Polypropylene/ABS Terpolymer Blends. Mixing and Mechanical Properties

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Synopsis

A typical commerical polypropylene and acrylonitrile–butadiene–styrene terpolymer were coextruded and injection molded in various ratios and as the pure components. The rheological properties of the pure components in a single screw extruder were analyzed. Tensile and impact properties were compared with those of the pure polymers. Stress relaxation was analyzed by a simple three-element model. The data were related to the processing conditions. The morphology of the blends was inferred from extractive and staining tests on the blends.

INTRODUCTION

A polyblend,[1–3] sometimes called a polymer alloy, is composed of two or more polymers blended but not otherwise treated initially. Compatibility of the polymers is a question of subdivision. If the polymers retain their identities in individual domains, the polymers are clearly incompatible.[4,5] There are relatively few examples of polymeric mixtures for which the state of subdivision is sufficiently fine, even molecular, that a single phase of new properties appears to exist comparable to a solid solution. The compatibility of the components may be increased by including a block or graft copolymer of the two components as a bridging material between the phases.[6] Also, incompatible pairs may be joined to give cured adhesion by cross linking to improve the strength properties, an approach used with elastomers in particular.[7] A recent review,[1] a published symposium,[2] and a monograph[3] list many references to the very considerable literature on this subject.

Many polyblends contain relatively small amounts of one of the polymers to improve the toughness or strength, processing characteristics, wear properties, surface appearance, stiffness or flexibility, tack or adhesiveness. This study is of an incompatible pair, semicrystalline polypropylene (PP) and a two-phase graft copolymer of styrene and acrylonitrile onto polybutadiene (ABS), in all proportions without the use of compatibilizing agents. Although blends may be made by mixing dispersions or lattices, or by evaporation of mixtures of solutions, this study is confined to the more direct industrial technique of melt extrusion blending of mixtures of pellets of the two polymers followed by appropriate grinding and extrusion molding steps. Both polymers find widespread use in the automotive industry particularly, where a blend of recycled or recovered material of variable composition might be used conveniently if the properties were adequate. Scott's program[8] would illustrate the growing interest in the subject.

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It was not expected that mutual solubility would be appreciable since the two polymers differ considerably in cohesive energy density and polarity. However, given adequate mixing and contact, adhesion between the phases would be expected,[9,10] but the strength of the bond would not be predictable since the amount of the nonwetted surface would not be known, nor would the depth and properties of the interfacial layer be controlled.[10-13]

The processing of the blends involved to varying degrees the steps of coextrusion in a screw extruder, grinding the extrudate, and molding specimens in a ram- or plunger-type extruder. The flow in the barrel of the extruder and through the die can roughly be equated to flow through capillaries and was analyzed by the technique of Rogers.[14-16] This subject has been reviewed in several monographs.[17-19]

The tensile and impact properties of polyblends may sometimes be better than those of the pure components but more often are poorer, hence the traditional assumption that blending is disadvantageous. Polystyrene mixed with either polypropylene or high-density polyethylene yielded uniform tensile properties when the mixing was good, regardless of the technique of mixing.[20] The less viscous component tended to form the continuous phase, but the exact morphology was influenced by the blend ratio,[21] particularly toward the extremes of composition. Superior properties may be obtained by suitably controlling the morphology. For example, the tensile strength of a polystyrene–polyethylene blend in tape form may be improved by hot stretching and quenching.[22] The dispersed phase is in the form of fibrils lying in the direction of draw. This improves the tensile strength in that direction.

In addition to the usual tensile tests, stress relaxation was measured on samples not strained to failure. The technique has been applied to ABS by Bergen and Wolstenholme[23] and to polypropylene by Faucher[24] and is similar to that used for crosslinkable polymers.[25,26] Likewise, the conventional Izod impact test was used with both notched and unnotched samples. Notched specimens yield more reproducible results.[27] Also energy dissipation can be visualized much better using the autographic technique.[28,29]

EXPERIMENTAL

Polypropylene (PP) Enjay E-115 Lot 9342, dried 3 hr at 80°C. $\overline{M}_n = 4.08 \times 10^4$ and $\overline{M}_w = 4.44 \times 10^5$ according to Han et al.[20]

Acrylonitrile–butadiene–styrene terpolymer (ABS) used was from Borg-Warner Chemicals, Marbon Division, Cycolac TH Natural NE-05033, dried 3 hr at 95°C, 20% PBd, 80% SAN of which 64% is styrene; $\overline{M}_n$ SAN = 35,000 to 40,000.

The blends were coded with a number indicating the percentage of the polymer identified immediately after the number, followed by one or more letters indicating extrusion (E), grinding (G) and injection molding (I). Thus 70% PP–EGI means a blend composed of PP 70% by volume, ABS 30% by volume, extruded; the extrudate is ground and the pellets are injection molded. Blends were made by calculating the weights of dried pellets required to yield 10, 30, 50, 70 and 90% by volume of polypropylene and mixing these quantities by dry blending before extrusion or molding.

Equipment and Procedures

The extruder (model 252, 0.75 in.) was fitted to a C.W. Brabender Instruments Plasticorder model PLV 300. The L/D ratio was 25/1. The capillary die was 3.05 mm in diameter and 20.6 mm long. Koch static mixing elements, about 2.5 in. long, were included. The screw speed was 2.09 rad sec^{-1} for comparison of samples and ranged from 1.05 to 5.24 rad sec^{-1} in the shear rate studies. Torque and pressures were recorded. The temperature was 200°C.

The grinder was a C.W. Brabender Instruments model S-20-9 using a 5-mm screen.

The injection molding was done with a Hillard Industries 1-oz laboratory model PM-225. The double-cavity mold conformed to ASTM specifications D638 type 1.[30]

Tensile strength and stress relaxation measurements were made using an Instron Universal Testing Instrument model TT-CM. An Instron Strain Gauge Extensometer model G-51-11 MA was used. Grip separation rates were 83 and 830 μm sec^{-1}. The sample length with parallel edges was 50 mm and it was assumed that the strain took place over this region. The sample preparation and test procedures followed ASTM D638.[30]

The impact strength was measured with a Tinius Olsen Impact Tester and an Autographic Impact Tester model 43-13 from Testing Machines Inc. The notcher was a Testing Machines Inc. Impact Notcher model 43-15-1. The sample preparation and testing procedures followed ASTM D256.[27] Usually ten but sometimes only five samples were tested.

For later calculations, the densities of the polymers at the extrusion temperature of 200°C were determined using a Custom Scientific Instruments Extrusion Plastometer model CS-217-804, by measuring the weight of extrudate of known volume at 200°C. The values were 750 and and 940 kg m^{-3} for PP and ABS, respectively. A value of 758 kg m^{-3} had been measured by Frank[31] for PP.

RESULTS AND DISCUSSION

Since the recommended extrusion temperature for ABS is 250°C and for polypropylene is 200°C some problems might be expected with blends. In practice the lower temperature was necessary with a longer dwell time. It was noted that jetting, which occurred with pure ABS, was not evident with PP or the blends presumably because of greater die swell.[32]

The flow from the extruder was the same whether or not the Koch mixers and breaker plates were present within the precision of measurements. Thus the shear rate in the die was unaffected by the presence of the mixers. Measurement of the average extrudate weight in 120 sec at screw speeds of 1.05, 2.09, 3.14, 4.19, and 5.24 rad sec^{-1} gave the volumetric flow rate (Q) whereby the shear rate (G_w) in the die could be calculated.

Analysis of Die Section

Determining the pressure drop through the die with the Koch mixers and breaker plate absent enabled the shear stress (τ_w) in the die, as well as the apparent viscosity η, to be calculated. The shear stress versus log shear rate data are plotted in Figure 1 and yielded straight lines and flow behavior indices of 0.48
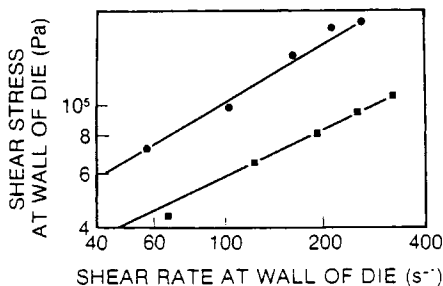
Fig. 1. Shear stress vs. shear rate in the die at 200°C. Upper ABS; lower PP.

and 0.60, respectively, for PP and ABS. The apparent viscosities at the five shear rates were 674, 543, 423, 375, and 325 Pa sec for PP, and 1283, 970, 872, 838, and 700 Pa sec for ABS. While, ideally, blending should be done under conditions represented by the intersection of the lines of Figure 1, it is obvious that no such condition exists in practice. However, since the apparent viscosities differ only by a factor of 2, good mixing should be obtained. Noel and Carley[33] obtained good mixing of PE and PP whose apparent viscosities were within a factor of five, and poor mixing is more likely to be experienced with the apparent viscosities differing 50- to 100-fold.

Densities of the extrudates were measured[34] and compared with the expected values and the values obtained from tensile and impact samples. Whereas the latter three agreed very well, the densities of the extrudates were low by small amounts [0.2–2%] for the pure polymers and blends. The lower values for the extrudate could be due to voids following die swell, and the largest decrease for PP might be attributable to a decrease in crystallinity. A value of 900 kg m^{-3} was expected for the semicrystalline polymer, but 880 kg m^{-3} was found as compared with 850 kg m^{-3} for amorphous PP.[35] A higher than expected density when mechanical blends of poly(vinyl chloride) and poly(ethylene-co-vinyl acetate) (35/65) were made was interpreted by Shur and Ranby[36] as evidence of compatability.

According to Rubin,[37] the apparent viscosities of plastics during injection molding are in the range of 70–700 Pa sec. The data agree very well for those of Han[38] for PP at comparable shear rates, 671 Pa sec for a shear rate of 65 sec^{-1}. It is probable that the higher apparent viscosities calculated for ABS reflect the use of a lower extrusion temperature than the recommended 250 °C.

It was mentioned above that the flow rate through the die was the same whether the Koch mixers and breaker plate were in or not. The overall pressure decrease, however, was greater. As an indication of magnitudes, the ratio of the pressure decrease through the die to the total decrease was 0.41 ± 0.014 for PP and 0.47 ± 0.032 for ABS, i.e., significantly less than half the pressure decrease that occurred in the die. The total pressure decrease increased with shear rate and with the presence of the Koch mixers and breaker plate, of course. The effective die lengths were 5.04 mm for PP and 4.43 mm for ABS.

Analysis of Screw Section

Torque was measured for the various screw speeds used and varied linearly on log–log plots. From the characteristics of the extruder screw and using the Krieger and Elrod equation,[15] the relationships between shear rate (G) and screw

speed were found to be $G_1 = 4.31\Lambda$ for PP and $G_1 = 3.97\Lambda$ for ABS, where Λ is the angular velocity in rad $\sec^{-1}$ and G_1 is $\sec^{-1}$. Values for β of 1.6 and for m of 1.73 and 1.50 were were used in the calculations.

The drag flow constant was calculated[16,17] as 1.43 cm^3. The volumetric flow rate varied linearly with screw speed so that drag flow shape factors for PP and ABS could be calculated and were 0.68 and 0.55, respectively. Further calculations indicated that the screw was only 76% full of PP and 62% full of ABS, giving effective helical lengths of 118 and 96 cm, respectively, for PP and ABS. The next step was to calculate the shear stress. The equations for PP and ABS were, respectively, $\tau_1 = 3.75 \times 10^3 T_d$ and $\tau_1 = 4.61 \times 10^3 T_d$, where T_d is the torque in Nm and τ_1 is the shear stress in Pa.

The shear stress–shear rate data for the screw section are in Figure 2. The slopes are 0.55 and 0.66, respectively, for PP and ABS, slightly greater than the corresponding values for the die section. Ideally, the two sets of data should be collinear, but agreement within a factor of three for PP and two for ABS is considered good. It is likely that the approximations required in the analysis of the screw extruder account for the discrepancy.

A similar analysis was not undertaken on the blends. The two polymers, however, were so similar that the data would be expected to approximate that shown.[39]

Stress–Strain Data

The stress–strain data for the polymers and blends at a strain rate of 1.7×10^{-3} $\sec^{-1}$ are in Figure 3. The curves change regularly with increasing PP content with failure occurring at low strains for the blends with 10–50 vol % PP. Increasing the strain rate to 1.7×10^{-2} $\sec^{-1}$ yielded a similar series (Fig. 4) with higher stresses and lower strains at break, except that the ABS samples broke at strains of about 0.02 without yielding. In both cases the sample containing 90 vol % PP or pure PP yielded above a strain of 0.08 (Fig. 5), the stress decreased to 20 MPa at strains of 0.10 to 0.15, and thereafter the strain increased with necking at constant stress to a strain of about 0.90, without failure at the lower rate of strain. The stress decreased to about 10 MPa between a strain of 0.8 and 1.0 with failure at the higher strain rate. It should be noted that whereas the ABS was not sensitive to the method of processing, there was about a 10% decrease in the tensile strength of PP when it was extruded, ground, and injection
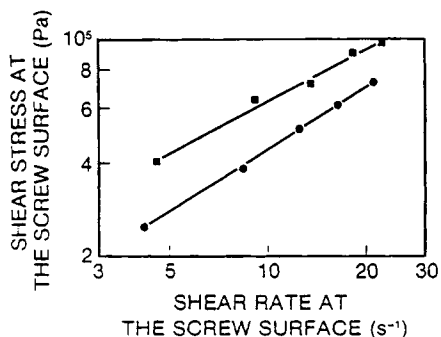

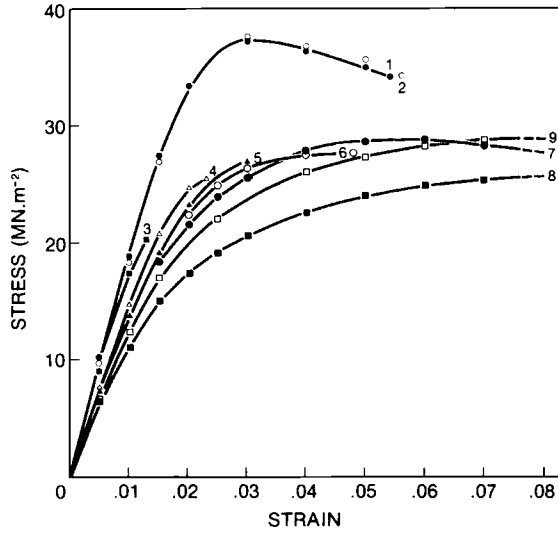Fig. 2. Shear stress vs. shear rate in the screw at 200°C. Upper PP; lower ABS.

Fig. 3. Stress vs. strain. Curve 1, 100% ABS-I; curve 2, 100% ABS-EGI; curve 3, 10% PP-EGI; curve 4, 30% PP-EGI; curve 5, 50% PP-EGI; curve 6, 70% PP-EGI; curve 7, 90% PP-EGI, curve 8, 100% PP-EGI; curve 9, 100% PP-I. Strain rate 1.7×10^{-3} sec^{-1}.

molded instead of just injection molded. This can be due to degradation or to reduced crystallinity. On the other hand, when blends containing 70 or 50 vol % PP were tested, the tensile was higher for the extruded, ground, injection-molded samples than for those injection molded only, indicating that a good dispersion was effective in counteracting any reduction in properties that the processing might have caused. The effect was negligible for the 30 vol % PP
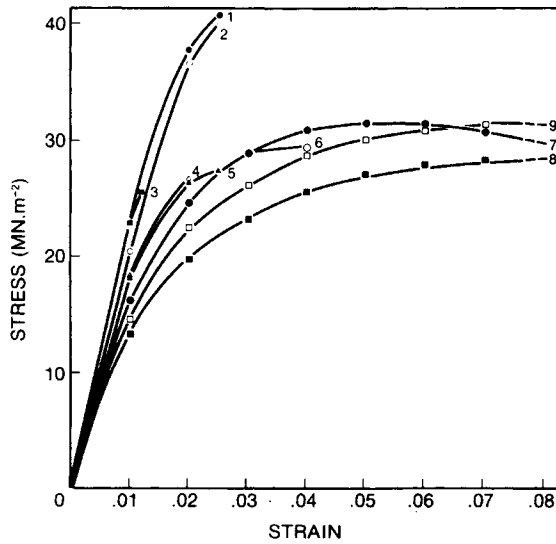

Fig. 4. Stress vs. strain. Curve 1, 100% ABS-I; curve 2, 100% ABS-EGI; curve 3, 10% PP-EGI; curve 4, 30% PP-EGI; curve 5, 50% PP-EGI; curve 6, 70% PP-EGI; curve 4, 30% PP-EGI; curve 5, 50% PP-EGI; curve 6, 70% PP-EGI; curve 7, 90% PP-EGI; curve 8, 100% PP-EGI; curve 9, 100% PP-I. Strain rate 1.7×10^{-2} sec^{-1}.
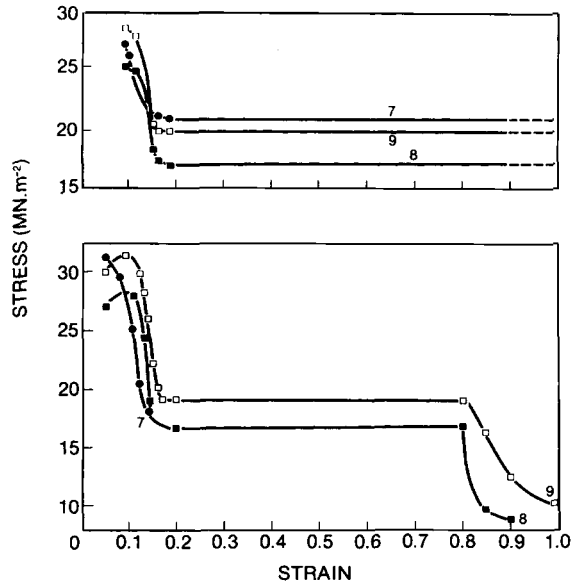
Fig. 5. Stress vs. strain at high strains. Curve 7, 90% PP-EGI; curve 8, 100% PP-EGI; curve 9, 100% PP-I. Strain rate upper set $1.7 \times 10^{-3} \text{sec}^{-1}$. Strain rate lower set $1.7 \times 10^{-2} \text{sec}^{-1}$.

blend. Han[20] noted less effect on tensile properties for well-mixed blends of polystyrene with polypropylene or high-density polyethylene.

The failure of PP was ductile with extensive necking (Fig. 6). At the other end of the scale, the failure of ABS was ductile with yielding and extensive crazing (whitening) at the lower strain rate and brittle at the higher strain rate. With
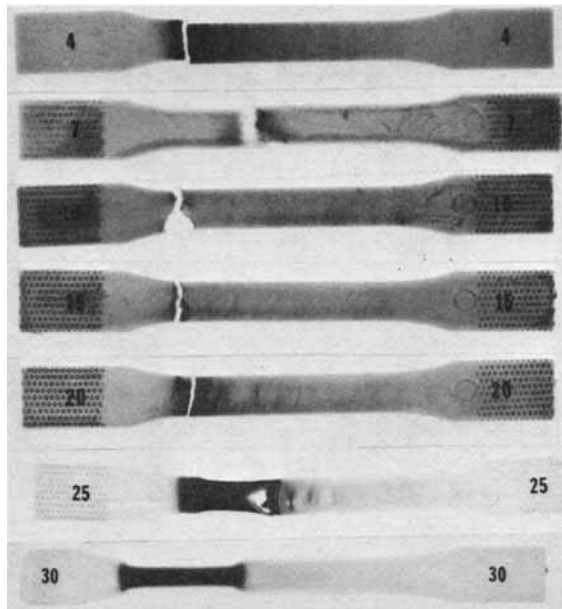

Fig. 6. Appearance of stress-strain samples after break. Photographed on a black background and reversed; stress whitening shows black. (4) 100% ABS-EGI; (7) 10% PP-EGI; (10) 30% PP-EGI; (15) 50% PP-EGI; (20) 70% PP-EGI; (25) 90% PP-EGI; and (30) 100% PP-EGI.

but 10 vol % PP present, the failure occurred at low strains with absence of crazes perpendicular to the direction of the strain. With 30 vol % PP there was irregular brittle fracture with no crazing, at 50 and 70 vol % PP there was crazing and brittle failure, and with higher PP contents the failure was ductile with crazing. At the lower rate of strain, stress whitening was more general, whereas at the higher rate of strain, it was concentrated near the break. The stress whitening of samples prepared by injection molding only was quite irregular.

The tensile yield strengths at both rates of strain decreased with increasing PP from that of ABS to a minimum with 10 vol % PP, then increased linearly to 90 vol % PP before decreasing slightly to that of pure PP. Samples just injection molded from pellets using the ram injection equipment gave lower results. The elongations at yield or break followed a similarly shaped curve with no final decrease for PP. As would be inferred from Figure 3, the change in strain after the yield point was very great for PP. It should be noted (see Morphology section) that the PP phase tended to be at the exterior of the tensile specimens and when present in only 10 vol %, the separation was particularly noticeable.

The plot of the moduli versus composition is seen in Figure 7, along with the upper and lower bounds calculated. The moduli of the blends lie between the values for the pure components. However, applying the semiempirical calculations used for composites,[40] in which the moduli usually differ by a factor of at least 10^3, obviously does not describe realistically this system for which the moduli differ by a factor of less than 2, and agree only at intermediate compositions by chance. Curves of similar shape have been reported for SBS block copolymer,[41] PS in SBR,[42] and PBd in SBR.[43]

Stress relaxation was measured by elongating the samples at a rate of 33 μm sec^{-1} to an elongation of 1 mm and following the stress with time up to 110 min. The decrease was very slow thereafter. The data are illustrated in Figure 8. It is obvious that as the amount of PP increases, the decrease in stress initially is more rapid, i.e., the relaxation of the PP phase becomes more important.

As in an earlier report,[44] the system was analyzed by a three-Maxwell-element equation yielding a total relaxation modulus curve very similar to the Young's modulus curve (Fig. 7) but displaced to lower values. The calculations of the parameters for the three Maxwell units in Table I indicated, as would be expected, an increasing prominence of the shorter relaxation times with increasing PP and an increasing effect owing to an intermediate relaxation time perhaps
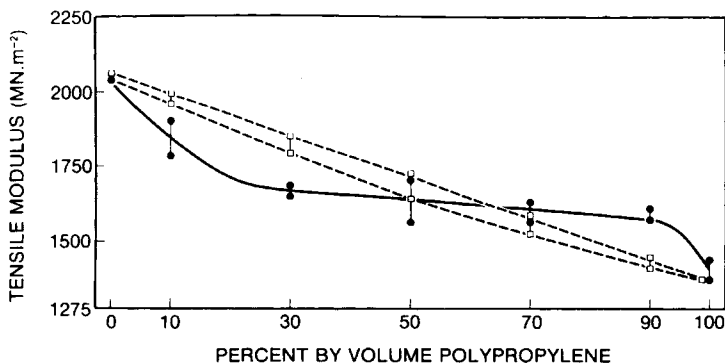

Fig. 7. Modulus vs. composition, solid line. Dashed lines calculated upper and lower bounds.
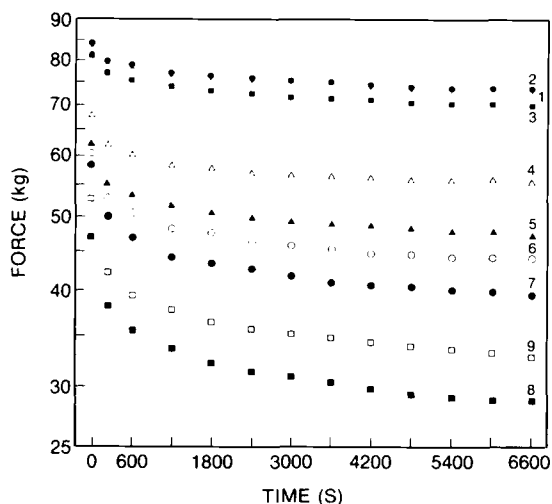
Fig. 8. Force time curves. Curve 1, 100% ABS-I; curve 2, 100% ABS-EGI; curve 3, 10% PP-EGI; curve 4, 30% PP-EGI; curve 5, 50% PP-EGI; curve 6, 70% PP-EGI; curve 7, 90% PP-EGI; curve 8, 100% PP-EGI; curve 9, 100% PP-I.

indicative of an interphase composed of the two polymers. The major contributor was the long relaxation time element.

The data in Table I were calculated using a time range between 3000 and 6600 sec for the first element, between 300 and 390 sec for the second, and between 0 and 360 sec for the third. Table I shows the values calculated for F, θ, and E. The force F decreases for element one and increases for element three as the PP content increases. There is little change for element three as the PP content increases. There is little change for element two, a slight trend upward with PP content. The corresponding relaxation times in sec (θ) and relaxation moduli E follow the same trends.

Figure 9 shows the percentage contribution to the total of each of these three elements as chosen above. Some irregularities in the modulus values may be related to residual stresses,[45] the removal of which may not have been accomplished uniformly in the samples.

Impact Data

The impact data using the Izod technique with notched and unnotched specimens yielded the data in Table II. The values for the notched specimens agree well with those in the literature for PP and, if assumptions are made as to the effect of sample thickness,[46] with those published for thinner samples of ABS (see *Modern Plastics Encyclopedia*).[60] The effect of processing technique is small or negligible for ABS, but the triple process of extrusion, grinding, and extrusion molding drastically reduced the unnotched impact strength of PP. As in the case of reduced tensile properties, this reduction could be attributed to degradation or to reduced crystallinity.

Blends containing 30–90 vol % polypropylene have notched impact strengths the same as PP, and electron scanning micrographs of the fracture surface show that it is PP. When the specimen is 90 vol % ABS a higher impact strength re-

TABLE I
Stress Relaxation Constants F and θ and Relaxation Moduli E at Initial Time

| Sample	Force (kg)			Relaxation time (sec)			Relaxation modulus (MPa)		
	F_1	F_2	F_3	θ_1	θ_2	θ_3	E_1	E_2	E_3
100% ABS-1	75.04	5.66	2.50	1.45×10^5	670	29	1710	130	60
100% ABS-EGI	77.07	4.13	2.60	1.16×10^5	613	66	1760	90	60
10% PP-EGI	72.28	5.07	3.65	1.62×10^5	1130	161	1650	120	80
30% PP-EGI	57.41	4.95	4.74	1.54×10^5	1060	105	1310	110	110
50% PP-EGI	50.82	4.61	6.57	8.22×10^4	1080	116	1160	110	150
70% PP-EGI	45.66	7.21	7.23	1.78×10^5	1400	120	1040	160	170
90% PP-EGI	42.60	6.43	9.17	8.73×10^4	1370	179	970	150	210
100% PP-EGI	30.87	7.28	8.85	8.65×10^4	1330	133	700	170	200
100% PP-I	36.23	6.35	10.22	6.64×10^4	1060	97	830	150	230
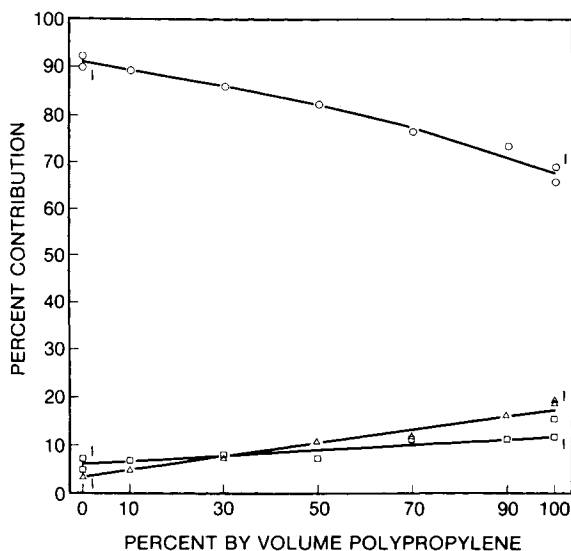
Fig. 9. Contribution to total modulus in percent vs. composition (O) first Maxwell element, (□) second Maxwell element, (△) third Maxwell element. (I) Samples injection molded only.

sults. It was shown (see Morphology section) that such a sample tended to be richer in PP on the surface and richer in ABS in the interior. Upon notching, the surface PP layer was removed and the crack propagated through the ABS-rich section. The electron scanning micrograph showed the presence of ABS in the fracture surface.

Stress whitening of the fracture surface increases with ABS content, unnotched specimens showed a larger and rougher surface, and partial breaks were fairly common for notched ABS samples. Samples prepared by injection molding only yielded higher impact strengths, some partial breaks, and rough and large fracture surfaces.

A similar set of samples was tested on an autographic impact tester. The data are in Table III and include the impact strength and breaking energy calculated in the usual way from the areas under the curves.[28] The data agree reasonably well with those in Table II. Oscillations in the trace due to sliding of the hammer and yielding of the polymer samples before fracture[29] resulted in curves, the area under which was hard to measure. Well-mixed blends deformed elastically

TABLE II
Notched and Unnotched Izod Impact Strengths

Sample	Notched Izod $(J m^{-1})$	Unnotched Izod $(J m^{-1})$
100% ABS-I	210	670
100% ABS-EGI	190	670
10% PP-EGI	60	120
30% PP-EGI	30	100
50% PP-EGI	30	120
70% PP-EGI	35	210
90% PP-EGI	40	580
100% PP-EGI	30	510
100% PP-I	37	850

TABLE III
Autographic Impact Testing Results and Characteristics of the Force–Time Curves

Sample	Izod Impact (J m^{-1})	E_b (N m)	Area under the curve (ref. 28)
Notched			
100% ABS-I	182	1.18	0.38
10% PP-EGI	42	0.27	0.08
30% PP-EGI	23	0.15	0.05
50% PP-EGI	25	0.16	0.05
70% PP-EGI	28	0.18	0.05
90% PP-EGI	39	0.26	0.08
100% PP-I	37	0.24	0.07
30% PP-I	99	0.64	0.20
50% PP-I	137	0.88	0.28
70% PP-I	46	0.30	0.09
Unnotched			
100% ABS-EGI	593	3.82	1.19
10% PP-EGI	82	0.53	0.10
30% PP-EGI	127	0.81	0.26
50% PP-EGI	137	0.88	0.27
70% PP-EGI	178	1.15	0.37
90% PP-EGI	487	3.14	0.90
100% PP-EGI	475	3.04	0.93

before fracture and brittle failure resulted.   Poorly mixed sample, i.e., injection molded only, showed larger fracture surface areas, rough and jagged.   The fracture time appeared to be about 2 msec in contrast with the time of 0.5 msec for the extruded, ground, injection-molded samples.   Also, the autographic traces indicated energy absorption during fracture[47] only for ABS samples and probably when samples contained an ABS-rich core.   When the polymers were well mixed, energy absorption during propagation was not detectable.   These would correspond to types III and I of the classification of Bucknall.[48]

These observations presented here are similar to those observed for graft polymers[49] and high impact polystyrene,[50] namely, that there is an optimal particle size for the disperse phase, and impact strength increases with particle size, while tensile strength decreases.   There seems to be no reason why mixed PP and ABS could not be used for applications requiring properties not far below those of the virgin material.   The state of subdivision might need to be controlled. A recent patent[51] compared a solution-cast blend of PP/ABS with a melt mixed blend.   It was found that the tensile strength was increased and that the average domain size was 200 μm^2 for the former versus 800 μm^2 for the melt processes. Another patent[52] reported improved flexural stiffness modulus when PP/ABS 70/30 was compared with PP.   As one would expect, the use of a graft copolymer[53] as compatibilizer[54] also improved the tensile strength of an ABS/PP blend 30/308.   The graft copolymer was 45/75 PP/poly(methyl methacrylate).

Morphology

ABS is extracted by methyl ethyl ketone, leaving the PP behind.   Likewise, ABS may be colored by reaction with perchloric acid, whereas PP is not.[55]   These two approaches were used to deduce something of the morphology by microscopic examination of the stained and extracted surfaces.

The morphology of the blends was examined using the fracture surfaces, the surfaces of the tensile and impact test pieces (Fig. 10), and the surfaces of additional tensile test samples broken at a strain rate of $6.6 \times 10^{-4} \sec^{-1}$. Samples prepared by extrusion, grinding, and injection molding containing 10 vol % of PP swelled in methyl ethyl ketone and the surface was darkened by perchloric acid treatment, indicating ABS on the surface. When 30 vol % of PP was present, the samples did not swell and the surface was not discolored, indicating virtually a complete layer of PP on the surface. This condition persisted, of course, with higher PP vol %. If the samples were just injection molded, all ratios of PP/ABS underwent swelling and indicated, by roughening on extraction, some ABS on the surface layer. A similar examination of the cross sections of the samples (Fig. 11) showed that the samples that had been extruded, ground, and injection
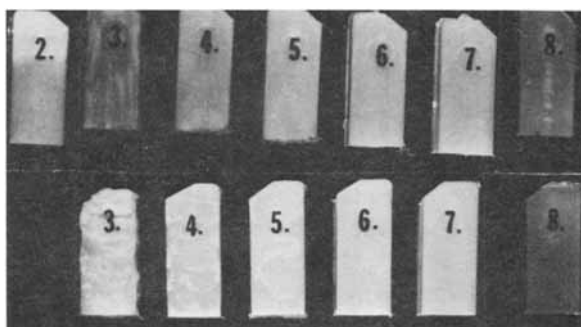

Fig. 10. Appearance of impact test pieces. Upper stained with perchloric acid, lower extracted with methyl ethyl ketone. (2) 100% ABS-EGI (partly immersed to show the darkening); (3) 10% PP-EGI; (4) 30% PP-EGI; (5) 50% PP-EGI; (6) 70% PP-EGI; (6) 70% PP-EGI; (7) 90% PP-EGI; and (8) 100% PP-EGI (appears black because of transluscence over black background).
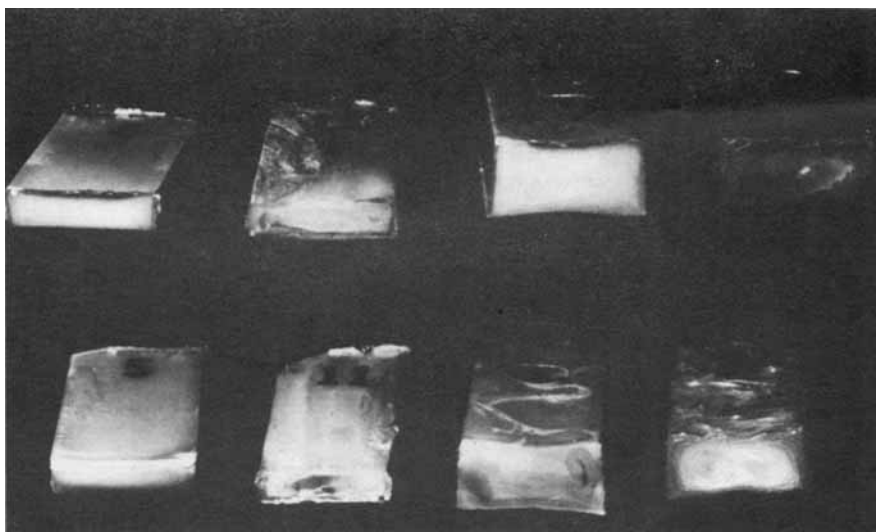

Fig. 11. Appearance of fracture surfaces. Upper stained with perchloric acid, lower extracted with methyl ethyl ketone; reversed so that stained ABS shows white. Left, tensile sample 50% PP-EGI; second left, tensile sample 50% PP-I; second right, impact sample 50% PP-EGI- right, impact sample 50% PP-I. Segregation in I samples evident, greater uniformity of EGI samples.

molded were more uniform in cross section, whereas those that had been injection molded only showed an ABS-rich interior.

Films compression molded from the runners produced in the molding step were examined by electron microscopy after exposure to methyl ethyl ketone. Films of PP and ABS were smooth by electron scanning microscopy. The appearance of the blends was characterized by cracks, presumably between the phases, short discontinuous cracks for well-mixed blends, and longer branched cracks for poorly mixed blends. Extraction of ABS by methyl ethyl ketone revealed that the component in the smaller volume percent consisted of discrete and narrow domains distributed evenly throughout well-mixed samples, and large distinct domains in poorly mixed samples (Fig. 12). Also, the appearance of extrudates with higher loadings of PP showed the typical smooth surface of one component which, being insoluble in methyl ethyl ketone, was polypropylene.

A strictly empirical test for extracted ABS was found to be at the absorbance of 360 nm, the calibration curve for which was remarkably linear. When extruded samples were extracted for 4 hr, those with 50 or more vol % PP yielded virtually no ABS, indicating that the surface was nearly pure PP. As the PP content is decreased, the tensile test pieces still exhibit a major coverage with PP; the samples that were extruded, ground, and injection molded, and test pieces for impact testing showed a greater amount of ABS on the surface, although still well below expected. On the other hand, samples injection molded only all showed a great deal more extractable ABS even with 70 vol % PP present.

Thus, the general observation is that with extrusion, grinding, and injection molding, more uniform dispersions are achieved than with just injection molding or extrusion alone. When the two polymers are coextruded, there is a tendency for polypropylene to be on the exterior surface, to the exclusion of ABS if the PP concentration is high and the dispersion good. Phase segregation has been discussed in detail.[56]

The tendency for segregation may be useful for those ultimate uses for which a PP layer or PP-rich layer may be advantageous, such as when the aging properties of PP would be an advantage. A number of recent patents and articles, however, suggest that in practice a minor proportion of ABS in PP may improve adhesion[57] and platability[58] when the viscosity of the PP phase is increased by
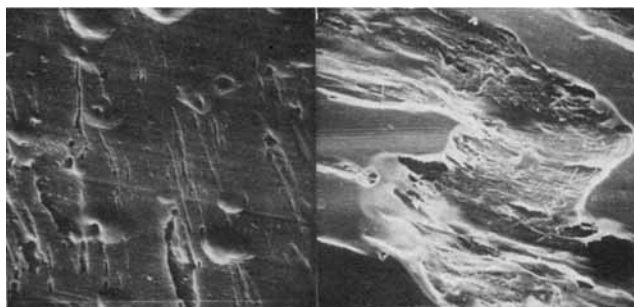

Fig. 12. Electron micrographs of compression molded samples prepared from the runners of injected molded samples, extracted with methyl ethyl ketone. Left, 70% PP-EGI, magnification 950×; right, 30% PP-I, magnification 200×.

a filler such as talc.[59] Presumably the ABS in both cases tends to be in the surface layers and to contribute the desired properties. It should be noted that all test pieces were made in single end-gated molds, hence no comments can be made as to problems arising from weld lines in more complex objects.

SUMMARY

Polypropylene and acrylonitrile–butadiene–styrene terpolymer were extruded using a single screw extruder on a Brabender Plasticorder. There was no intersection of the shear stress versus log shear rate lines. The densities of the extrudate were lower than expected but in keeping with the known incompatibility of the polymers. The shear rate data permitted the calculation of drag flow shape factors of 0.68 and 0.55 for PP and ABS, respectively, and indicated that the screw effectively operated 76 and 62% full, respectively. Shear stress–shear rate data for the screw and the die sections were plotted, and although the lines for the two sections were not collinear, the differences were only a factor of 3 for PP and 2 for ABS. The coextruded materials were examined by solvent extraction and staining. Polypropylene tended to be at the surface of an extrudate in proportions greater than in the blends, whereas the discrepancy was much less in molding. The properties of the blends are surprisingly good in all ratios. There is an indication that the better the dispersion the better the tensile strength, and the poorer the dispersion the better the impact strength, but a numerical value associated with these effects was not determined. The stress relaxation rate increased with polypropylene content. The mode of failure changed from that associated with ABS to that associated with polypropylene as the content of the latter is increased.

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