

Ethylene–Methacrylic Acid Copolymers as Stress Whitening Suppressants in Polypropylenes

R. RENGARAJAN,* S. K. KESAVAN,† K. L. FULLERTON, and S. LEE‡

Department of Chemical Engineering, The University of Akron, Akron, Ohio 44325-3906

SYNOPSIS

Impact-modified polypropylenes were prepared by incorporating copolymers of ethylene–methacrylic acid (E-MAA) with different cations (zinc or sodium) and varying degrees of neutralization. These blends gave low stress whitening on impact. This phenomenon was due to the unique morphology of the blend. It was found that unneutralized acid copolymer and the zinc ionomer formed chainlike structures in the polypropylene matrix. These uniform chains crisscrossed the polypropylene matrix providing impact strength to the matrix. The matrix deformed on impact by the shear yielding mechanism, thus suppressing stress whitening. The impact modifier in the matrix did not form micro crazes in the matrix but formed several layers of crisscrossing chains. On the other hand, the sodium ionomer did not form chainlike structures. The impact modifier was dispersed evenly in the matrix. This type of morphology resulted in a higher degree of stress whitening. The failure on impact was due to crazing and not by shear yielding. This size of the impact modifier in the polypropylene matrix varied significantly depending on the melt processing equipment used. The dependence of polymer alloy mechanical properties on the composition has been studied to help in ionomer comparison.

INTRODUCTION

During the past decade, impact-modified polypropylenes have gained great importance both technologically and commercially. The impact-modified polymers are commonly used in the manufacture of injection-molded parts, such as battery cases, automotive instrument panels and other large articles. It is important that these articles be free of manufacturing blemishes and be resistant to stress-induced optical defects, commonly known as stress whitening or blushing.

During injection molding of large parts, the melt is allowed to solidify in the mold and the molded part is ejected out of the mold. During ejection, the knock-out pins force the parts out of the cavity. The locations of impact of knock-out pins on the part are subjected to high stress, and they undergo stress

whitening. This results in distinct white marks on the molded parts thus spoiling the aesthetics of the molded part. This phenomenon is more predominant in certain dark colors. In most cases, such blushing shows up over and above the hiding power of the pigment.

Impact modification of a thermoplastic is provided by impact modifiers whose primary role is to create multiple failure sites instead of a single fracture site. These fracture sites are formed by the deforming polymer. Voids created by the deforming polymer scatter light that manifests itself as a white mark on the plastic. The white mark on the impacted thermoplastic reveals the first stage of failure in that plastic. This white mark is well known as stress whitening, as crease whitening, or as blushing.

Several studies have been undertaken^{1,2} to suppress or eliminate stress whitening. Impact strength of crystalline polypropylene can be improved by blending with rubbery impact modifiers such as ethylene propylene copolymers (EPR), ethylene propylene diene monomers (EPDM), styrene butadiene styrene (SBS), styrene ethylene butadiene styrene (SEBS), polyethylenes (LDPE, LLDPE, MDPE,

* Currently with A. Schulman Inc., Akron, Ohio.

† Currently with Allied-Signal Inc., Troy, Michigan.

‡ To whom correspondence should be addressed.

and HDPE), and polybutylene copolymers.³⁻¹⁰ Although the impact strength of the modified systems may be favorably influenced by the type of the modifier and its compatibility with the polypropylene component, the desired physical properties cannot be obtained by blending alone. However, excellent properties have been obtained by using block copolymerization of propylene with ethylene. Stress whitening that arises in these products is commercially detrimental and is difficult to control. The tendency of stress whitening increases as the impact strength of the copolymers increases.

Studies performed by researchers to reduce stress whitening by blending with polyethylene, ethylene-propylene copolymers, and other thermoplastic elastomers have resulted in several morphological studies of the blends that give a quantitative assessment of the stress whitening.

Commercially available low-blush systems contain blends of HDPE and a small amount of propylene-ethylene copolymer that compatibilizes this system. These blends result in low-blush levels but can suppress blush only to a certain level of copolymer. Beyond this level, crazing mechanism takes over resulting in excessive stress whitening. Similar blends are reported in the literature,¹¹ but the dominant mechanism of failure is by crazing.

Crazing was the primary mechanism of impact modification in rubber-modified thermoplastics¹² and shear yielding a secondary mechanism operating in the polymer system. It was decided to investigate the possibility of using impact modifiers that would improve the impact strength of the polymer and cause deformation primarily by the shear yielding mechanism. It is well known that the phenomenon of stress whitening is not associated with deformation occurring by shear yielding.¹³ Polymers that do not exhibit the stress whitening behavior were chosen to be blended with polypropylene to investigate the morphological properties of the blends. The alloy developed in this study is expected to suppress stress whitening in colored high-impact polypropylenes.

EXPERIMENTAL

Materials

Several preliminary screening experiments were performed to study the potential of ionomers as stress whitening suppressants. The content of the impact modifier was fixed at 20% of the total weight. Materials were considered candidates for further study if the difference in the lightness and darkness

values as measured by a spectrophotometer (DL^*) was less than 9.0, while also having a minimum notched izod impact strength of 4.0 ft-lb/in.

It was found from the preliminary experiments that the unneutralized ethylene-methacrylic acid copolymer (E-MAA) and the terpolymer described later seemed to result in good impact and flow properties and also gave low levels of stress whitening. It was decided to investigate the family of ionomers to arrive at a system that would result in the desired properties.

E-MMA copolymers are produced by copolymerizing ethylene with methacrylic acid. By varying the degrees of polymerization, the molecular weight of the acid copolymer can be varied to result in either a hot melt adhesive grade or a high molecular weight thermoplastic grade.

The degree of neutralization, the free acid content of the polymer, and the percentage of sodium or zinc can be varied to result in a whole range of polymers.

It was decided to select a representative sample from each group for our analysis. Therefore, the following four grades, furnished by DuPont, were chosen for the analysis.

1. SURLYN 8528: Ethylene-methacrylic acid copolymer 10% acid 50% neutralized sodium-based ionomer. It will be denoted as sodium ionomer in this work.
2. SURLYN 9020: Ethylene-methacrylic acid copolymer 10% acid 50% neutralized zinc-based ionomer, denoted as zinc ionomer.
3. SURLYN 8020: Ethylene-methacrylic acid isobutyl acrylate terpolymer neutralized with sodium salt, denoted as terpolymer.
4. NUCREL 035: Ethylene-methacrylic acid copolymer (10% acid unneutralized), denoted as acid copolymer.

Specimen Preparation Procedure

Polypropylene was mixed with the stress whitening modifiers described above in a low-intensity Hobart mixer for 15 min. The blend was then injection molded in a Van Dorn molding machine (mold cavity dimensions $6 \times 8 \times 0.125$ in.). The sprue was then cut off the specimen, and the specimen was conditioned at 21°C and 55% relative humidity for 24 h before performing the stress whitening tests. Analysis of blushing was performed by an Applied Color Systems spectrophotometer.

Impact locations were selected on the injection-molded plaque so as to average out the variations in packing. These locations were impacted with a $\frac{3}{8}$

in. diameter cup weight, 8 lb, falling from a height of 5 in. This free-falling impact measured 40 in.-lb. An average of three readings was taken from each plaque. The spectrophotometer reading was recorded at eight impacted locations on each plaque and an average value was recorded as the L of the sample. Three such plaques were tested. In each case the DL^* was computed as the difference in the L of the unimpacted location and L of the tested average impacted points. DL^* was averaged over the three specimens tested. Copolymer was added in the alloys in amounts ranging from 10 to 50 wt % in steps of 10 wt %.

Specimens for optical microscopy were prepared as follows. A small specimen was prepared by microtoming along the thickness of an injection-molded plaque. The sample was mounted in epoxy and photographed at 400X magnification.

Processing of Blends

Based on the preliminary results, the most promising blend/blends were selected based on the following criteria:

1. Uniform dispersion of the impact modifier.
2. Good overall impact strength (notched izod > 4.0 ft-lb/in.).
3. Low stress whitening ($DL^* < 9.0$).
4. Good flow properties (melt flow index > 8.0 g/10 min).

The compound was processed through a high-shear, co-rotating, intermeshing, twin-screw extruder. The objective was to disperse the additives uniformly in the polypropylene matrix to ensure uniform mechanical properties.

Mechanical Property Testing

The mechanical properties of the polypropylene ionomer were obtained according to ASTM Standard Test Methods: tensile strength, ASTM D638; elongation, ASTM D638; notched izod impact, ASTM D256; melt flow index, ASTM D1238; and flexural modulus, ASTM D790.

Stress Whitening or Blushing

Stress whitening tests conducted on the spectrophotometer showed that, as the levels of ionomer or acid copolymer increased, the stress whitening decreased. The stress whitening, denoted by DL^* , is the difference in lightness and darkness between the

standard unimpacted specimen and the impacted specimen.

Stress whitening, as denoted by DL^* , increased initially up to a 20% level of terpolymer and then appeared to decrease gradually, as shown in Figure 1. The initial increase in stress whitening was due to the uneven dispersion and/or insufficient amount of impact modifier in the base polypropylene matrix. In the case of the sodium ionomer, stress whitening seemed to increase steadily until about 30% levels and then decreased, as evidenced by Figure 1.

In the case of the acid copolymer the stress whitening increased slightly as loading was increased from 10 wt % to the 20 wt % level, then decreased as the levels of impact modifier increased. The uneven dispersion or insufficient impact modifier caused the initial increase in stress whitening.

Compounding (melt processing) the terpolymer into polypropylene by means of the twin-screw extruder resulted in lower values of DL^* , which are related to lower stress whitening (Fig. 1). At 10% terpolymer levels, stress whitening remained the same as the results from the physical blend.

Overall, from a comparison between the three impact modifiers used in the study, stress whitening seemed to be the lowest in the acid copolymer, very closely followed by the terpolymer, with the sodium ionomer being the worst. The minimum levels required to suppress stress whitening in the case of the acid copolymer and the terpolymer were 40%, if physically blended pellets were used. If melt processing is done through high-shear processing equipment prior to injection molding, then a lower amount of 20–30% may be sufficient to suppress stress whitening.

Visually, the difference between the acid copolymer and terpolymer on blushing was nonexistent. Only a spectrophotometer could perceive the minute difference.

Effects of the Type of Analysis on the Data

Spectrophotometer analyses were performed under three different conditions: (1) transmitted light, white background; (2) transmitted light, black background; and (3) reflected light.

It was found that the blends made were translucent, and, therefore, transmitted light with a white background. This reflected light gave erroneous results. It was decided to use the transmitted light with a black background to measure stress whitening. While using transmitted light with a black background, the light passing through the sample was absorbed by the black background.

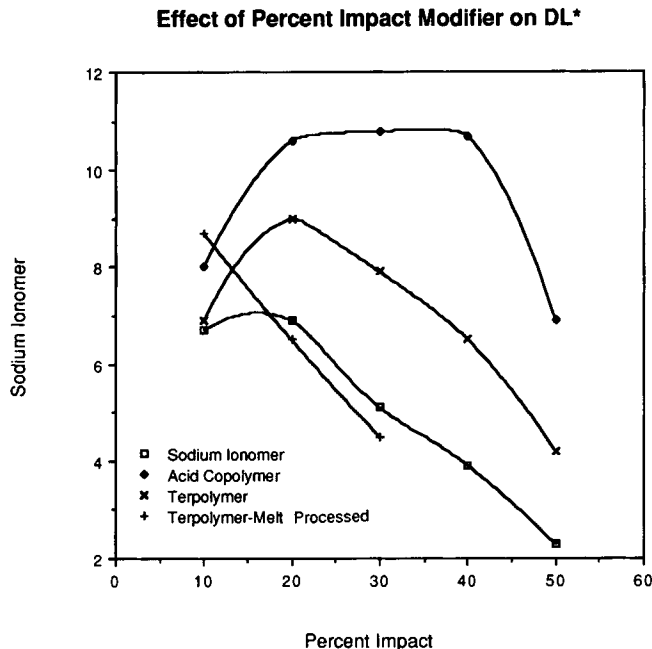


Figure 1 Effect of composition on the lightness–darkness value (DL^*).

In the case of the sodium ionomer, some areas in the specimen withstood the impact and did not break, while in certain other areas the specimen shattered. This was due to the uneven dispersion of the impact modifier in the system. This phenomenon was predominant in lower sodium ionomer levels. This type of behavior was not found in the terpolymer and acid copolymer systems. The specimens that failed on impact were not used to measure stress whitening.

When the terpolymer was melt processed through the twin-screw extruder, the stress whitening slightly decreased. The minimum amount of terpolymer required to suppress the stress whitening was lowered from 40 to 30%.

Although the stress whitening data DL^* showed that the acid copolymer was slightly better than the terpolymer, it was decided to choose the terpolymer for further trials based on the following factors:

1. The ultimate elongation was the same in both the melt flow direction and the transverse direction for an injection-molded specimen. This ensured uniform melt orientation in all directions.
2. The photomicrographs showed that the impact modifier oriented in both directions to ensure uniform impact.
3. Overall mechanical properties were much

better than the blends with the acid copolymer (data presented later).

4. The objective was also to achieve a melt flow index in the range between 9 and 12 g/10 min, but the addition of acid copolymer dramatically raised the melt flow index of the blend (data presented later).

RESULTS AND DISCUSSION

Thermal Analysis

It was found that all of the blends studied gave dual glass transition temperatures, indicating immiscibility and phase separation in the blends.

It was reported by Boyer¹⁴ that atactic, isotactic, and syndiotactic grades of polypropylenes exhibited dual glass transition temperatures, one at -10°C and the other at 40°C . Since most monomers and acid copolymers encounter a dual endotherm, one around 50°C and the other around $80\text{--}95^{\circ}\text{C}$, it was not possible to determine whether the shift in the baseline in the enthalpy temperature diagram was due to the onset of an endotherm or due to the upper glass transition temperature [$T_g(U)$] of polypropylene. The isotactic homopolymer polypropylene used in the present analysis exhibited only a single glass transition temperature at around 0°C .

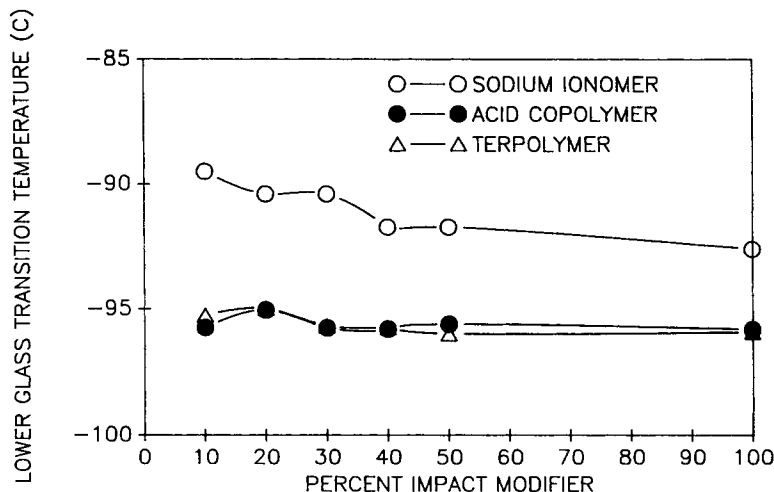


Figure 2 Effect of composition on the lower glass transition temperatures of the alloys.

The compositions and the glass transition temperatures of the blends of polypropylene (PP) and sodium ionomer are given in Figures 2 and 3. It can be found that the sodium ionomer seemed to have a glass transition around -92°C . Its addition to polypropylene (having a glass transition temperature of 0°C) at various levels from 10 to 50% did not seem to raise or lower the glass transition temperatures of either one. It could also be concluded that these blends are immiscible at all proportions, resulting in a phase-separated blend.

Figures 2 and 3 show the composition and the ductile brittle transitions (T_g 's) of the blends with the terpolymer. Although the blends resulted in a clear finished product, the thermal analysis revealed

a dual transition behavior. It was originally perceived that the terpolymer component (isobutylacrylate) would aid miscibility and thus result in a single transition temperature, but the blends of PP with the terpolymer resulted in dual transition temperatures and phase separation. It can be concluded that the blends are immiscible and phase separated at all blend ratios.

An analysis performed on the blends of acid copolymer and polypropylene revealed that these blends also exhibited a similar behavior like other chemically similar blends (Figs. 2 and 3). Although the transition temperatures were similar to that of terpolymer, these blends were slightly opaque. It could also be concluded at this point that the type

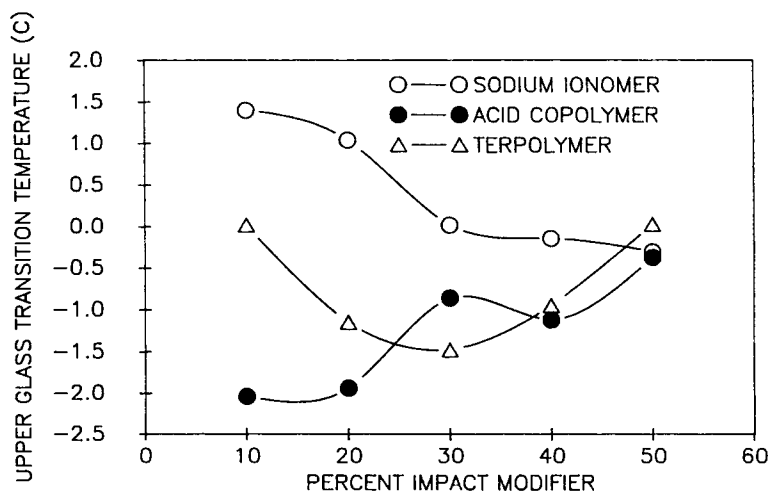


Figure 3 Composition dependence of upper glass transition temperatures of the alloys.

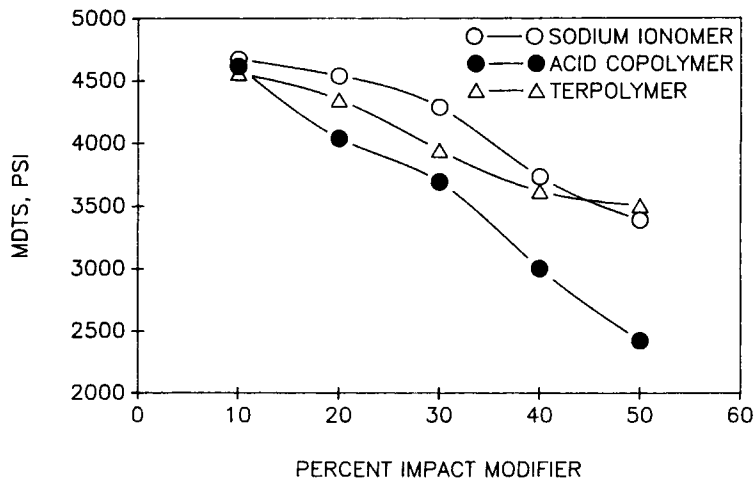


Figure 4 Effect of composition on the tensile strength measured in the melt flow direction.

of ion, amount of ion, percent acid, and percent neutralization did not play any role to aid miscibility or to form a single glass transition temperature.

Tensile Strength (Machine Direction)

From Figure 4 it can be seen that the tensile strength decreased with an increase in impact modifier level. The decrease in tensile strength was more significant in the case of the acid copolymer than in the case of the sodium ionomer or terpolymer. The decrease in tensile strength was nearly linear and, in the case of the terpolymer, the tensile strength seemed to level off above a 40% terpolymer level.

Tensile Strength (Transverse Direction)

The specimen obtained in the transverse direction exhibited a similar loss in tensile strength, as seen from Figure 5. The tensile strength was consistently lower than that obtained in the machine direction.

In either case the tensile strength was comparable to those of the other low-blush (low stress whitening) systems (Table I).

Elongation (Machine Direction)

The elongation increased with an increase in the ionomer (Fig. 6), acid copolymer, and terpolymer

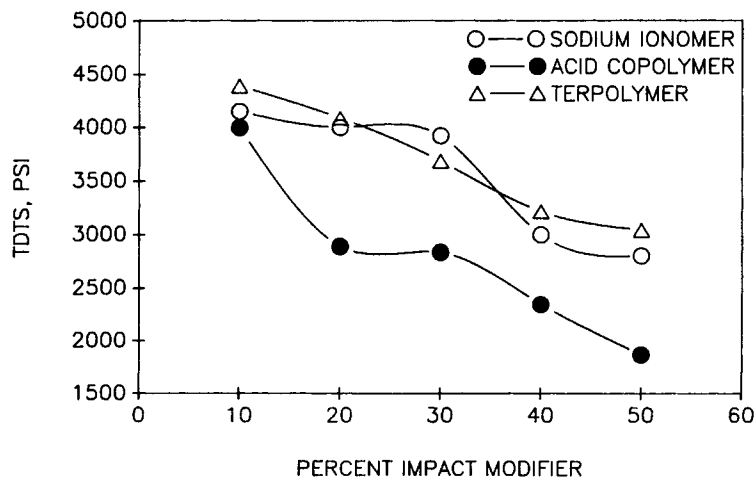


Figure 5 Effect of composition on the tensile strength measured in the transverse direction.

Table I Mechanical Properties of Low-Blush Systems

	Low-Blush Systems		
	1	2	3
Tensile strength (psi)	3650	3120	3456
Elongation	130%	145%	200%
Notched izod impact (ft-lb/in.)	3.0	2.9	4.2
<i>DL</i> *	12.9	14.4	16.3
Melt flow index (g/10 min)	8.1	6.5	10.1

content. The terpolymer exhibited the highest elongation at and above 30% additive levels. This higher elongation revealed excellent mechanical compatibility. This was borne out by microscopic examination of the polypropylene-terpolymer blends.

Elongation (Transverse Direction)

The elongation was tested in the transverse direction to the melt flow of the polymer. Figure 7 reveals that the elongation was very low and practically absent in the case of the acid copolymer and sodium ionomer. In the case of the terpolymer the elongation did not decrease in the transverse direction. The terpolymer seemed to orient itself in both directions. It showed that the loss in elongation in the transverse direction implied uniaxial orientation of the impact modifier. In the case of the terpolymer there appeared to be biaxial orientation of the impact

modifier. This resulted in good elongation in both directions.

Flexural Modulus

Impact modification traditionally reduces the stiffness of a polymer system, resulting in lower flexural modulus. Loss in flexural modulus with an increase in impact modifier level was observed in all three impact modifier systems. This effect can be seen from Figure 8. Loss in stiffness or flexural modulus was comparable to the other commercially available high-impact low-blush systems (Table I).

Notched Izod Impact Strength

The objective of the present study was to develop a high-impact composition (greater than 4.0 ft-lb/in. izod impact strength). From Figure 9 it can be seen that the terpolymer and the acid copolymer exhibited excellent impact properties above a 20% impact modifier level. The addition of sodium-based ionomer to the polypropylene did not seem to have a significant effect in enhancing the impact strength of the polypropylene. It was found that the sodium-based ionomer did not disperse evenly in the polypropylene matrix and a certain degree of reagglomeration occurred, resulting in the loss of impact strength.

Melt Flow Properties

Rheological melt flow properties were measured using an extrusion plastometer (using ASTM D 1238

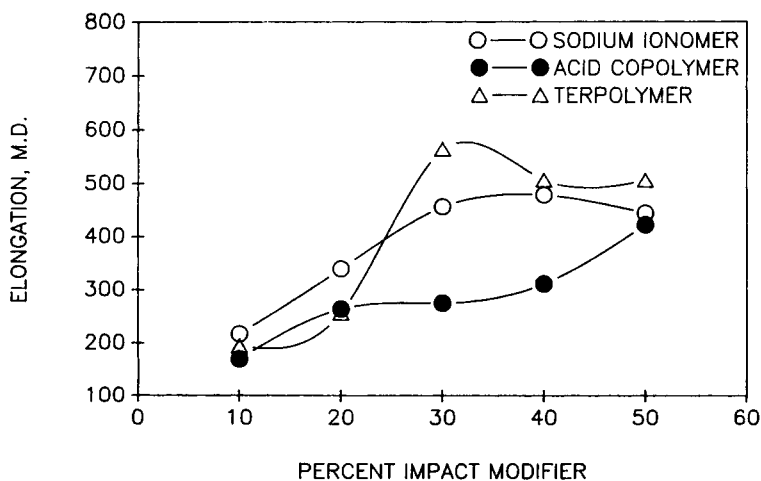


Figure 6 Composition dependence of elongation measured in the melt flow direction.

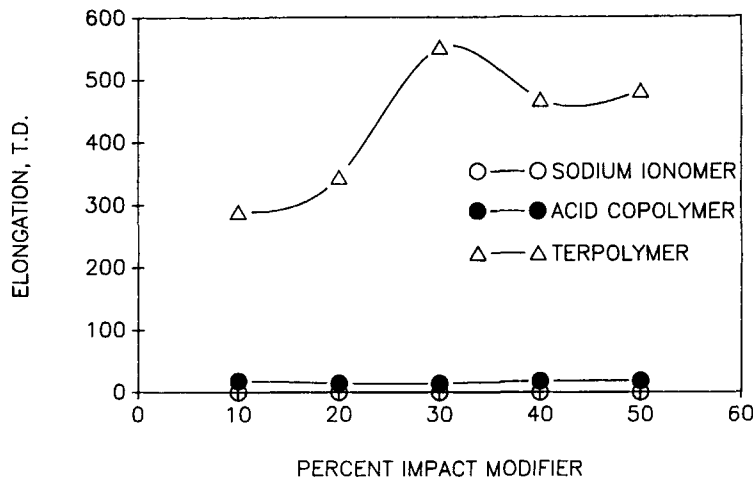


Figure 7 Effect of composition on the elongation measured in the transverse direction.

condition L, 230°C, 2160 g). The melt flow data are plotted in Figure 10. It can be seen that the melt flow index increased as the level of the acid copolymer in the blend increased. This was due to the inherent high-flow index of the acid copolymer. In the case of the sodium-based ionomer and the terpolymer, the melt index did not seem to be influenced as the level of impact modifier increased.

Effects of the Type of Processing Equipment on the Overall Mechanical Properties

Notched Izod Impact Strength

The notched izod impact strength increased with an increase in terpolymer content and, at comparable loadings of the impact modifier, compounding

through a twin-screw extruder improved the notched izod impact strength by about 30%.

Table II compares the notched izod impact values obtained by mechanical blending of the pellets and compounding prior to injection molding.

Melt Flow Index

Table III shows the comparison of the melt flow data performed by blending and by processing. As evidenced, the flow properties were not influenced by the type of processing equipment.

Zinc Ionomer

It can be found from Table IV that the zinc-based ionomer resulted in lower mechanical properties when compared to the sodium-based monomer.

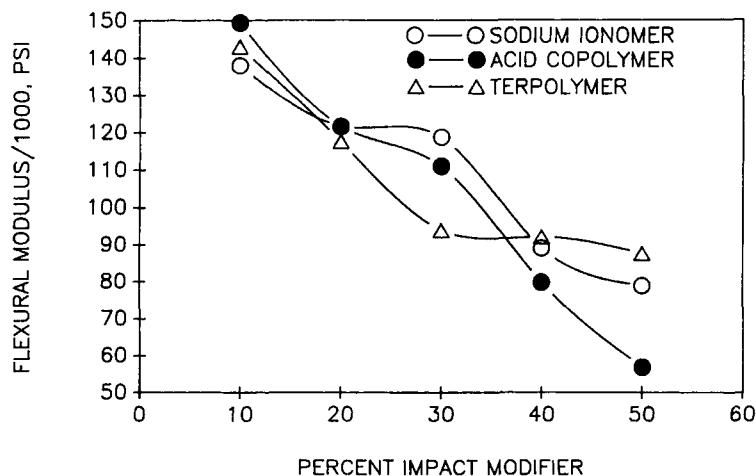


Figure 8 Flexural modulus as a function of ionomer type and concentration.

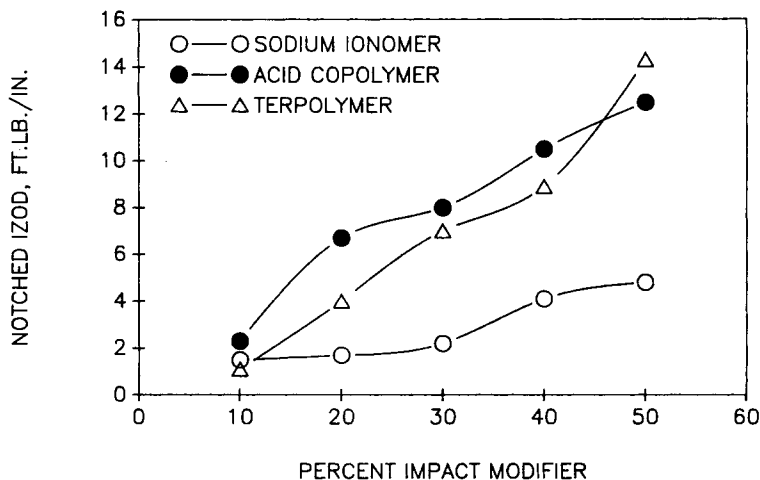


Figure 9 Effect of ionomer composition on the notched izod impact strength of the blends.

Lower physical properties exhibited by zinc ionomer in polypropylene led us to use sodium ionomer as a modifier in the blends.

ANALYSIS OF OPTICAL MICROGRAPHS

Polypropylene-Sodium Ionomer Blends

It can be seen from Figure 11 that the circular globules are the dispersed ionomer phase and the continuous phase is that of polypropylene. At 10% level of sodium-ionomer in polypropylene there seems to be a random distribution of the ionomer melt globules distributed in the matrix. The size of the dispersed phase seems to be uneven with a very wide

size distribution. At 20% level a similar phenomenon was observed resulting in a very uneven size distribution of the impact modifier phase, as seen in Figure 11 (b). At 30% ionomer level the size of the larger globules seemed to decrease. This could be due to the mutual attrition of the ionomer particles or the polypropylene phase resulting in the reduction of the globular size of the impact modifier [Fig. 11 (c)].

Above a 40% impact modifier level, there seemed to be reagglomeration [Fig. 11 (d)] of the already dispersed ionomer resulting in either a very large globule or a very small, finely dispersed impact modifier. This reagglomeration can be attributed to 60/40 weight ratio of polypropylene and ionomer wherein the ionomer is competing with the polypropylene to achieve the continuous phase. At a 50%

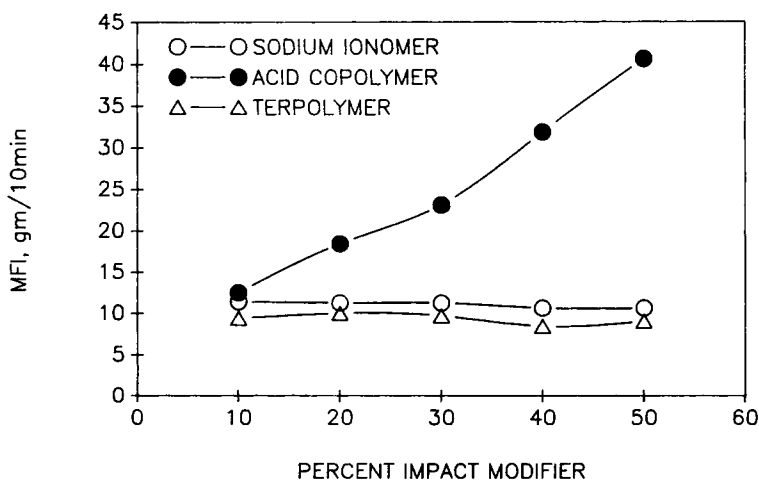


Figure 10 Melt flow indices of the blends as a function of composition.

Table II Notched Izod vs. Composition

Impact Modifier Level	Notched Izod Impact Strength	
	Mechanical Blending	Compounding
10% Terpolymer	1.06	2.1
20% Terpolymer	4.0	6.9
30% Terpolymer	7.18	8.2

Table III Melt Flow Index vs. Composition

Impact Modifier Level	Melt Flow Index (ASTM D 1238) (g/10 min)	
	Compounding	Mechanical Blending
10% Terpolymer	10.0	9.5
20% Terpolymer	9.49	9.96
30% Terpolymer	9.3	9.47

level, several large globules were seen due to reagglomeration [Figure 11(e)].

Polypropylene–Acid Copolymer Blends

It can be seen from Figure 12(a) that the acid copolymer particles appear to be dispersed in a random fashion and the particulates about to form a continuous phase. There are discrete particles as well as continuous phase formation. In Figure 12(b) globules in the dispersed phase tend to form a continuous phase and are finely distributed. They are oriented in a line about to form a continuous phase or about to form layers of acid copolymer between layers of polypropylene. In Figure 12(c) the pattern seen

above was observed again with a more uniform trend of layer formation by agglomeration of the discrete particles. In Figure 12(d) the continuous phase formation is on the verge of occurring, with a part of the micrograph showing a continuous phase and the other part exhibiting the tendency to form the continuous phase. In Figure 12(e) complete phase separation can be seen, and the particle breaking away from the continuous phase can also be observed.

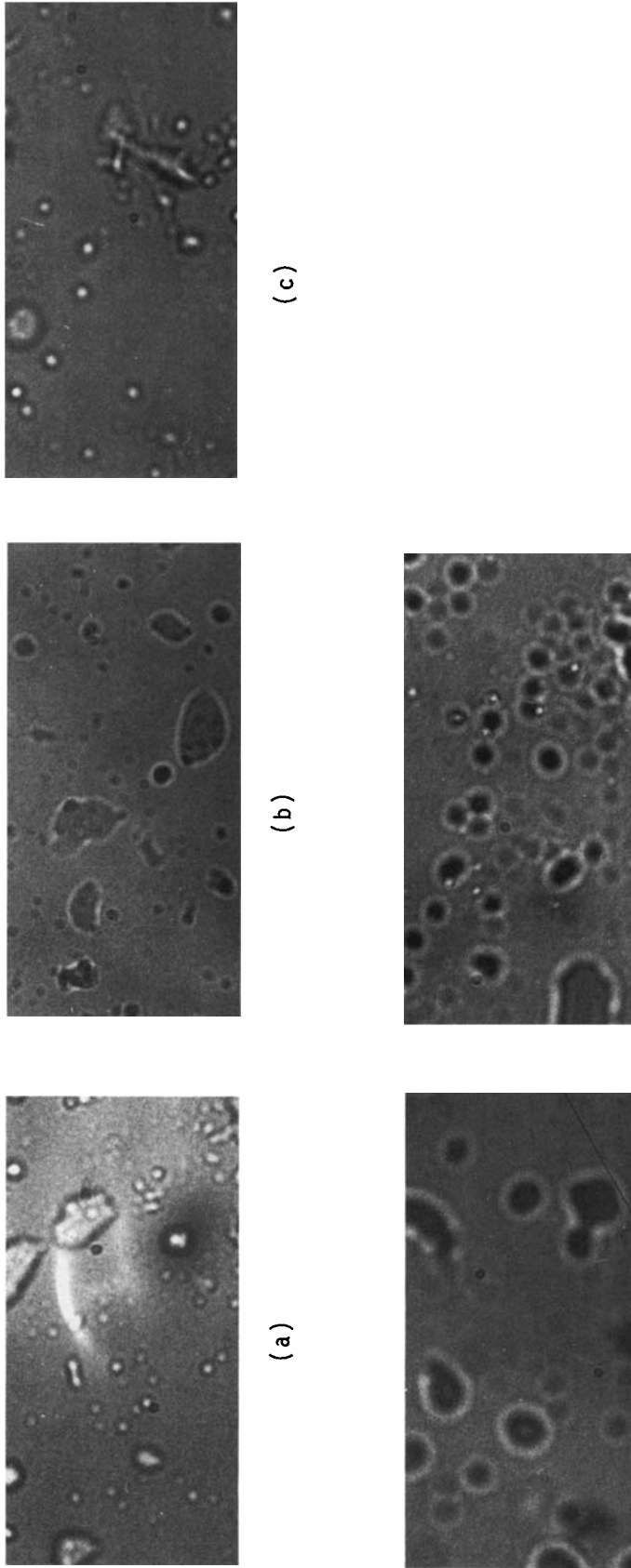
It was found that, in the case of the acid copolymer, the discrete phase formed was very uniform in size and seemed to orient itself in a certain organized fashion. This could contribute to the reduction in stress whitening, since the layer formation enabled the impact modifier layer to withstand the impact and yield by shear yielding. The tendency to stress whiten was suppressed as the impact modifier layer yielded by shear yielding. This mechanism resulted in lower levels of blushing and also resulted in enhanced impact strength.

Polypropylene–Terpolymer Blends

In Figure 13(a) the melt seemed to be dispersed evenly in fine globules and some amount of reagglomeration is visible. The amount of ionomer was not sufficient to enable the formation of a continuous phase. In Figure 13(b) we observe that the globules are smaller and further reduced in size and appear to form chains or exhibit the tendency to form a continuous phase in both the melt and transverse directions. The particle size seemed to be very small when compared to the other two chemically similar systems investigated. The continuous phase formation was visible [Figure 13(c)] with agglomeration of the particles to form a continuous phase in either direction. The agglomeration of particles did not result in an increase in particle size, which is detrimental to the impact strength. Figure 13(d) shows that the continuous phase formation was ev-

Table IV Zinc vs. Sodium Ionomer Property Analysis

	Zinc	Ionomer		Sodium Ionomer		
	10%	30%	50%	10%	30%	50%
Tensile strength (psi)	3050	2040	1540	4147	3921	2787
Elongation	80%	120%	150%	244%	456%	450%
Notched izod (ft-lb/in.)	0.8	2.0	3.0	1.4	2.1	5.0
Flexural modulus (10%) (psi)	1.1	1.0	0.8	1.4	1.2	0.8
Melt flow index (g/10 min)	8.2	7.8	6.4	11.5	11.1	10.8



(a) (b) (c) (d) (e)

Figure 11 Optical micrographs of sodium ionomers in polypropylene (400X magnification). Ionomer content: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, (e) 50 wt %.

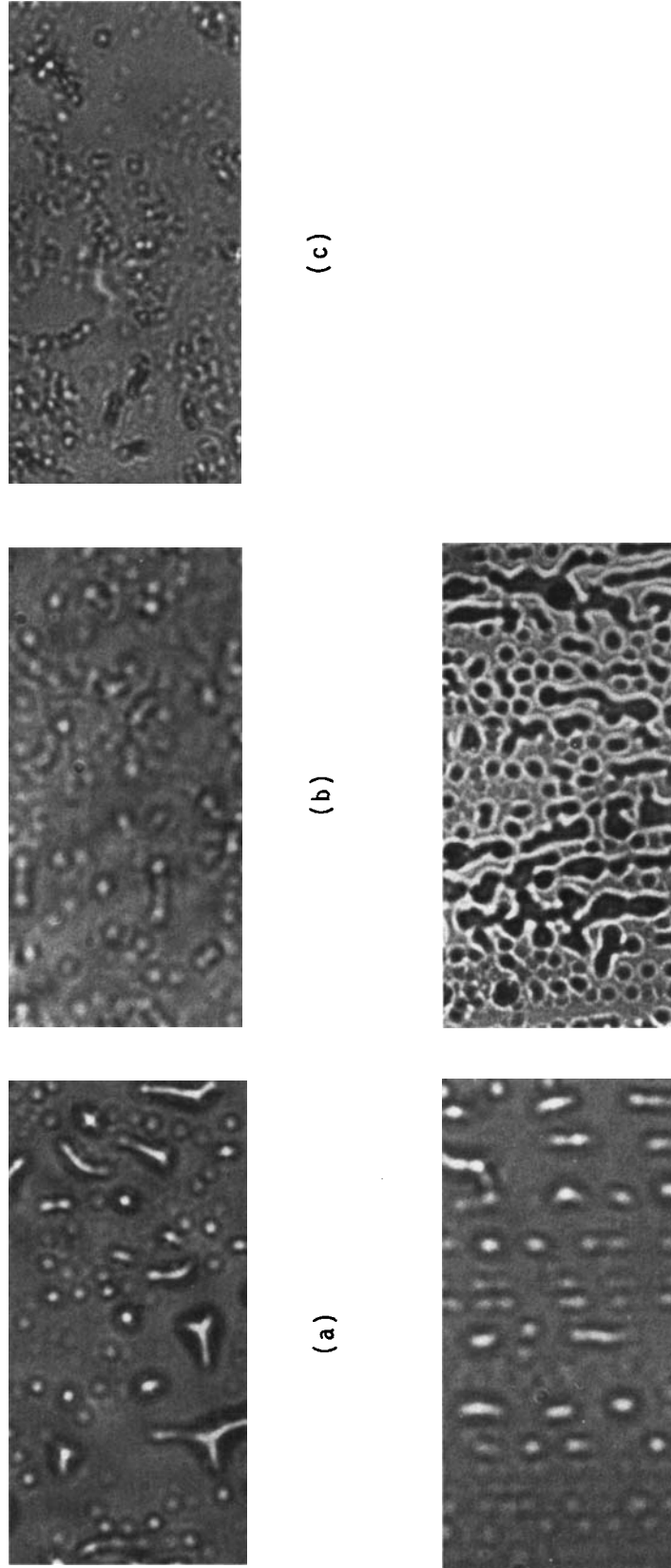


Figure 12 Optical micrographs of acid copolymer-polypropylene blends (400X magnification). Copolymer content: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, (e) 50 wt %.

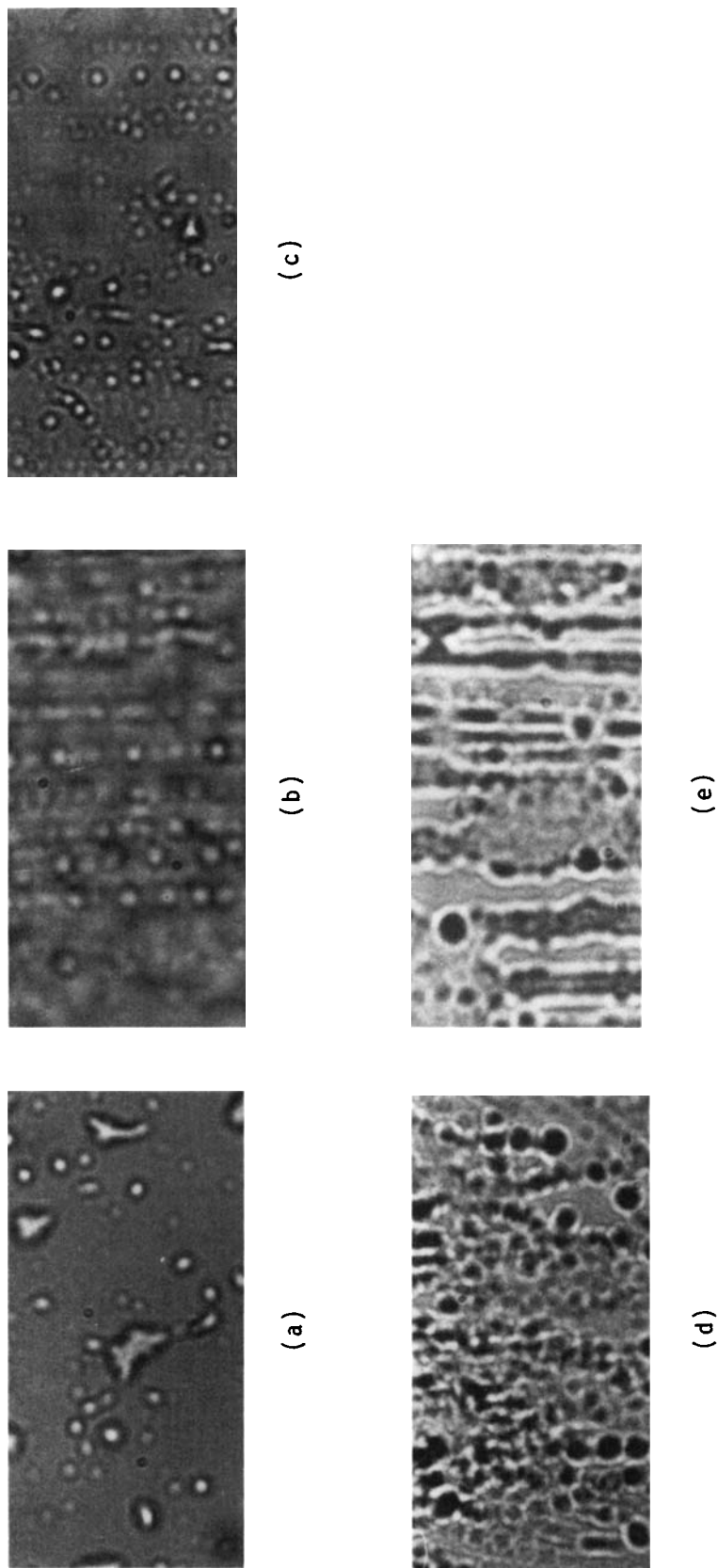
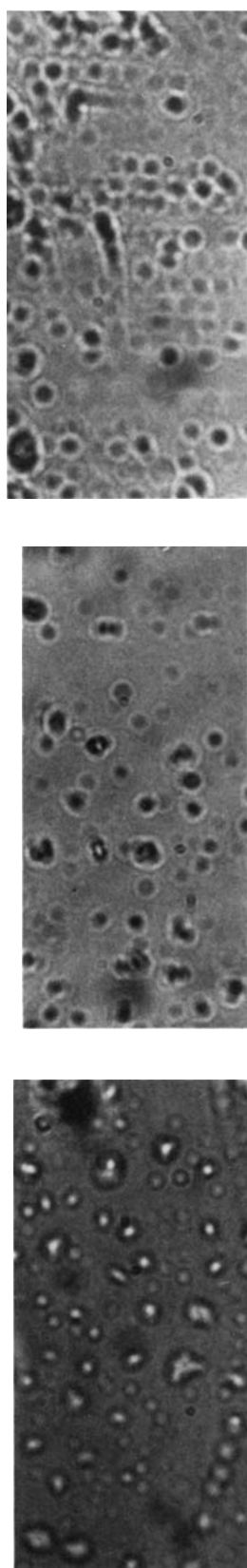


Figure 13 Optical micrographs of terpolymer-polypropylene blends (400X magnification). Terpolymer content: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, (e) 50 wt %.



(a) (b) (c)
Figure 14 Optical micrographs of terpolymer-polypropylene blends processed in a twin-screw extruder (400X magnification). Terpolymer content: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %.

ident with very little reagglomeration. It is interesting to note the competing effects of polypropylene and the terpolymer [Figure 13(e)] to form the continuous phase.

Since the addition of terpolymer seemed to result in an overall enhancement of the specified properties and the continuous phase formation resulted in the desired low-blush values, it was decided to determine the minimum amounts of terpolymer required to form a continuous phase and result in low blush, uniform impact at all locations. It was decided to use high shear melt processing equipment to distribute the impact modifier phase evenly in the matrix. It was anticipated that the high shear equipment would help in the formation of the monolayers and thus suppress stress whitening.

It can be seen from Figure 14(a) that high shear melt processing gave results similar to that of the physical blend. It also shows that there was a minimum amount of ionomer required to form the monolayer irrespective of the type of melt processing equipment. That minimum level was set to be 20% for the melt-processed blend and 40% for the physical blend of pellets. Figure 14(b) reveals that layer formation is imminent. Continuous phase formation seems to occur. In Figure 14(c) the layer formation appears to be complete with some agglomeration.

Fifty percent loading of the terpolymer is desirable to ensure continuous layer formation if high-intensity shear mixing is not available. A similar low stress whitening can be observed at a 30% impact modifier level when melt is processed prior to injection molding.

CONCLUSIONS

The ethylene-methacrylic acid family of polymers suppressed stress whitening by phase separation and formation of a continuous layer/layers within the polypropylene matrix. The layer formation to suppress stress whitening and to enhance the impact was favored by the acid copolymer and the terpolymer. This formation shared the impact energy to promote the failure to occur by shear yielding rather than crazing. The shear yielding mechanism does not result in stress whitening. This was caused by the formation of a continuous monolayer of the impact modifier. The formation of a monolayer seemed to be accelerated by high-intensity shear mixing of the components. By high shear compounding, the amount of impact modifier required to form a continuous monolayer, to reduce stress whitening, and to achieve the required degree of impact was also

lowered. High shear processing oriented the impact modifier in an organized fashion thus resulting in uniform impact strength lower levels of stress whitening.

The addition of the terpolymer and the acid copolymer at 30% levels and above in polypropylene resulted in good impact properties and excellent overall mechanical properties. Good impact strength was achieved at 30% by compounding the terpolymer with the polypropylene in a co-rotating, intermeshing twin-screw extruder.

To obtain reproducible and consistent results on stress whitening and monolayer formation if high shear processing equipment is not used, it is preferable to use an equal amount of impact modifier and polypropylene. If high shear processing equipment is available, 20–30% of the terpolymer was sufficient to give the required impact strength and stress whitening. The sodium ionomer did not form a continuous monolayer at or below a 40% impact modifier level. It was found that, in the case of the sodium ionomer, excessive reagglomeration took place, resulting in uneven impact strength.

The acid copolymer seemed to form a monolayer at lower loadings (20% Nucrel 035) and resulted in good impact strength and gave poor overall mechanical properties.

Other commercially available impact-modified polypropylenes had the tendency to stress-whiten more as the impact strength increased, but the current system(s) exhibited an exactly opposite phenomenon: blushing decreased as the impact strength increased.

The blends exhibited dual glass transition temperature, which is the primary characteristic of an incompatible blend. It was found that the family of ethylene–methacrylic acid was incompatible with polypropylene and the terpolymer also exhibited a similar phenomenon. It was due to this incompatibility that phase separation seemed to occur, lowering the stress whitening.

Optical microscope analysis clearly revealed the formation of monolayers of the impact modifier when the impact modifier used was either a terpolymer or an acid copolymer.

The authors would like to thank Dr. Robert W. Roberts and Ms. Beth Berthinee for their assistance in this work and in preparing this manuscript. Thanks are also due to A. Schulman, Inc. for its support.

REFERENCES

1. A. R. Schultz and B. M. Beach, *Macromolecules*, **7**, 902 (1974).
2. E. Turi, *Thermal Characterization of Polymeric Materials*, Academic Press, New York, 1981, p. 412.
3. S. Newman, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978.
4. L. A. Utracki, *Polym. Plast. Technol. Eng.*, **22**, 27 (1984).
5. J. Karger-Kocsis, A. Kallo, A. Szafner, and G. Bodor, *Polymer*, **20**, 37 (1979).
6. J. Karger-Kocsis and V. N. Kuleznev, *Polymer*, **23**, 699 (1982).
7. W. J. Ho and R. Salovey, *Polym. Eng. Sci.*, **21**, 839 (1981).
8. L. D'Orazio, R. Greco, C. Mancarella, E. Martuscelli, G. Ragosta, and C. Silvestre, *Polym. Eng. Sci.*, **22**, 536 (1982).
9. L. D'Orazio, R. Greco, C. Mancarella, E. Martuscelli, G. Ragosta, and C. Silvestre, *Polym. Eng. Sci.*, **23**, 489 (1983).
10. F. C. Stehling, T. Huff, C. S. Speed, and G. Wissler, *J. Appl. Polym. Sci.*, **26**, 2693 (1981).
11. H. E. Bair, *Anal. Calorim.*, **2**, 51 (1970).
12. C. B. Bucknall, *Toughened Plastics*, Applied Science Publishers, London, 1977, p. 136.
13. F. Altendorfer and H. Janeschitz-Kriegl, *Kunststoffe*, **74**(6), 325 (1984).
14. J. C. Boyer, *Structured Polymer Properties*, Marcel Dekker, New York, 1973.

Received March 28, 1991

Accepted August 1, 1991