The Effects of Fillers, Crosslinking Agents, and Domain Size on the Physical Properties of PE–PCV Blends

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Synopsis

Blends of polyethylene and poly(vinyl chloride) were prepared on a Brabender Plasticorder, and attempts were made to improve the very inferior physical properties of the product. The blends were found to have domain structures, and it was shown that their physical properties could be improved very considerably if the domain sizes could be reduced drastically. However, in melt blending, there was a limit to the reduction of domain sizes. A noticeable improvement in properties was achieved through the use of various fillers and crosslinking agents. Small changes in crystallite size and percentage crystallinity were observed where certain additives were used. It appeared that the additives that were most effective in enhancing physical properties acted by improving load transfer at the interface between the two polymer phases.

INTRODUCTION

The physical properties of blends of incompatable polymers are known to be inferior to those of their polymer components.[1] Segregation of polymeric wastes into generic types poses various problems, and an improvement in blend properties which would remove the necessity for such segregation is of considerable interest in the reuse of waste materials. It has been shown that the properties of a polyethylene–poly(vinyl chloride) blend can be improved by the addition of chlorinated polyethylenes to the blend,[2,3] while Barentsen and Heikens[4] have reported marked improvements in the properties of low-density polyethylene–polystyrene blends by the addition of a 50:50 graft copolymer of the two homopolymers. This paper reports on the effects of various fillers, crosslinking agents, and variations in the domain[5] size on the properties of polyethylene–poly(vinyl chloride) blends. The particular blend composition chosen for this study was based on a local survey[6] which showed that domestic waste was likely to contain disposable plastics bottles in the mass ratio 55% polyethylene to 45% poly(vinyl chloride).

EXPERIMENTAL

The materials used are detailed in Table I. Blends containing 55% PE and 45% PVC by mass were prepared on a Brabender Plasticorder PLV 151 equipped with a Type 5 roller mixing head of 60-ml capacity and a quick loading chute. The pellets were premixed before their addition to the mixing chamber. Blending was done in a preheated head at 170°C for 20 min at a rotor speed of 20 rpm.

TABLE I
Polymers and Additives

Abbreviation	Description	Source
PE	high-density poly(ethylene)	Hoechst
PVC	poly(vinyl chloride)	I.C.I.
PS	polystyrene	Shell
EVA	ethylene–vinyl acetate copolymer	Bayer
SBR	styrene–butadiene rubber	Synthetic Rubber Co.
EPDM	ethylene propylene diamine	Enjay Chem. Soc.
Neoprene	chloroprene rubber	du Pont
CB	carbon black	Phillips C.B.
Asbestos	Gooche asbestos	Maybaker
DCP	dicumyl peroxide	BDH
TAIC	triallyl isocyanurate	Allied Chem.

Blends were compression molded for 4 min at 45 kPa (1 kPa = 145 psi) in a rectangular mold preheated to 140°C. The mold was force cooled before opening. Test pieces for tensile and impact tests were cut from these molded plates. Five duplicate tests were done on all blends.

A Hounsfield tensometer with a testing speed of 1.5 cm/min was used for tensile tests, and a Ceast Izod impact tester was used for determining impact resistance. Blends containing fillers were prepared by adding half of the polymer pellets to the mixing head, followed by all of the filler and then the remainder of the pellets.

In experiments involving the use of crosslinking agents, it was necessary to limit crosslinking as far as possible during the mixing process in the Brabender head where the blend was subjected to large shear forces, while at the same time ensuring adequate mixing of the polymers and the polymers with the initiator. Crosslinking should occur mainly in the mold once a good dispersion had been achieved and where bonds formed would no longer be disrupted. Preliminary experiments in the Brabender showed that relatively little crosslinking occurred during the first 4 min following addition of the peroxide to a blend at 155°C. Blends were therefore prepared by mixing the polymers at 155°C and 20 rpm for 20 min to ensure thorough mixing of the phases; peroxide was added, and mixing was continued for a further 4 min. The blends were transferred to the preheated compression mold where crosslinking was completed by maintaining the sample at 170°C for 20 min. Gregorian and Bafford[7] showed that for the complete cure of polyolefins, the crosslinking time should be about ten times the half-life of the peroxide at that temperature. DCP has a half-life[8] of 1.2 min at 170°C.

Thermogravimetric (TGA) and differential scanning calometric analyses (DSC) were conducted in a nitrogen atmosphere on a du Pont 990 thermal analysis system. The heating rate was programmed at 5°C/min. Calculations of the percentage crystallinity of the PE were based on a value of 282 Jg^{-1} (1 J = 0.239 cal) for the enthalpy of fusion of a single crystal.[3]

RESULTS AND DISCUSSION

Blends of incompatible polymers have domain structures and the domain size and shape may be expected to play a significant role in determining proper-
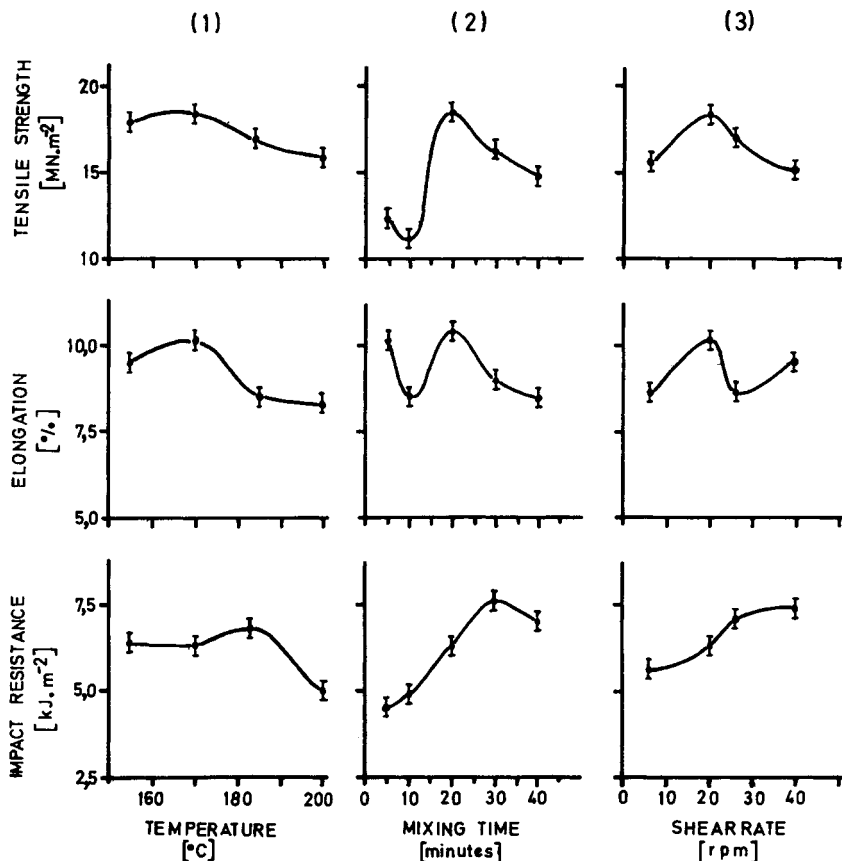
Fig. 1. Effects of processing variables on physical properties of blend: (1) 20 min, 20 rpm; (2) 170°C, 20 rpm; (3) 170°C, 20 min.

ties.[1,5,10] The morphology generated depends on the processing step. The effects of blending temperature, time, and shear rate in the mixing head on the blend properties were investigated (Fig. 1.), and blending conditions of 170°C for 20 min at a rotor speed of 20 rpm were found to yield a product with optimum properties. Microscopic examination of the blends showed a refinement of the domains with increased mixing time up to 20 min, after which time a certain coarsening in structure was evident. This coarsening was very pronounced in blends prepared at higher temperatures, while higher temperatures and/or longer mixing times also lead to a discoloring of the sample indicating degradation of the PVC.

PE had the lower melt viscosity at the temperatures of blending and of molding and formed the continuous phase and PVC the dispersed phase. This structure is consistent with the results of Han and Yu[5] who showed that the material with the lower melt viscosity would constitute the continuous phase.

Reproducibility of the blending and molding conditions were checked by carrying out tests on 15 tensile specimens cut from a number of similarly blended and molded samples. These yielded average values for tensile strength of 18.42 ± 0.46 MN m^{-2} (1 MN m^{-2} = 145 psi) and percentage elongation 10.3 ± 0.6%.

TABLE II
Properties of Pure Polymers and Normal Blend

Polymer	Tensile strength, MN m^{-2}	Elongation, %	Impact resistance, kJ m^{-2}[a]
PVC	37.0	14.0	36.0
PE	19.5	>110	>130
PE–PVC	18.4	10.3	6.2

[a] 1 kJ m^{-2} = 0.4744 ft lbf in^{-2}.

TABLE III
Effects of Fillers on the Physical Properties of Blends

Filler type	Filler	Mass % added	Tensile strength, MN m^{-2}	Elongation, %	Impact resistance, kJ m^{-2}
Fibrous	asbestos	10	17.9	9.2	10.9
		20	14.5	8.0	8.4
Particulate	carbon	5	20.9	8.8	7.6
	black	10	18.0	7.9	6.8
Rubber-like					
SBR		5	15.5	9.6	12.9
EPDM		10	10.3	9.0	11.9
Neoprene		5	13.6	10.1	7.1
Neoprene		10	10.9	10.5	7.9
EVA		5	15.7	17.4	14.3
EVA		10	12.1	25.7	20.1
Normal blend		—	18.4	10.3	6.2

Additives

Table III shows that the physical properties of the filler modified blends were little different from those of the unfilled material, and small changes observed were consistent with that expected for particulate and for rubber-filled polymers, respectively. Only the EVA-filled blends showed noticeably different properties. The copolymer is almost completely amorphous, and the acetate group is claimed to have an adhesive effect with most polymeric materials. Its effect may thus have been to improve adhesion between the phases. DSC analysis of the compounded blend yielded curves that coincided closely with those for the normal PE–PVC blend, showing that the structure and percentage crystallinity of the PE phase remained unaltered by addition of EVA.

Crosslinking

In crosslinking experiments, optimum physical properties were obtained using 2% DCP (Table IV). These results agree with the work of Hoffman[11] who found that the degree of crosslinking obtainable can be significantly increased by increasing the peroxide concentration, but that additions beyond a certain optimum value no longer produced significant improvements in properties.

Examination of the fracture surfaces of tensile and impact specimens revealed lumps of varying sizes in the blends. TGA of these lumps showed that they comprised mainly PVC while an analysis of selected areas surrounding the lumps showed these regions to be rich in PE. A DSC analysis of lump material showed

TABLE IV

Effects of Crosslinking, and of Crosslinking with Additives,
on the Physical Properties of Blends

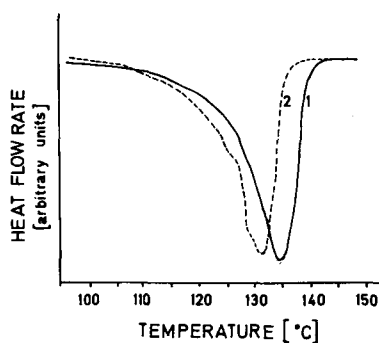| Crosslinking agent	Filler, mass-%	Tensile strength, MN m^{-2}	Elongation, %	Impact resistance, kJ m^{-2}
1% DCP	0	15.5	10.5	16.2
2% DCP	0	16.1	15.0	25.6
3% DCP	0	13.2	11.4	19.8
3% DCP	5% CB	21.3	16.6	15.4
3% DCP + 2% TAIC	5% CB	18.1	19.0	37.2
3% DCP	10% EPDM	18.7	15.5	8.8
3% DCP + 2% TAIC	10% EPDM	16.3	18.2	16.0

Fig. 2. DSC scans of (1) normal blend; (2) blend crosslinked with 3% DCP.

no crystallinity, thus supporting the TGA evidence. DSC analyses of random
samples of the blend crosslinked with 3% DCP showed the same percentage
crystallinity (36%) as was found in the absence of a crosslinking agent (35%).

Clearly, crosslinking was not severe enough to noticeably decrease the degree
of crystallinity in the PE. The crystalline regions in the areas surrounding the
lumps melted at slightly lower temperatures than was found for crystalline re-
gions in the normal blend (Fig. 2). This may indicate that crystallites were
somewhat smaller in the crosslinked blend. The improvements effected in the
percentage elongation and impact resistance using 1% and 2% DCP can there-
fore be ascribed to improved adhesion between the phases impeding the develop-
ment of crazes and cracks on deformation. Load transfer between the softer PE
and the harder PVC particles is improved. The deterioration in the elongation
at break and impact resistance on further increasing the percentage DCP may be
due to the more highly crosslinked PVC domains being too hard to respond
noticeably to deformation of the surrounding material. The presence of the
PVC lumps was very noticeable in these samples.

The slight deterioration in tensile strengths of all the crosslinked blends com-
pared to the normal blend could be explained in terms of the formation of smaller
crystallites as suggested above.

Crosslinking with Additives

The properties of blends containing additives plus crosslinking agents are
shown in Table IV. Triallyl isocyanurate (TAIC) added to some blends is
used as an accelerating agent for the crosslinking process of peroxides.[11]

TABLE V
DSC Analyses of Crosslinked Blends Containing Fillers

Blend	% Crystallinity	Peak temp., °C
PE–PVC	35	133
PE–PVC–10% EPDM	53	133
PE PVC–10% EPDM–3% DCP	46	127
PE–PVC–10% EPDM–3% DCP– 2% TAIC	43	123
PE–PVC–5% CB	54	133
PE–PVC–5% CB–3% DCP	48	128

DSC scans of these blends showed that increased crosslinking led to a decrease in the DSC peak temperatures similar to those described above. No distinct PVC lumps were evident and the percentage crystallinity in the EPDM-filled samples was considerably higher than in the normal blend (Table V). EPDM is compatible with PE and may have acted as a plasticizer reducing the PE melt viscosity and hence increasing the degree of crystallinity. In the presence of carbon black, the percentage crystallinity showed a similar increase. Carbon black particles may act as nuclei for crystal growth and hence increase the degree of crystallinity in these samples. Its use is known to decrease the crystallite size in PE but no such size reduction was evident from the melting ranges and peak values of the DSC scans. It should be remembered that the percentage crystallinity was low in our samples, and a size reduction may only be evident in highly crystalline samples where the growing nuclei readily overlap. In the presence of both EPDM and CB, the degree of crystallinity was found to decrease on increasing the crosslinking as was to be expected.

It can be seen from Table IV that the tensile strength of the blends produced under these conditions were very similar to those of the normal blend though a deterioration in tensile strength was evident with increased crosslinking in the absence of fillers, and may similarly be ascribed to a decrease in crystallite size (as reflected in the lower DSC peak temperature) or to the more highly crosslinked PVC becoming less ductile. Rigid PVC particles resist deformation, and large stress concentrations will develop in the surrounding PE matrix during testing. The slightly higher tensile strength (21.3 MN m^{-2}) of the CB-filled sample compared to that of the EPDM-filled blend (18.7 MN m^{-2}) may be ascribed to the reinforcing properties of CB and the plasticizing properties of the rubber-like EPDM. Both blends have a similar percentage crystallinity.

The closely similar improvements in the percentage elongation with both the solid CB filler and the rubber-like EPDM filler suggested that improved adhesion resulting from crosslinking was the most important factor in determining elongation. This conclusion was supported by the improved impact resistance where better adhesion between phases would impede the development and propagation of microcracks. The CB-filled sample was far superior to the EPDM-filled blend, though in the absence of a crosslinking agent (Table III), the EPDM-filled blend showed better impact resistance. This could be ascribed to the combined effects of CB filler in strengthening the softer PE phase, together with improved adhesion to the larger rigid PVC domains.

Influence of Dispersed Polymer Particle Size

Continuation of mixing beyond a certain time did not improve the properties of the blend and microscopic examination revealed that the domain size did not decrease beyond a certain point. It has been shown[5] that even where polymer powders are substituted for pellets, much the same degree of dispersion finally results. In an effort to increase the degree of dispersion of the two phases, it was decided to coprecipitate these from a common solvent.

The solubility of PE is extremely low even at elevated temperatures, and a large disparity exists between its solubility and that of PVC. This experiment was therefore carried out using a PVC-PS mixture. Equal masses of PVC and PS were dissolved separately in tetrahydrofuran (THF), and the solutions were added together. The solution was stirred vigorously and the polymers co-precipitated by the rapid addition of methanol. The precipitate was dried thoroughly.

A portion of the coprecipitated mixture was molded and tested. Another portion was mixed in the Brabender at the standard conditions used in this study and then molded and tested.

Use of the PVC-PS blend necessitated preparation of a reference melt blend from premixed pellets at the standard conditions as well as the mixing of pure PS on the Brabender. PS formed the continuous phase and PVC the dispersed phase as in the PE-PVC blends.

The tensile strength of the precipitated blend was far superior to that of any of the melt blends and was of the same order of magnitude as that of the pure materials (Table VI). The pelleted melt-blended sample had a considerably inferior tensile strength as had the precipitated sample that was subsequently melt blended. It has been shown[12] that phase separation occurs, even in solution yet the results here clearly illustrate that if the domain size can be reduced a marked improvement in tensile strength can be expected. On melt blending, domain sizes increase owing to the incompatibility of the polymers and the tensile strengths of the samples decrease.

The precipitated sample showed an improved percentage elongation over the melt-blended samples. This could be explained in terms of improved dispersion and the existence of smaller stress concentration around the smaller PVC "filler" particles. Improved adhesion between phases would also result from the increased interpenetration of polymer chains between phases.

The impact resistance of all blends was poor as was to be expected for a mixture of two polymers that are in themselves brittle.

TABLE VI
Effects of Processing on the Physical Properties of PVC-PS Blends

Blend	Tensile strength, MN m^{-2}	Elongation, %	Impact resistance, kJ m^{-2}
Pure PVC	37.0	14.0	36.0
Pure PS	32.0	10.0	6.1
Precipitated PS-PVC	37.5	9.2	3.8
Precipitated and melt blended	15.9	6.5	3.8
Pellets melt blended	20.2	7.6	4.8

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