Reactive Extrusion of Poly(Vinyl Chloride) Compounds with Polyethylene and with Ethylene-Vinyl Acetate Copolymers

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Synopsis

The mechanical properties of poly(vinyl chloride)/polyethylene blends can be improved by a reactive extrusion process in the presence of an organic peroxide and a coupling agent. With a judicious loading of dibenzoyl peroxide and triallyl isocyanurate coupling agent, such blends generally exhibit significantly greater ultimate tensile strengths and dynamic moduli. The nature of the sample posttreatment after compression molding is shown to have a major impact upon the relative magnitude of these differences. Evidence is also presented to suggest that such improvements result from a superior physical interlocking between blend components, rather than through the formation of co-crosslinked graft segments (which would, presumably, impart a compatibilization effect). Similar extrusion trials with a poly(vinyl chloride)/poly(ethylene-*stat*-vinyl acetate) mixture revealed a general worsening of material properties with increasing dibenzoyl peroxide levels. These observations can be rationalized by examination of the degradation reactions that likely occur in these reacting systems.

INTRODUCTION

Dunkelberger[1] has pointed out that the properties of neat poly(vinyl chloride), (PVC), render it essentially a useless thermoplastic material since it readily degrades at normal processing temperatures to release hydrochloric acid through a "zipper" mechanism.[2] Fortunately, modern stabilizer technology permits the processing of this polymer in both its rigid and flexible forms. Generally, monomeric compounds, such as phthalic acid derivatives (e.g., dioctyl phthalate and diisodecyl phthalate) or adipic acid derivatives (e.g., dibutyl adipate and diisooctyl adipate), have been used for plasticization of PVC[3] to almost any desired degree of flexibility. It is also of interest to assess the feasibility of using polymeric additives that possess a similar capacity to plasticize the PVC resin or to improve its impact resistance.

In this regard, polyolefinic materials have elicited considerable interest as potential modifiers for PVC resins. The blending of PVC with polyethylene[4-15] or with poly(ethylene-*stat*-vinyl acetate)[16-22] (EVA), has received most of the recent attention in the literature. Both of these systems generally form immiscible mixtures whose final product properties are dictated by the individual characteristics of the blend components as well as by their interaction at the interface between the two polymers.

While blends of PE and PVC are observed to be inherently brittle, the addition of chlorinated polyethylene,[5] or suitable graft copolymers (e.g., PE-g-PVC[4] and PE-g-PMMA[12]), or other effective solid-phase dispersants[10] can

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dramatically increase the ductility of the resulting composites. Other researchers have discovered that crosslinking agents, such as dicumyl peroxide, could also be useful modifiers for enhancing the mechanical properties of both binary PVC/PE blends[7,11] and ternary PVC/PS/PE mixtures.[8] In these cases, it was presumed that graft copolymers formed *in situ* would have acted as "compatibilizing agents" for the respective homopolymers.[11] The most recent investigations report significant increases in the ultimate mechanical properties of PVC/PE mixtures that have been co-crosslinked in a static molding operation through the incorporation of peroxide and coupling agent.[13-15]

Along the same vein, blends of PVC and EVA have shown some degree of improvement in impact properties largely at the expense of a reduction in tensile strength, flexural strength, hardness, and heat distortion temperature.[16] The more recent evaluations on PVC/EVA blends have demonstrated that truly miscible mixtures can be formed when the vinyl acetate content of the selected EVA component ranges from about 60 to 75 wt%,[17] since the polar parts of the EVA macromolecule interact strongly with the polar groups of the PVC chain.[19] EVA copolymers can be crosslinked by free radical mechanisms. On the basis of relative bond strengths, radicals may be generated by the abstraction of hydrogen atoms (preferentially those hydrogens attached to main chain tertiary atoms) or through cleavage of the C—O bond of the

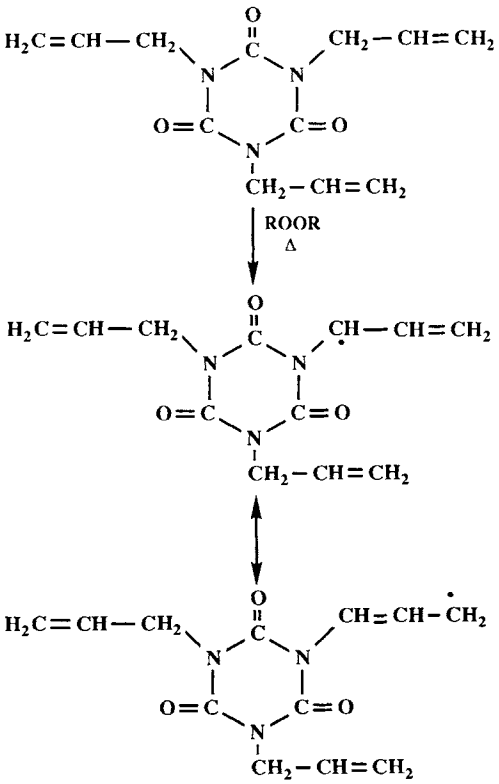


Fig. 1. Proposed radical generation of TAIC coupling agent.

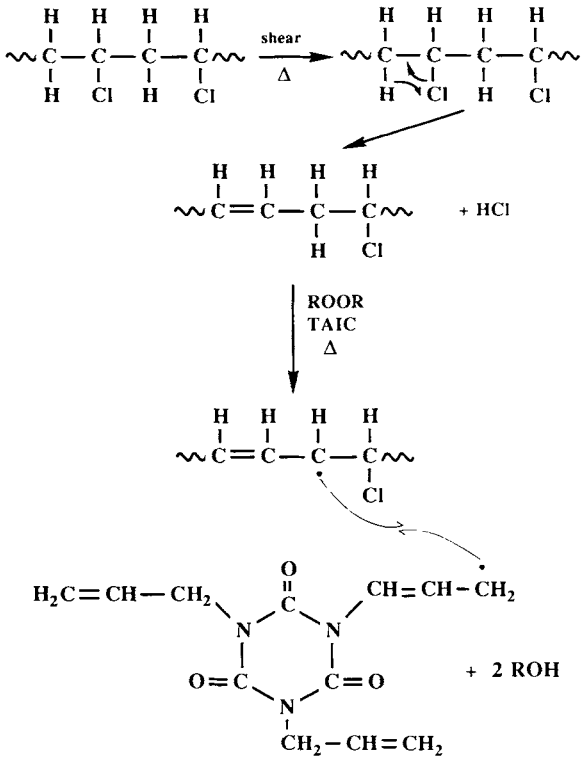


Fig. 2. Proposed coupling reaction between TAIC and PVC.

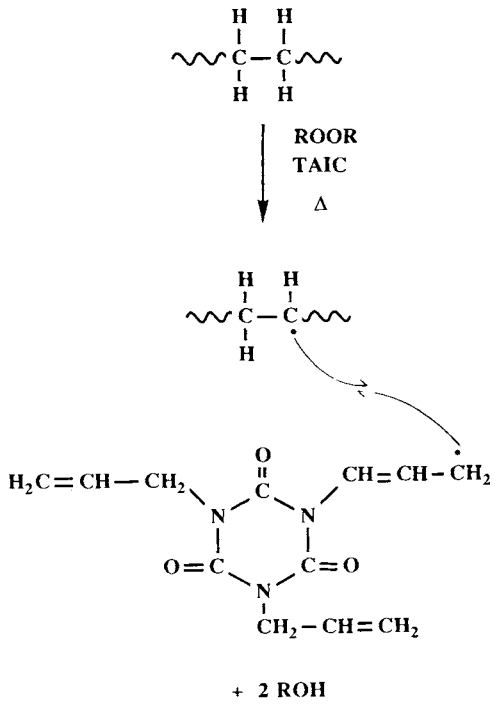


Fig. 3. Proposed coupling reaction between TAIC and LLDPE.

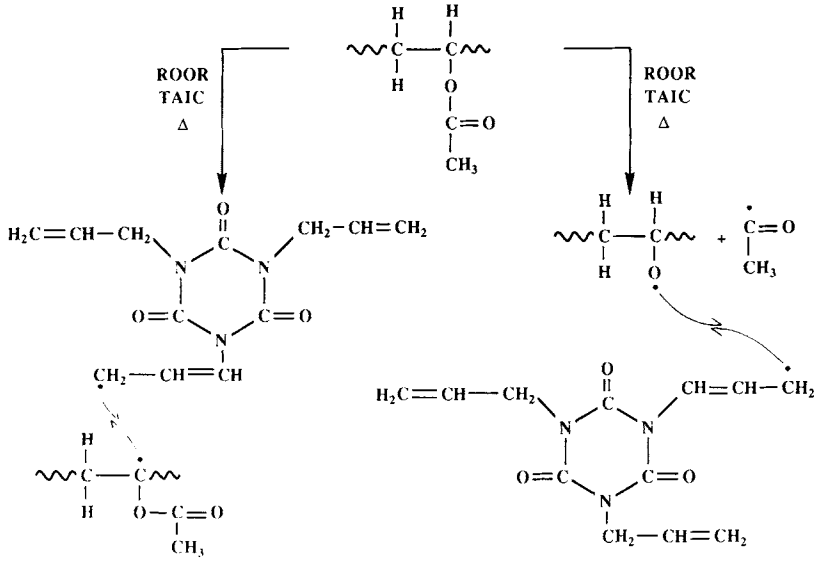


Fig. 4. Proposed coupling reactions between TAIC and EVA.

acetate group. A more unlikely scenario involving radical attack with subsequent bonding occurring preferentially at the mobile CH_3 group of the vinyl acetate unit has also been advocated by Rätzsch and Schönefeld.[23] The formation of co-crosslinked PVC/EVA blends, similar to the PVC/PE systems mentioned above, has remained an unexplored area.

In this report, the feasibility of producing co-crosslinked PVC/PE and PVC/EVA blends via a continuous reactive extrusion process is examined. With the addition of a suitable peroxide (e.g., dibenzoyl peroxide) and coupling agent (e.g., triallyl isocyanurate), it might be possible to induce the formation of intrachain graft structures between different polymer phases in these blends. Schematically, one could envision that an available radical center on TAIC (Fig. 1) could form a chemical linkage by recombination with a macroradical on PVC,[24,25] (Fig. 2), PE (Fig. 3), or EVA (Fig. 4).

EXPERIMENTAL

Selection and Preparation of Blend Components

A low-molecular-weight poly(vinyl chloride) resin (PVC-1) was used for all of the blending operations. To prevent extensive degradation of the PVC phase during reactive processing, a stabilization package was incorporated into the resin to allow for exchange reactions with any labile chlorine atoms in allylic or tertiary positions.[26] As a consequence of replacing any easily abstractable chlorine atoms with stable groups, further decomposition of the PVC is suppressed. Allylic hydrogen atoms, however, would still be available for abstraction; these sites would be the most probable locations for grafting reactions (as illustrated in Fig. 2). Thus, PVC-1 was compounded with 1.0 wt% magnesium oxide and 1.0 wt% of an organotin mercaptide heat stabilizer.[27-29] Blending was accomplished in a single-screw extruder fitted with a 3:1

compression ratio screw. The temperatures of the metering and die zones were kept below about 415 K during the compounding stage.

The compounded PVC-1 was characterized by its molecular weight distribution as determined from size exclusion chromatography (SEC). The Mark–Houwink constants for the PVC resin were calculated to be $K = 1.61 \times 10^{-6}$ m^3/kg and $a = 0.765$ at 418 K in 1,2,4-trichlorobenzene by a reported procedure.[30,31] No observable degradation was witnessed in the SEC analyses of the PVC samples as evidenced by the lack of any pH change in solutions stored at 418 K for several hours.

A butene copolymer LLDPE, P-6, with comparable melt viscosity (as determined by similarity in observed shear stress during extrusion at 443 K in a single-screw extruder at an apparent shear rate of about 10 s^{-1}) to the compounded PVC-1 resin was chosen as an acceptable blend component for the reactive extrusion trials. Molecular weight characterization and branching estimates were obtained by established procedures.[32,33] An ethylene-vinyl acetate copolymer, EVA-3, was also selected for blending with PVC-1. In this case, the most suitable candidate (also with respect to similar melt viscosities under extrusion conditions) was a high-pressure autoclave process EVA with approximately 28 wt% vinyl acetate content. Molecular weight determination was accomplished by similar methods after taking into account the specific refractive index correction for the particular EVA copolymer.[34] The branching characteristics and vinyl acetate content of the EVA were estimated by quantitative ^{13}C NMR according to a procedure detailed elsewhere.[35] Both of the olefinic blend components used were free of any antioxidants.

Sufficient quantities of PVC-1/P-6 and PVC-1/EVA-3 blends were prepared by the following procedure:

1. The blend components were initially tumble-mixed to provide good macroscopic dispersion within the mixture
2. The blend was then melt-mixed by single-screw extrusion at 428 K (with a 3 : 1 compression ratio screw) through a small orifice (length and diameter of capillary are 12.70 mm and 3.18 mm, respectively) with two 80 mesh screens and a breaker plate placed just before the die entrance
3. The extrudate was mechanically reduced to fine particles that passed through a mesh 40 sieve
4. The appropriate additive package consisting of dibenzoyl peroxide and triallyl isocyanurate was deposited uniformly upon the blend surface by dissolution in diethyl ether (followed by removal of solvent under forced convection and stirring)
5. Residual solvent was eliminated under vacuum at 313 K for a minimum of 4 days

Extrusion Conditions and Characterization of Blends

Reactive extrusion experiments were conducted on a DAVO counterrotating twin-screw extruder with intermeshed screw configuration (length of the screw was 0.52 m and the corresponding L/D was equal to 24). A die having a diameter of 4.5 mm was used for all extrusion trails. All PVC-1/P-6 blends were extruded with a flat temperature profile of 443 K applied across all

zones. For the PVC-1/EVA-3 mixtures, the temperature of the feed zone was reduced to 393 K to facilitate extrusion (at higher temperatures, sample "bridging" in the throat became problematic due to the tackiness of the EVA component). The second zone was adjusted to 423 K while the final two zones were set at 443 K. For all blends, screw speed was constant at 60 rpm and a throughput rate of 15 g/min (corresponding to a mean residence time of about 4 min) was controlled with a calibrated auger feeder.

The characterization of the PVC-1/P-6 extrusion products was carried out by removing ungrafted PVC by exhaustive solvent extraction. A 50 : 50 (v/v) mixture of carbon disulfide and acetone was found to be an ideal solvent for PVC-1 while being a nonsolvent for P-6. Thus, thin films of the extrudates were exposed to this solution at room temperature over a two week period. The extracted samples were freed from residual solvent by drying under vacuum at 333 K for 24 h. Thin films with uniform thickness of 0.10 mm were compression molded at 443 K. The resulting infrared absorption peaks at 1250 cm^{-1} (corresponding to the C—Cl stretch of the PVC macromolecule) were measured on a Perkin-Elmer Model 983 spectrometer.

A similar characterization for PVC-1/EVA-3 blend products was not feasible because all solvent systems capable of dissolving the PVC component also tended to dissolve low-molecular weight fractions of the EVA substituent. Furthermore, the carbon–oxygen linkage in the acetoxy group also absorbs strongly in the 1250 cm^{-1} region.

Specimen Preparation and Mechanical Testing

Tensile test specimens were prepared in compression molds under identical fabrication conditions. The procedure used for PVC-containing blends involved a 5 min warm-up for the blend at 443 K (directly in the molding plates) followed immediately by another 5 min period under an applied pressure of about 5 MPa. Specimens were then rapidly quench-cooled under cold water. One-half of all samples produced in this fashion were subsequently annealed in an air oven set at 353 K for 50 h. These samples were then brought slowly to room temperature at a cooling rate of 10 K per hour. All tensile test samples were exposed to a relaxation period of two to three days. The tensile testing was performed at constant grip speed and at 298 K using a cross-head speed of 1 and 10 mm/min for the PVC-1/P-6 and PVC-1/EVA-3 blends, respectively. For all trials, the gage length was adjusted to 22 mm. The reported mechanical properties for each blend are based on the results of 10 to 12 replicate specimens.

The dynamic rheological properties of selected PVC-1/P-6 blends were evaluated on a Rheometrics Model 605 Mechanical Spectrometer. Samples with nominal dimensions of 63.50 × 12.70 × 3.17 mm were tested in a torsional shear geometry with the loss and storage moduli being determined in a temperature sweep from 140 to 360 K. The applied strain was 0.10% and several testing rates, with frequencies ranging from 0.16 to 7.38 Hz, were employed. This strain was in the linear viscoelastic region for these materials.

Morphological Characterization of Reactive Extrusion Products

The morphology of PVC-1/P-6 and PVC-1/EVA-3 blend fracture surfaces was examined with a JOEL JSM-840 scanning electron microscope. The

analyses were conducted on specimens that had undergone slow deformation from tensile strain applied at ambient conditions; photomicrographs were obtained from broken samples of tensile testing, both before and after exposure to a solvent treatment. A 50 : 50 (v/v) mixture of carbon disulfide and acetone was used as the extraction solvent for the PVC phase of the poly(vinyl chloride)/polyethylene blends. The PVC/EVA blend series was not examined after solvent exposure for reasons cited above. All fracture surfaces were sputtered with a thin gold layer of approximately 10 nm to eliminate any "charging" by the SEM sample.

RESULTS AND DISCUSSION

Preliminary Co-crosslinking Investigations with PVC / PE Systems

Initial studies were conducted to determine the feasibility of the static co-crosslinking process using the materials with molecular weight characteristics as outlined in Table I. It should be noted from Table II that the LLDPE used in this work contained only significant concentrations of ethyl branches. The particular ethylene-vinyl acetate copolymer (EVA-3), on the other hand, had virtually no branching originating from its hydrocarbon segments; the methine carbon of the vinyl acetate unit was the only location where branching had been observed. This conclusion is supported by ^{13}C NMR spectra. A nonbranched vinyl acetate unit should have the ratio of methine to carbonyl resonance areas being equal to unity, whereas an increasing amount of chain transfer at the methine carbon would be reflected in a decrease in this ratio. While one can argue that EVA-3 has branching at the methine carbon site ($A_{methine}/A_{carbonyl} = 0.74$), one can only speculate that these branches are long in nature (since the presence of the vinyl acetate unit should hinder short-chain branch formation by back-biting mechanisms[35]).

Following the methodology of Nakamura et al.,[13] blends of PVC-1 and P-6 [with each component containing 4 wt% of triallyl isocyanurate (TAIC) and varying levels of α,α'-*bis*-(*t*-butylperoxy)diisopropylbenzene (BDPB)] were prepared on a two-roll mill and subsequently hot pressed at 433 K for 30 min to yield the co-crosslinked PVC/PE blends. As illustrated in Figure 5, the mechanical properties observed here are at variance with the values previously quoted in the literature.[13] The most striking discrepancy is that the reported co-crosslinked blends are claimed to display substantial degrees of ductility, whereas similar composition blends produced in this laboratory exhibit essentially brittle failure regardless of the level of peroxide incorporated into the polymer blend matrix. One may speculate that the dissimilarities in the molecular weight characteristics of the various resins used in each work could have contributed (at least to some extent) to these observed differences.

For the extrusion trials, dibenzoyl peroxide (DBP) was selected as the free radical generator to ensure that all peroxide would completely decompose to its acyloxy radicals during its transit through the extruder. The initial experiments using a single-screw extruder suggested that the DBP loadings for the PVC-1/P-6 and PVC-1/EVA-3 blends should not exceed approximately 0.75 and 0.50 wt%, respectively. At higher peroxide levels, the resultant blend

TABLE I
Molecular Weight Distributions of Blend Components

Designation	Material[a]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	SD(N)[b]	SD(W)[b]	Skew(N)[c]	Skew(W)[c]
PVC-1	PVC	54,000	116,000	188,000	2.2	—	—	—	—
P-6	LLDPE	36,000	167,000	416,000	4.6	69,000	204,000	6	4
EVA-3	EVA	83,000	154,000	515,000	1.9	77,000	236,000	10	29

[a] Commercial PVC resin was stabilized, commercial LLDPE resin was used as received, commercial EVA copolymer resin was used as received.
[b] Standard deviation of number (N) and weight (W) distributions.[40]
[c] Skewness of number (N) and weight (W) distributions.[40]

TABLE II
Branching Characteristics of Olefinic Blend Components from ^{13}C NMR Analyses

Estimates of branching (per 1000 backbone carbons)	P-6	EVA-3
Amyl	< 0.00001	< 0.00001[a]
Butyl	< 0.00001	< 0.00001[a]
Ethyl	21.0	< 0.00001[a]
Long chain (> 6 carbons in chain)	< 0.00001	< 0.00001[a]
$(A_{CH}/A_{CO})^b$	—	0.74
Vinyl acetate content[c] (wt%)	0.0	28.3

[a] Branching concentrations apply only to hydrocarbon component of copolymer.
[b] Ratio of methine carbon resonance area to carbonyl carbon resonance area.
[c] Applying the method of.[35]

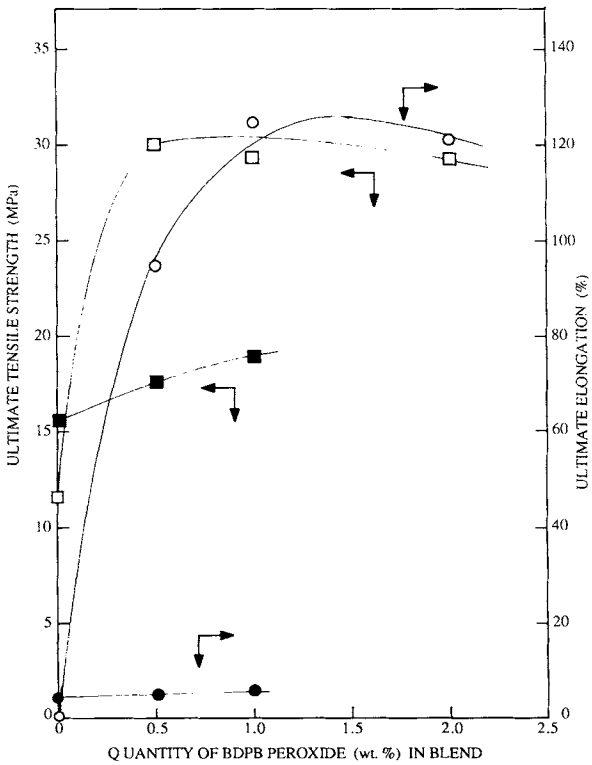


Fig. 5. Mechanical behavior of statically co-crosslinked PVC/PE blends: (○) Data points from Nakamura[13] of ultimate elongation for 100 : 50 (wt%) PVC/PE blends containing 4 wt% TAIC and varying levels of BDPB peroxide (samples pressed at 433 K for 30 min; posttreatment unknown). (□) Data points from Nakamura[13] of ultimate tensile strength for 100 : 50 (wt%) PVC/PE blends containing 4 wt% TAIC and varying levels of BDPB peroxide (samples pressed at 433 K for 30 min; posttreatment unknown). (●) Data points from this work of the ultimate elongation for 100 : 50 (wt%) PVC-1/P-6 blends containing 4 wt% TAIC and varying levels of BDPB peroxide (samples pressed at 433 K for 30 min followed by quench-cooling in water). (■) data points from this work of the ultimate tensile strength for 100 : 50 (wt%) PVC-1/P-6 blends containing 4 wt% TAIC and varying levels of BDPB peroxide (samples pressed at 433 K for 30 min followed by quench-cooling in water).

mixtures generally produced materials that were intractable and which exhibited extreme discoloration and poor thermoplasticity. These upper limits of peroxide levels were used as a guideline for subsequent twin-screw extrusions. In all subsequent work presented here, the blend ratio of PVC to olefinic modifier was kept at 100 : 50 for comparative purposes.

Blend Composition and Extrusion Characteristics

With twin-screw extrusion, suitable blend mixtures having compositions as outlined in Table III could be readily extruded. For both polymer blend systems, some discoloration was present in the extrudates. Generally, as the level of peroxide was increased, so was the intensity of the discoloration. This behavior is not unexpected for these reacting systems since both chain crosslinking and chain degradation processes would run simultaneously during the free radical reactions.[23] Furthermore, the rate of HCl liberation in the PVC phase is accelerated by the presence of radical-producing additives[36] and the resulting highly conjugated polyene structures in the PVC macromolecule become intensely colored through the formation of carbonium salt complexes.[26]

In considering the PVC-1/P-6 series, the torque requirements in twin-screw extrusion were observed to increase with the level of dibenzoyl peroxide incorporated in the blend mixture. Any grafting reactions between or within polymer phases would result in increases in both molecular weight and melt viscosity of the mixture; those effects would manifest themselves through a concomitant increase in observed torque levels during the extrusion process. Thus, this trend gives credence to the assertion that polymer coupling reactions must be occurring during the extrusion process. For the PVC-1/EVA-3 system, no indication of increasing torque levels could be reported. Conversely, the small observed decrease in the required torque between trials 5 and 7 of Table III suggests that a reduction in the blend's melt viscosity may have resulted from some degradation processes.

TABLE III
Observed Torque Measurements of Reactive Extrusion Blends

	Blend composition					Torque reading on twin-screw extruder (N · m)
Blend	PVC-1[a]	P-6	EVA-3	Dibenzoyl peroxide (wt%)	Triallyliso-cyanurate (wt%)	
1	100	50	—	—	—	47.0 (±0.5)
2	100	50	—	0.25	4.0	47.0
3	100	50	—	0.50	4.0	48.0
4	100	50	—	0.75	4.0	51.0
5	100	—	50	—	—	46.0
6	100	—	50	0.25	4.0	46.0
7	100	—	50	0.50	4.0	45.0

[a] The PVC resin was compounded with a stabilization package consisting of 1.0 wt% magnesium oxide and 1.0 wt% organotin mercaptide stabilizer.

Stress–Strain Behavior of Reactive Extrusion Blends

The mechanical tensile properties of the blend component homopolymers are summarized in Table IV. The ductility of PVC-1 was highly dependent upon the fabrication process. That is, quench-cooled specimens exhibited substantial plastic deformation (for rigid PVC) whereas similar, but annealed, samples underwent essentially brittle failure. As a result, the required energy to rupture values can fluctuate by approximately two orders of magnitude depending upon the nature of the posttreatment. Behavior of this nature has been well known for semicrystalline polymers like polyethylene[37] where slow cooling produces more highly crystalline, and therefore more rigid and brittle, structures. The magnitude of this effect in PVC is somewhat surprising, however, because the level of crystallinity in this polymer is relatively low.[38]

As one would have expected, the physical properties of the olefinic materials are dramatically different from the poly(vinyl chloride) compound. While their ultimate tensile strengths are far inferior (compared to PVC-1), both P-6 and EVA-3 can undergo very great plastic deformation prior to catastrophic failure. Furthermore, the annealing process is observed to have negligible consequences for the polyethylene resin and resulted in only minor deterioration in the material properties for the ethylene-vinyl acetate copolymer.

Table V presents the tensile properties of the poly(vinyl chloride)/polyethylene blend products after reactive extrusion. For the quench-cooled series, statistically significant increases in ultimate tensile strength, elongation to break, and Young's modulus can be observed for all blends containing DBP and TAIC (relative to the additive-free "control"). In practice, most of the improvement in material properties is realized at the lowest level of peroxide considered in this work (i.e., 0.25 wt% DBP); further increases in the peroxide loading generate only small incremental gains in the tensile strength to failure and minimal changes to the ultimate elongation or Young's modulus values. After the annealing process, the additive-treated blends maintain their higher ultimate strength and greater rigidity (as reflected by the Young's moduli) relative to the control blend 1-AN. The difference in elongation to break, however, becomes negligible given the sample estimate error.

The dynamic mechanical storage and loss moduli of two PVC-1/P-6 blend products are illustrated graphically in Figures 6(a) and 6(b), respectively. In

TABLE IV
Typical Tensile Properties of Blend Components

Material	Ultimate tensile strength (MPa)	Ultimate elongation (%)	Young's modulus (MPa)	Energy to rupture[a] (J)
PVC-1	52.4	100	1095	6.8
PVC-1[b]	40.2	6	1444	9.1×10^{-2}
P-6	16.6	650	208	13.0
P-6[b]	16.1	650	206	12.0
EVA-3	15.7	730	13	12.9
EVA-3[b]	13.9	675	13	10.7

[a] For samples with nominal dimensions of 1.5 × 5.0 mm.
[b] For samples annealed as described in text.

TABLE V
Physical Properties of PVC-1/P-6 Reactive Extrusion Blend Products

Blend[a] (code in Table III)	Ultimate tensile strength			Ultimate elongation			Young's modulus	
	Median (MPa)	Mean (MPa)	σ_{mean} (MPa)	Median (%)	Mean (%)	σ_{mean} (%)	Mean (MPa)	σ_{mean} (MPa)
1	14.5	14.7	1.5	5.5	5.3	0.3	713	21
2	20.3	20.5	0.9	7.0	7.4	0.5	836	24
3	21.6	21.4	0.7	7.0	6.7	0.6	838	31
4	23.4	23.6	0.9	6.5	6.8	0.6	828	19
1-AN	18.6	18.3	1.6	5.5	5.4	0.2	800	14
2-AN	24.1	24.1	1.0	5.5	5.8	0.6	971	27
3-AN	25.3	24.7	1.5	5.5	5.4	0.3	963	28
4-AN	24.1	24.5	1.1	5.5	5.7	0.2	951	28

[a] Those blends designated with "AN" have been annealed as described in text.

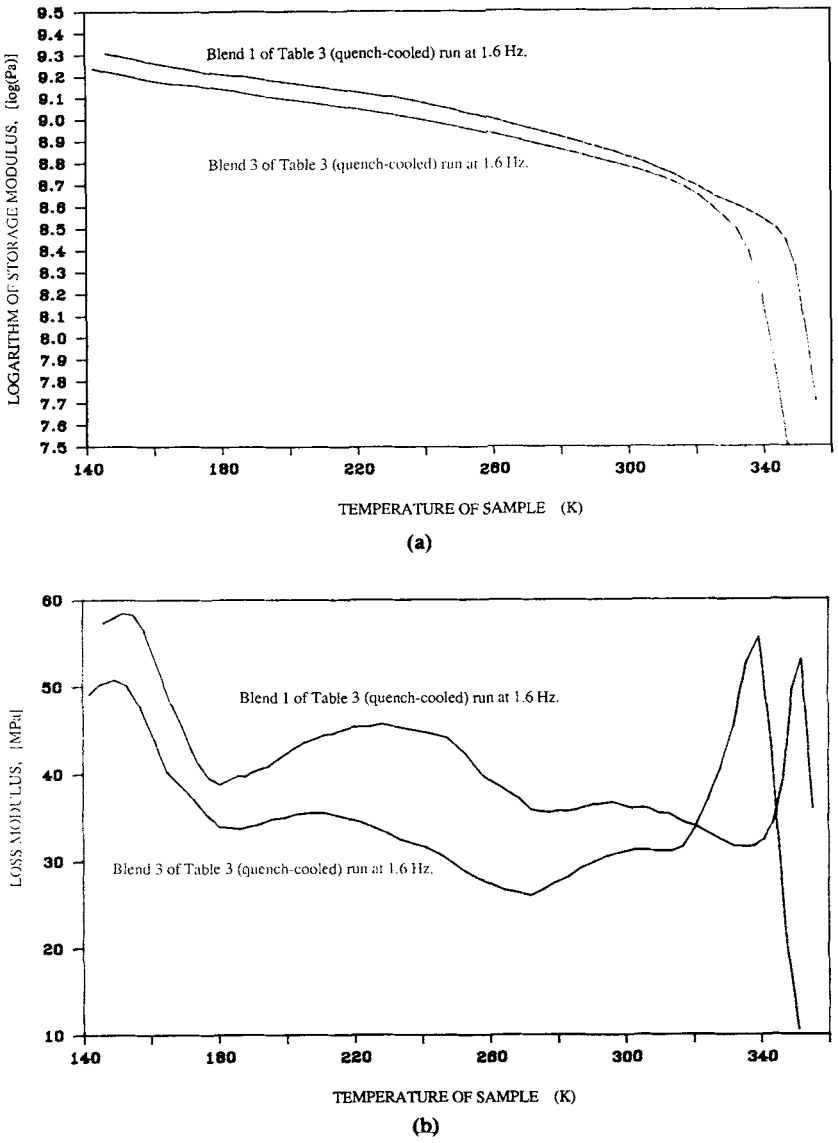


Fig. 6. (a) Dynamic mechanical behavior of selected PVC-1/P-6 blends (storage modulus versus temperature). (b) Dynamic mechanical behavior of selected PVC-1/P-6 blends (loss modulus versus temperature).

the glassy region from about 140 to 260 K, the magnitude of the storage modulus (G') of the blend treated with 0.5 wt% DBP and 4.0 wt% TAIC is approximately 20% higher than that of the comparable additive-free blend; at higher temperatures, the magnitude of this difference lessens. In the glass transition region of PVC-1, the G' curve for the additive-treated blend is shifted to higher temperature by approximately 10 K. This displacement is likely a result of two factors: first, any light crosslinking between PVC macromolecules would lead to the formation of longer macromolecules which should increase T_g and, second, crosslinking within the PE domains would

result in a reinforcing action upon the PVC phase that could hinder the long-range segmental motion of the PVC chains. The loss modulus (G'') undergoes a similar shift in the rubbery region of these two blends (which is controlled by the T_g of the PVC phase). The observed increase in loss modulus for the blend containing peroxide and coupling agent additives (relative to the additive-free material) is to be expected since any crosslinking or branching reactions would lead to an increase in blend's viscosity. Therefore, more energy would need to be supplied to the specimen to impart the applied 0.10% strain and, hence, the loss modulus would rise. In addition, the loss modulus curves of Figure 6(b) also suggest that crosslinking within the PE phase causes minor upward shifts in its glass transition temperature. Similar trends are observed at both the lower and higher frequencies employed in this work. The only distinction is that for a testing rate employing higher frequency oscillation, the storage and loss moduli will be correspondingly larger with an accompanying horizontal shift to higher temperature.

Exhaustive solvent extraction of the PVC-1/P-6 extrusion products conclusively demonstrated that essentially all of the poly(vinyl chloride) components could be removed from these blend mixtures. The measured absorbances at 1250 cm^{-1} were zero for the extracted residues of blends 1 to 4 suggesting that "between" phase grafting reactions are negligible for the PVC/PE system considered in this work; any branching or crosslinking reactions occur primarily "within" each phase. Furthermore, since all of the PVC could be readily extracted, it is reasonable to conclude that crosslinking reactions within the PVC phase did not lead to extensive network formation. Thus, one could also infer that the superior ultimate tensile properties of the additive-containing blends are likely not the result of any compatibilization effects from *in situ* graft copolymer formation (as suggested by earlier investigations[11,13-15]), but rather a consequence of a more efficient physical interlocking between blend components on the molecular level.

The tensile properties of the PVC-1/EVA-3 blends, as illustrated in Table VI, follow a profoundly different trend than that exhibited in the polyethylene-modified system. In this case, additions of even minor levels of DBP caused a significant worsening in the blend's ultimate properties and a small lowering in its Young's modulus values. These observations, which apply to both quench-cooled and annealed blend specimens, are consistent with the decreasing torque requirements witnessed for the extrusion of blends 5 to 7 of Table III. This evidence suggests that the free radical reactions induced in the extrusion process lead primarily to chain degradation as opposed to chain coupling. A previous examination of the behavior of PVC/EVA blend mixtures has concluded that the dehydrochlorination of PVC can cause simultaneous destabilization of *both* PVC and EVA.[39] As illustrated in Figure 7, the diffusion of hydrogen chloride into the EVA phase catalyzes the loss of acetic acid while the migration of the acetic acid into the PVC phase catalyzes further dehydrochlorination reactions. Acid hydrolysis of the vinyl acetate group, leading to the formation of poly(vinyl alcohol) structures, could also occur within the EVA phase. Under the experimental conditions employed in this work, one would anticipate that such small molecular species could easily diffuse across the phase boundaries.

TABLE VI
Physical Properties of PVC-1/EVA-3 Reactive Extrusion Blend Products

Blend[a] (code in Table III)	Ultimate tensile strength			Ultimate elongation			Young's modulus	
	Median (MPa)	Mean (MPa)	σ_{mean} (MPa)	Median (%)	Mean (%)	σ_{mean} (%)	Mean (MPa)	σ_{mean} (MPa)
5	18.1	18.0	0.8	22.5	22.8	3.7	432	17
6	15.2	15.2	1.1	13.0	12.9	1.5	335	30
7	13.7	13.7	0.8	14.5	14.5	2.7	350	14
5-AN	19.8	19.8	1.0	13.0	13.6	1.5	400	14
6-AN	19.7	19.9	1.5	10.5	11.2	1.4	385	26
7-AN	15.8	16.8	1.9	10.5	11.0	1.5	395	17

[a] Those blends designated with "AN" have been annealed as described in text.

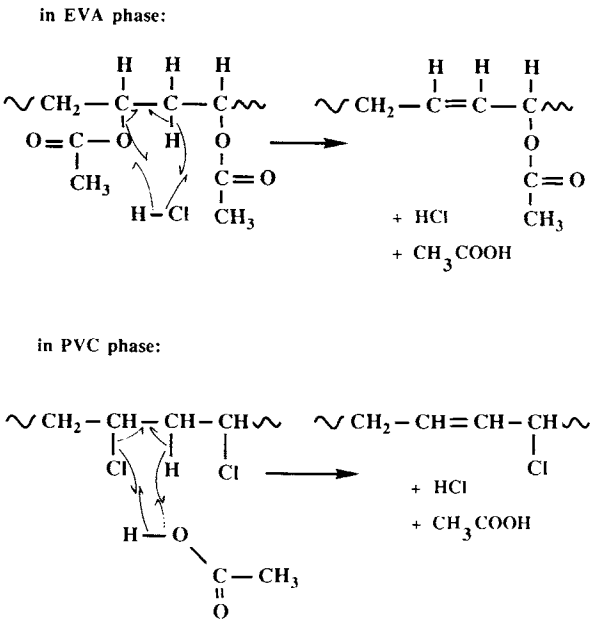


Fig. 7. Degradation mechanism in PVC/EVA blends.

The energy to rupture measurements for the PVC/olefin blend products are presented in Table VII. These results closely parallel with the trends observed earlier. That is, for the quench-cooled PVC-1/P-6 blends, a 2.5-fold increase in the energy to rupture is realized for the additive-treated mixtures. This is presumably a reflection of a superior physical interlocking between the dissimilar macromolecular components. These differences are largely eliminated after the annealing period as the macromolecules have had some opportunity

TABLE VII
Energy to Rupture Measurements for PVC/Olefin Reactive Extrusion Blend Products

PVC-1/P-6 blends		PVC-1/EVA-3 blends	
Blend composition[a] (code in Table III)	Average energy to rupture[b] relative to control sample (%)	Blend Composition[a]	Average energy to rupture[b] relative to control sample (%)
1 (control)	100 (4.2×10^{-2} J)	5 (control)	100 (4.5×10^{-1} J)
2	255	6	41
3	245	7	38
4	257		
		5-AN	55
1-AN	155	6-AN	31
2-AN	164	7-AN	29
3-AN	167		
4-AN	174		

[a] Those blends designated with "AN" have been annealed as described in text.
[b] For samples with nominal dimensions of 1.5 × 5.0 mm.

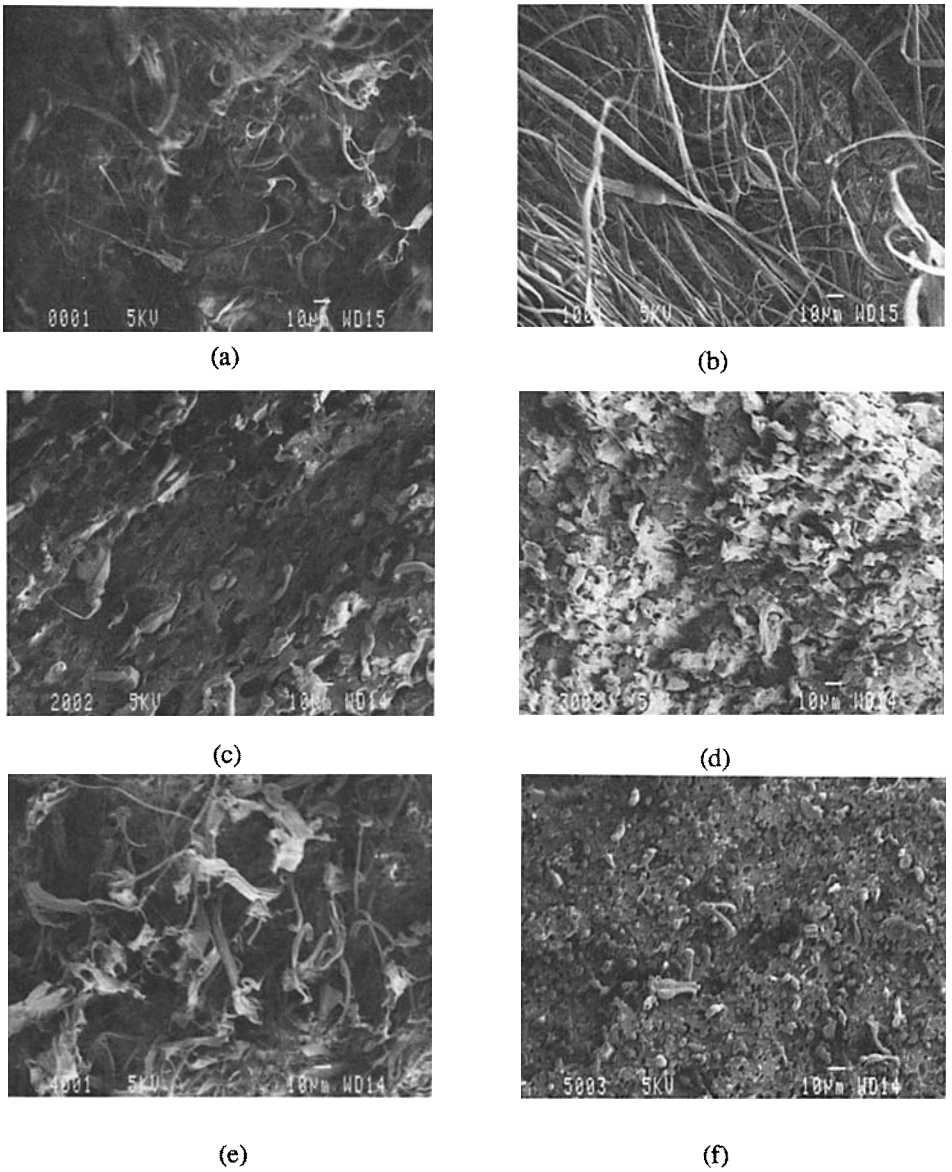
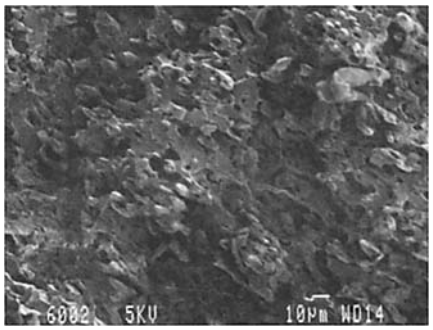


Fig. 8. Photomicrographs of PVC-1/P-6 blend fracture surfaces: (a) Blend 1 of Table VII.5 (quench-cooled). (b) Blend 2 of Table VII.5 (quench-cooled). (c) Blend 3 of Table VII.5 (quench-cooled). (d) Blend 4 of Table VII.5 (quench-cooled). (e) Blend 1-AN of Table VII.5 (annealed). (f) Blend 2-AN of Table VII.5 (annealed). (g) Blend 3-AN of Table VII.5 (annealed). (h) Blend 4-AN of Table VII.5 (annealed). (i) Blend 1 of Table VII.5 (quench-cooled and exposed to solvent mixture for 7 days). (j) Blend 2 of Table VII.5 (quench-cooled and exposed to solvent mixture for 7 days). (k) Blend 3 of Table VII.5 (quench-cooled and exposed to solvent mixture for 7 days). (l) Blend 4 of Table VII.5 (quench-cooled and exposed to solvent mixture for 7 days).

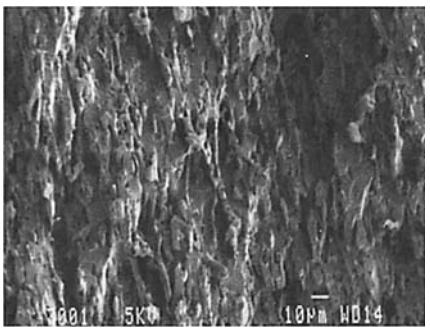
to disentangle and segregate into their respective domains. With regard to the PVC-1/EVA-3 blends, the energy to rupture of quench-cooled specimens is greatly reduced for the additive-treated materials for reasons cited above. The annealing posttreatment aggravates the condition even further, presumably because of additional degradation reactions of the type suggested in Figure 7.

Morphology of Reactive Extrusion Blends

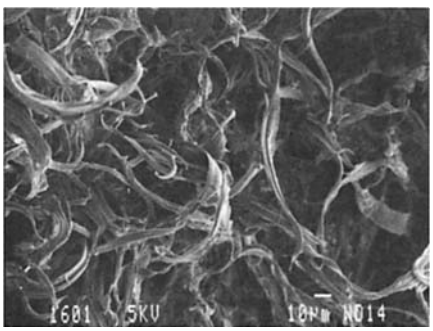
Scanning electron microscopy (SEM) of the PVC/olefin blends has given some insight to their morphological characteristics. With the quench-cooled



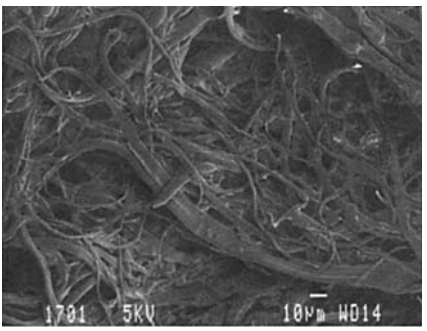
(g)



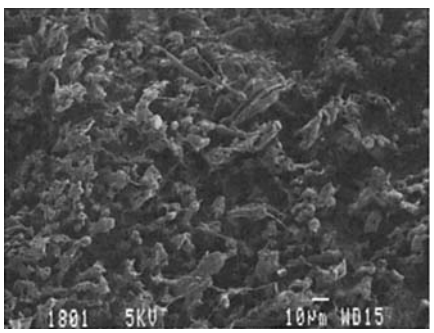
(h)



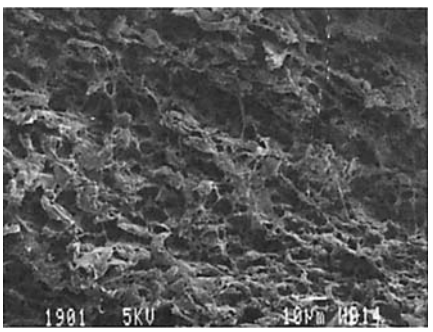
(i)



(j)



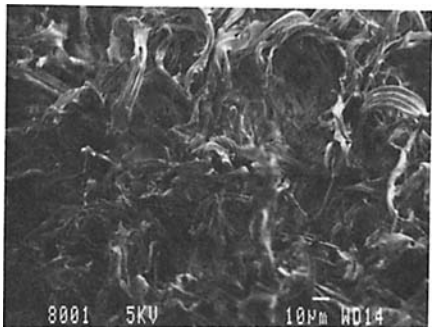
(k)



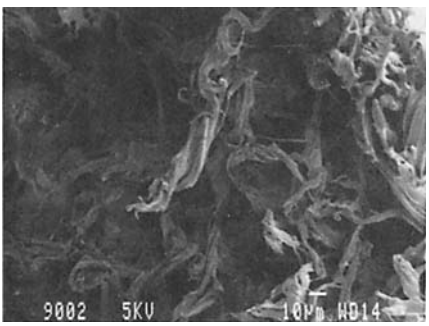
(l)

Fig. 8. (*Continued*)

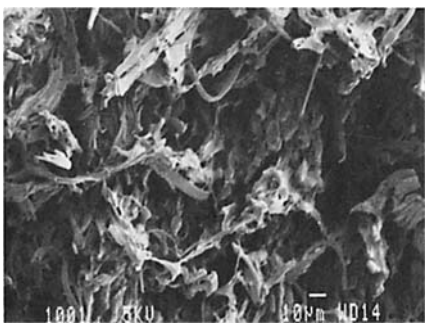
PVC/PE series (i.e., blends 1 to 4), the structure of the additive-free PVC-1/P-6 blend fracture surface displays extensive fibrillar characteristics [see Fig. 8(a)]. With the addition of 0.25 wt% DBP and 4.0 wt% TAIC, the morphology of the fracture surface is similar to a sea of highly intertwined fibers that possess some ability to undergo plastic deformation through "necking" [see Fig. 8(b)]. At higher peroxide levels (0.50 and 0.75 wt% in the blend composition), a two-phase co-continuous morphology becomes the dominant feature [see Figs. 8(c) and 8(d)]. Thus, in considering the sequence of



(a)



(b)



(c)

Fig. 9. Photomicrographs of PVC-1/EVA-3 blend fracture surfaces: (a) Blend 5 of Table VII.6 (quench-cooled). (b) Blend 6 of Table VII.6 (quench-cooled). (c) Blend 7 of Table VII.6 (quench-cooled).

blends 1 to 4, one can readily observe that the resultant morphologies tend to display less fibrillar character and more co-continuous phase structure. This trend is probably a direct consequence of the hindered macromolecular mobility within those blends that are crosslinked to some extent.

The morphologies of the annealed blends (1-AN to 4-AN) have similar topography in comparison to the series described above. The only significant difference is observed between Figures 8(b) and 8(f) where the latter blend morphology does not exhibit the highly oriented fibrillar structures that are present in the former sample. For the quench-cooled PVC-1/P-6 blend series that have been exposed to a solution which selectively dissolves the PVC component [Figs. 8(i) to 8(l)], one can readily observe that the polyethylene residues reflect decreasing fibrillar orientation with increasing peroxide loadings. As can be observed from Figure 8(l), the removal of the poly(vinyl chloride) component leaves behind the polyethylene in a form that resembles an open-cell foam.

As shown in Figure 9(a), the morphology of the additive-free PVC-1/EVA-3 blend fracture surface is largely indistinguishable from its PVC/PE counterpart [Fig. 8(a)]. But contrary to that observed for the PVC/PE series, the level of DBP incorporated into the PVC-1/EVA-3 mixtures does not appear to have any prominent influence upon the resulting morphological structure. In fact, the SEM photomicrographs of blends 5, 6, and 7 [corresponding to Figures 9(a), 9(b), and 9(c), respectively] bear more similarities than differences.

CONCLUSIONS

Blends of PVC with polyolefins generally result in mixtures that have poor overall physical properties. The effectiveness of reactive extrusion processes for improving these material properties is highly dependent upon the nature of the selected polyolefin. For example, the PVC-1/EVA-3 extrudates produced in this work displayed a significant worsening in their ultimate mechanical properties when free radical generators and coupling agents were incorporated into the blend formulation. This deterioration in material properties was attributed to degradation processes that occurred within both phases. However, if poly(vinyl chloride)/polyethylene blends are exposed to a similar extrusion process, an improvement in mechanical properties (in particular, the ultimate tensile strength and dynamic moduli) can be realized through a judicious loading of peroxide and coupling agent. These beneficial modifications most probably arise not from the in situ generation of graft copolymer interfacial agents but, rather, from the establishment of superior physical interlocking between blend components.

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