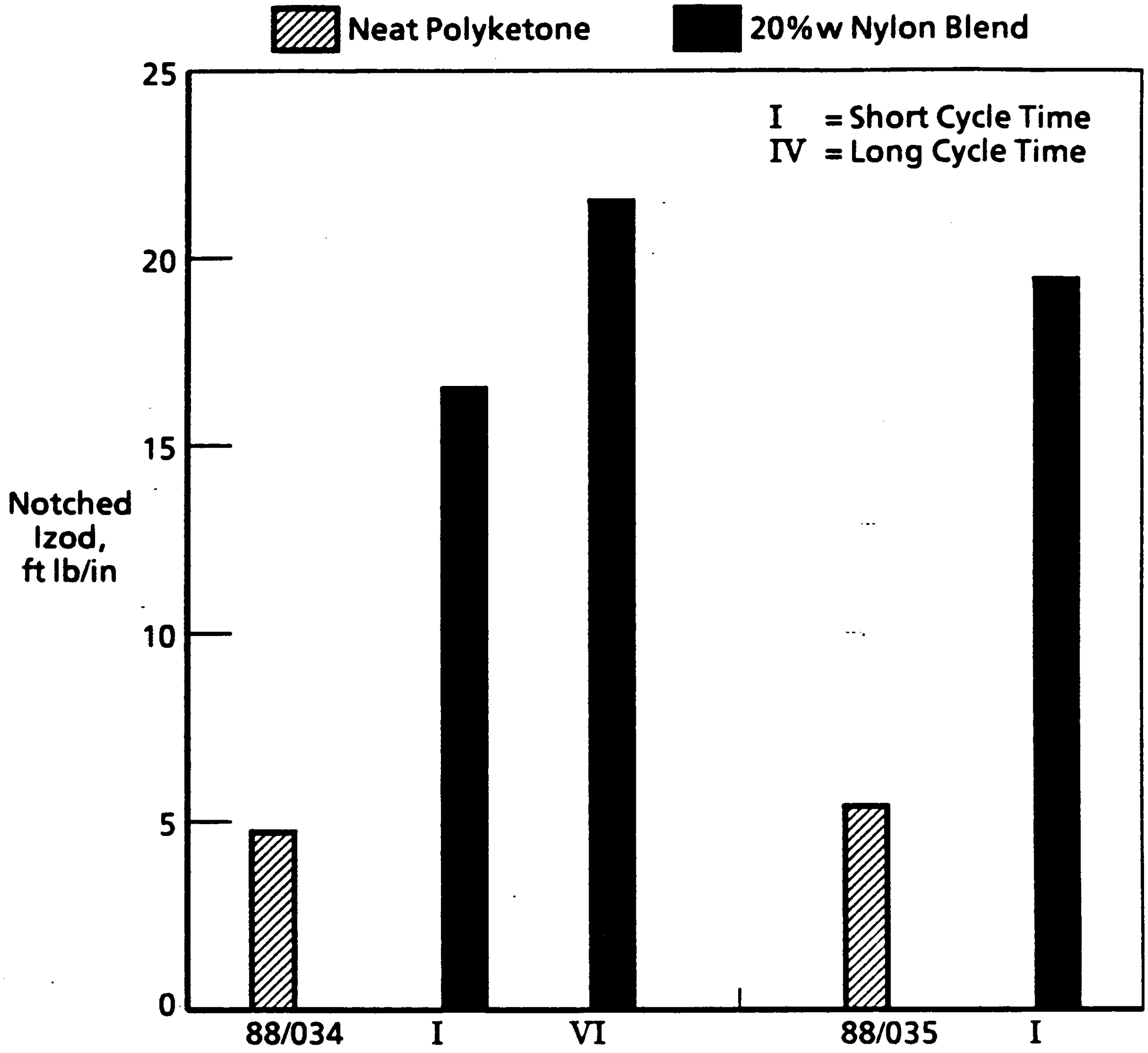

Figure 26. Notched Izod Measured at Room Temperature for CARILON™ E/Nylon 66 Blends

013647-26

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APPENDIX I

APPENDIX 1

Melt Compounding Procedure

All the blends in this work were compounded on a Haake 30mm co-rotating, intermeshing, twin screw extruder. The total screw L/D is equal to thirteen, and the screw configuration is shown in Figure A1. The mixing dynamics in this type of screw have been discussed by Lutz.

Blends were compounded directly from dried, mixed pellets (although the Nucrel 535 component was in cryoground powder form). Typically, the extruder was operated at 200 rpm, however, series MG-1 and MG-2 were compounded at 300 rpm screw speed. The extruder was usually operated near maximum available torque to minimize total residence time. Thus throughput was maximized. Table A2 gives the operating conditions for an exemplary series of blends. For reasonably melt stable blends, extruder throughputs were in the range of 10-15 lbs/hr, and approximate residence times in the barrel were in the range of 1-2 minutes.

The formulations of specific blends are listed below (Table A1) arranged according to the chapters in which they are discussed.

Sample Designation	**CARILON Polymer** pph (batch)	**Nylon 66** pph	**Additive** pph
Section III			
MG1-H	100 (88/023)	0	0
MG1-A	100 (88/023)	0	1 (Nuc535)
MG1-B	95 "	5	"
MG1-C	90 "	10	"
MG1-D	85 "	15	"
MG1-E1	80 "	20	"
MG1-F	75 "	25	"
MG1-G	70 "	30	"
MG2-A	0 "	100	0
MG-2B	0 "	100	1 (Nuc535)
MG-2C	2 "	98	"
MG-2D	4 "	96	"
MG-2E	6 "	94	"

MG-2F	8 (88/023)	92	"
MG-2G3	15 "	85	"
MG-2H	20 "	80	"

Sample Designation	CARILON Polymer pph (batch)	Nylon 66 pph	Additive pph
Section IV			
MG6-B	80 (87/053)	20	1 (Nuc535)
MG6-D	80 (88/010)	20	"
MG6-F	80 (88/024)	20	"
MG6-H	80 (88/022)	20	"
MG6-J	80 (88/005)	20	"
MG6-L	80 (88/023)	20	"
MG6-N	80 (87/029)	20	"
MG14-B	80 (88/043)	20	"
MG20-B	80 (88/040)	20	"
Section V			
MG7-A	100 (88/022)	0	1 (Nuc 535)
MG7-B	80 (88/022)	20	"
MG8-A	100 (88/010)	0	"
MG8-B	80 (88/010)	20	"
MG20-A	100 (88/040)	0	"
MG20-B	80 (88/040)	20	"
MG13-A	80 (88/022)	20	"
MG13-B	100 (MG13-A)	0	0
MG13-C	100 (MG13-B)	0	0

Section VI			
MG18-A	80 (88/022)	20	10 (Nuc 535)
MG18-B	"	"	3 (Nuc 535)
MG18-C	"	"	1 (Nuc 535)
MG18-D	"	"	0.3 (Nuc 535)
MG18-E	"	"	0.1 (Nuc 535)
MG18-F	"	"	0

Sample Designation	**CARILON Polymer** pph (batch)	**Nylon 66** pph	**Additive** pph
Section VI (cont.)			
MG27-A	80 (88/022)	20	1(Nucrel 535)
MG27-B	"	"	1(Primacore)
MG27-C	"	"	1(Surlyn)
MG27-D	"	"	1(Stear. Ac.)
MG25-E	"	"	"
MG25-C	"	"	1(Sty-AA Cop)
MG25-D	"	"	1(PAcryl Ac)
Section VII			
MG12-A	100 (88/034)	0	0
MG12-B	100 (88/034)	0	1 (Nuc 535)
MG12-C	80 (88/034)	20	"
MG23-B	100 (88/035)	0	"
MG23-C	80 (88/035)	20	"

Table A2. Extruder operating conditions for MG18 blend series.

Sample	Zone Temperatures (set/act.)(deg C)			Melt Temp. (deg C)	RPM	Amps	Thruput (lb/hr)
	#1	#2	#3				
MG18A	240/224	230/241	240/258	275	200	17	14.7
MG18A	240/226	230/249	240/262	281	200	17	15.8
MG18C	240/228	230/251	240/263	293	200	17	13.1
MG18D	240/228	230/251	240/264	290	200	17	12.9
MG18E	240/229	230/252	240/266	305	200	17	12.5
MG18F	240/221	230/253	240/269	317	200	17	10.3

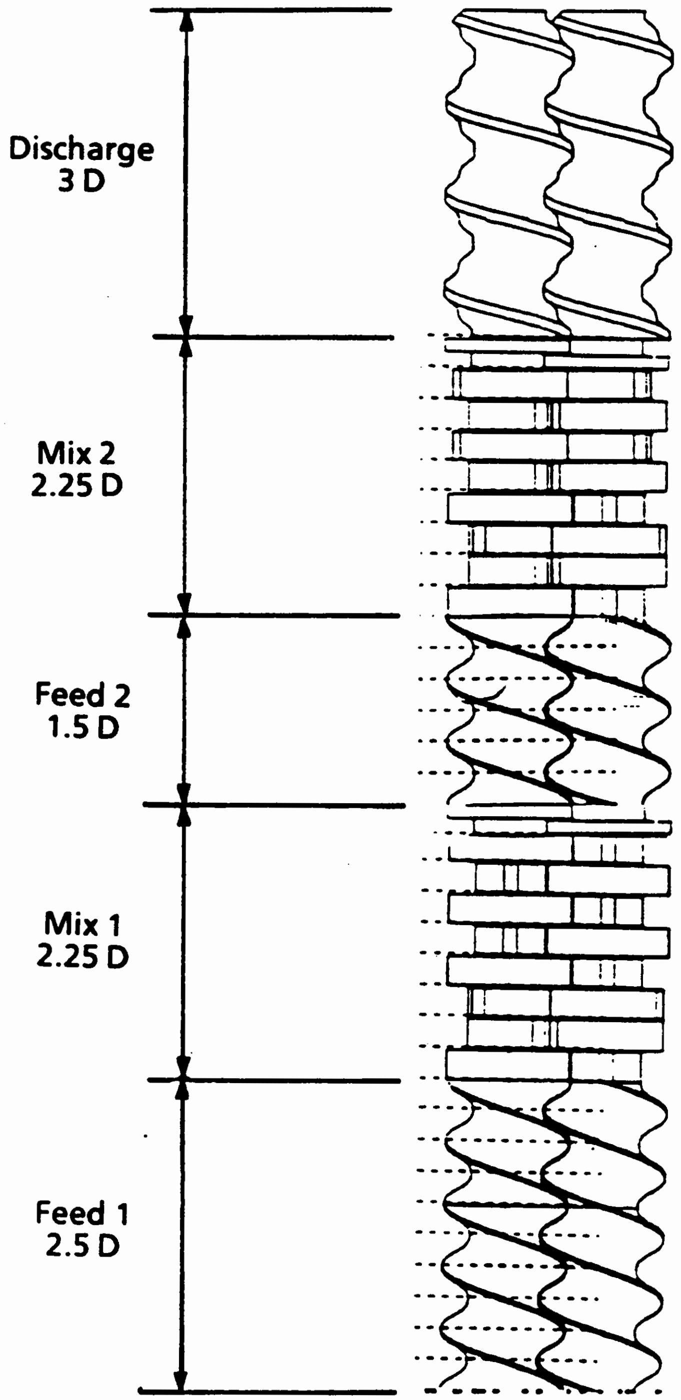

Figure A1. Diagram of Screw Configuration Which was Used in the Present Work

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APPENDIX II

APPENDIX 2

Relationship between Molding Cycle and Residence Time

The specimens tested in this work were molded on a 25-ton Arburg injection molding machine with a 25mm screw with 18/1 L/D. An important consideration in these studies was total residence time and the relationship between residence time and cycle time (see section IV). The ratio of (average) residence time/cycle time is, of course, equal to the ratio of shot volume to barrel capacity and thus depends upon the tooling, the barrel, and the screw which is used.

In this study, residence time was determined by dropping a color concentrate pellet into the barrel directly after shot injection and before screw reciprocation. The subsequent shots were then collected and examined for colorant content. In Figure A2, molded parts are shown for the seven shots following the introduction of the color concentrate. This was done for a number of different molding cycles. This figure shows that the maximum color concentration, regardless of cycle time, is observed on the third shot after injection. Also, the fourth shot contains significantly more pigment than the second. Thus the average residence time is between 3.0 and 3.5 times the cycle time; a reasonable estimate is probably 3.25. Thus, we have used the relationship:

Average Residence Time = 3.25 X Cycle Time

Of course, this equation is relevant only to this combination of machine, screw, and mold.

The residence time distribution appears to be independent of cycle time as one would expect. Figure A2 also shows that there is an observable (although small) fraction of material which is subject to a very long residence time (shots 5, 6, and 7), but there is virtually no material with a very short residence time (shot 1). The inhomogeneity of color content within the molded parts is indicative of the notion that injection molders are poor mixing devices. Consequently, in cases when blend properties are strongly residence time dependant, some inhomogeneity of properties may be encountered.

Cycle time was varied in this study over the range of about 16 seconds to three minutes. For each sample the specific molding conditions used were denoted with a Roman numeral suffix. Table A3 gives the molding cycles which were used.

Table A3. Standard Molding Cycles.

Cycle	**Delay** (sec)	**Inject** (sec)	**Hold** (sec)	**Cool** (sec)	**Pause** (sec)	**Total** (sec)	**Mold T** (deg C)

Table A3. Standard Molding Cycles.

Cycle	Delay (sec)	Inject (sec)	Hold (sec)	Cool (sec)	Pause (sec)	Total (sec)	Mold T (deg C)
I	1.0	2.0	2.5	10	1.0	16.5	65
II	1.0	2.0	2.5	10	9.9	25.4	65
III	9.9	2.0	2.5	10	9.9	33.4	65
IV	9.9	2.0	2.5	30	9.9	53.4	65
V	9.9	2.0	2.5	60	9.9	83.4	65
VI	9.9	2.0	2.5	99.9	9.9	124.2	65
VII	9.9	2.0	62.5	99.9	9.9	184.2	65

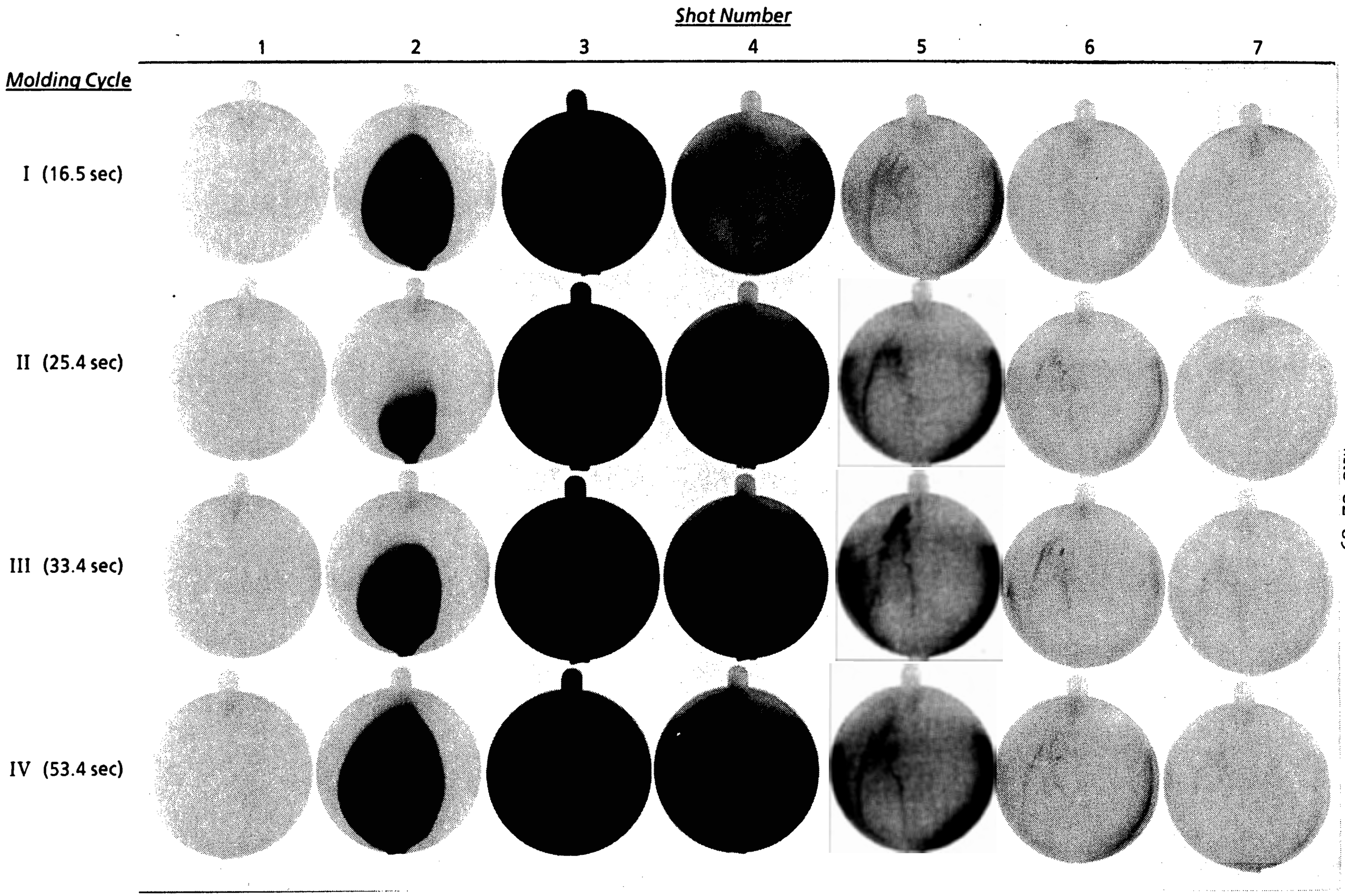

Figure A2. Photograph of Successive Shots Following the Introduction of a Color Concentrate Pellet Into the Barrel Maximum pigmentation is observed in the third shot. The residence time distribution is independent of cycle time.

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