

Mechanical Properties of a Polymer Blend Obtained through *In Situ* Crosslinking of the Dispersed Phase

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ABSTRACT: Blends of a polypropylene matrix and a miscible phase of ethylene vinyl acetate and ethylene methyl acrylate copolymers were produced by twin-screw extrusion. The miscible phase can be crosslinked *in situ* through a catalyzed transesterification reaction. Mechanical properties of reactive and nonreactive blends were characterized. Impact properties increase with the concentration of elastomeric phase and are improved by the crosslinking reaction. Yield stress and Young modulus are not modified by the reaction, but tensile stress and elongation at break are improved, which suggests the development of network structure at the interface. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1385–1390, 1997

Key words: reactive blend; mechanical properties; polypropylene

INTRODUCTION

In recent years, different authors have reported that a major improvement in some mechanical properties of polymers could be obtained from blending processing.^{1–3} For instance, conventional polypropylene (PP) has several distinctive engineering properties, but its impact strength at low temperature is moderate, due to the high glass transition temperature of the polymer ($T_g \sim 0^\circ\text{C}$). Therefore, the impact strength at low temperature of conventional PP is generally enhanced by blending with various polymers, such as rubber polymers.^{4–8} On the other hand, the end-use properties of these polymer blends are mainly dependent on the structure that develops during processing.^{9–12}

Actually, rubber particle size and rubber–matrix adhesion are two important factors determining the toughness of polymer rubber blends.¹³ Therefore, a reactive processing operation, where some type of chemical reaction can be expected during the melt mixing stage, seems an original way to improve the impact properties.¹⁴

In the present work, we studied the effect of an *in situ* crosslinking of the dispersed phase on the impact toughness and tensile-strength properties of a based PP blend. This blend is constituted by a PP matrix, in which is dispersed by twin-screw extrusion a phase made of two miscible copolymers (ethylene vinyl acetate, EVA, and ethylene methyl acrylate, EMA). The chemical reaction of crosslinking of the EVA-EMA phase is an exchange reaction of ester groups of the two copolymers, in the presence of dibutyltin oxide as precursor of the catalyst system. It was shown in previous experimental and theoretical studies^{15,16} that the crosslinking of the elastomeric phase permitted the control and the stabilization of the morphology, i.e., particle size distribution in the melt.

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EXPERIMENTAL

The experimental work on blend elaboration was carefully described in previous work.^{15–17} Consequently, we only focus hereafter on the main elements necessary for a clear understanding of the present article.

Materials

Polymers used were provided by Elf-Atochem company. PP is an Appryl 3120MN1 (melt index 12), EVA (Evatane 2803) and EMA (Lotryl 29MA03) are commercial copolymers, containing respectively in weight 28% of vinyl acetate and 29% of methyl acrylate.

The crosslinking of the EVA–EMA phase in the molten state is due to the transesterification reaction of ester groups of EVA and EMA copolymers. This reaction was well characterized by chemical and rheological experiments.¹⁸ Furthermore, it was shown¹⁹ that the gel fraction and the extent of the reaction can be linked together from Flory's theory on rubber elasticity. Consequently, the gel fraction can be used as a quantitative estimation of the network structure of the dispersed phase.

Processing Equipments

Extrusion experiments were carried out with an intermeshing self-wiping corotating twin-screw extruder (Clextral BC 45, centerline distance: $C_1 = 45$ mm, screw diameter: $D = 50$ mm, barrel length: $L = 1.825$ m, $L/D = 36.5$). The extrusion conditions were adjusted from previous results in order to obtain a high level of crosslinking of the EVA–EMA phase at the die exit. These conditions are as follows: screw speed: 100 rpm, feed rate: 15 kg/h, melt temperature at the die exit: 200°C. With such processing conditions, a mean residence time of about 3 min was measured in the extruder.

Samples Preparation

In Table I are reported the different blend compositions used in the study and the network structure of the EVA–EMA phase at the die exit, char-

Table I Composition of PP/EVA–EMA Blends and Gel Fraction of the EVA–EMA Phase

Blend Composition % of EVA–EMA (in Weight)	Gel Fraction
5	—
10	0.60
20	0.50
30	0.50
40	0.15
50	0.20

acterized by the gel fraction. The concentration of dibutyltin oxide in the EVA–EMA phase was reduced to 2% for the proportions of EVA–EMA of 40 and 50% in the blend (for which a cocontinuous phase was observed), because the crosslinking of the EVA–EMA phase led to very high pressure at the diehead. After extrusion, the blends were injection molded at 200°C under 10 MPa into 2 mm thick bars, which were used for the mechanical tests (impact and tensile tests).

Mechanical Tests

Impact strength was characterized at -30°C on a pendulum-type Charpy machine, according to ISO 179. The sample is percuted by a pendulum at constant speed and the corresponding break-up energy is recorded.

A conventional Instron testing machine was used for the tensile characterizations. A constant speed of 50 mm/mn was selected, according to ISO R527. The tensile force is recorded as a function of the deformation. From these measurements, we can deduce the yield stress σ_y , the yields strain ϵ_y , the Young modulus ($E = \sigma_y/\epsilon_y$), and elongation and tensile strength at break.

These experiments were carried out as a function of the blend composition, and for both reactive and nonreactive (it means without catalyst) blends.

RESULTS AND DISCUSSION

Impact Strength

The dependence of impact strength on composition of the blend, with and without crosslinking of the EVA–EMA phase, is shown in Figure 1.

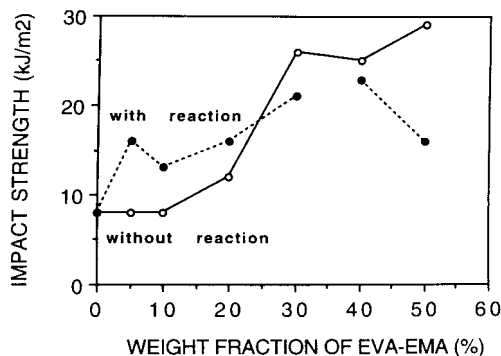


Figure 1 Impact strength as a function of blend composition. ●: with chemical crosslinking reaction; ○: without chemical reaction.

Without Chemical Reaction

We can observe that impact strength increases monotonously with increasing the concentration of the elastomeric phase. At concentrations lower than 30%, these results are in good agreement with those of Thomas²⁰ on PP/EVA blends. Following the criterion for rubber toughening proposed by Wu,¹³ these results mean that the blends at those concentrations present a homogeneity of their morphological structure, with a low particle size ($d < 0.8 \mu\text{m}$), which was confirmed by scanning electronic microscopy observations.^{15,17} At higher concentrations (40 and 50%, respectively), Wu's criterion can no more be applied, as we observe a cocontinuous morphology. In this region, the impact strength remains approximatively constant. Then, these results put in evidence that a concentration of around 30% of EVA–EMA elastomeric phase is an optimal concentration for improving the impact strength of PP.

With Chemical Crosslinking Reaction

It was shown in a previous study¹⁵ that for the fully crosslinked dispersed phase (gel fraction ~ 0.4), the final morphology remained remarkably stable during successive processing steps. Nevertheless, the increase of the viscosity and the elasticity of the dispersed phase during the development of the crosslinking reaction shifted the equilibrium between breakup and coalescence (or coagulation) and led to larger particles compared with the uncrosslinked blend with the same mixing history. For example, at a concentration of 20% of EVA–EMA, the mean diameter of the particles increases approximatively by a factor two as the reaction develops (from 0.36 to 0.70 μm ,

respectively). Despite this fact, Figure 1 shows that the *in situ* crosslinking of the dispersed phase tends to improve impact strength for concentration of EVA–EMA lower than 30%. These results cannot be exclusively explained from the Wu's generalized criterion for rubber toughening²¹ because the morphology of the crosslinked EVA–EMA phase is not homogeneous and presents higher particle size with coagulation aspect, as shown in Figure 2. The observation, in a previous work,¹⁵ of a low-frequency plateau of the elastic modulus suggested high interactions at the interface, due to the formation of a network-type structure. Therefore, these results suggest that the matrix/elastomeric phase interaction is also an im-

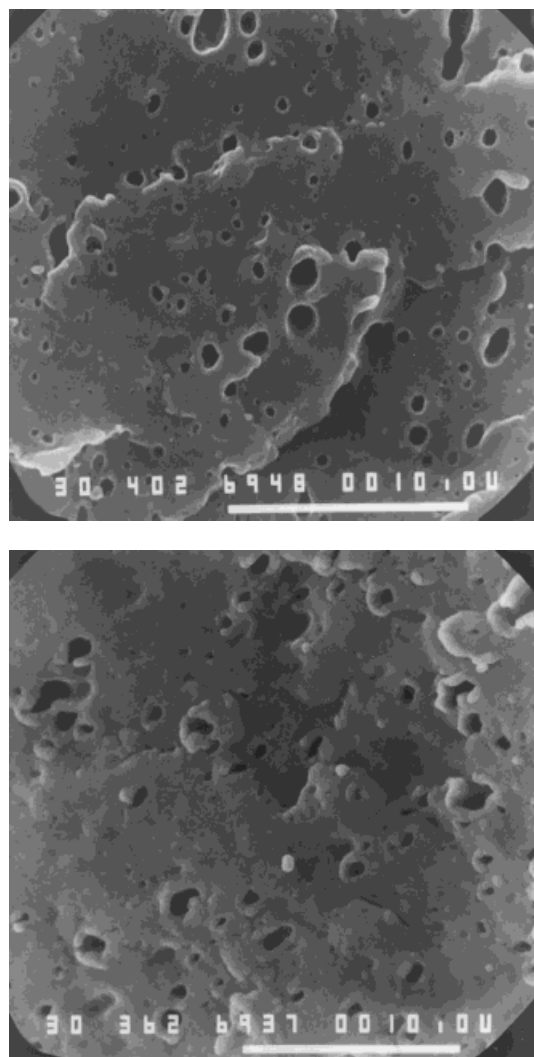


Figure 2 SEM pictures of (a) nonreactive and (b) reactive blend, after solvent extraction of the dispersed phase. 80/20 blend composition.

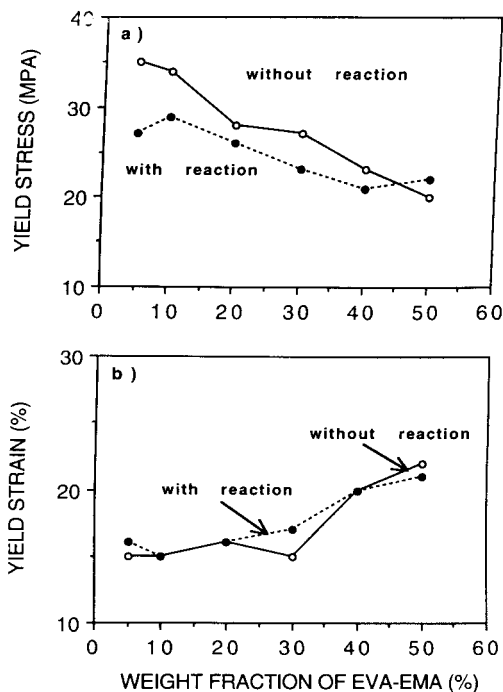


Figure 3 Yield stress (a) and yield strain (b) properties as a function of blend composition.

portant factor for improving impact strength, in the limit of the applicability of the Wu's criterion on domain size and dispersed phase spacing. These results will be confirmed in the later part from tensile properties.

At the values above 30% of EVA-EMA corresponding to a smaller amount of catalyst, the impact strength drastically decreases. Such a behavior can be attributed to the cocontinuous morphology, with a brittle behavior of the slightly crosslinked EVA-EMA phase (gel fraction < 0.2)

Tensile Properties

Yield Stress (σ_y) and Yield Strain (ϵ_y)

The yield stress and the yield strain of the blend at different compositions are shown in Figure 3(a) and (b), respectively. Figure 3(a) shows that yield stress slowly decreases with increasing the content of the elastomeric phase. These results qualitatively agree with those of Thomas on PP/EVA blends,²⁰ who explains that yield stress depends of the crystallinity of PP, which was observed to decrease with the elastomeric composition. Furthermore, it was observed by other authors that PP-based blends, such as PP/EPR,²²

PP/HDPE/EPDM,²³ and PP/PE,²⁴ similarly behave. On the other hand, the crosslinking of the dispersed phase lead to slightly lower values of the yield stress. This difference with the nonreactive system may be attributed to the thermal degradation of the polypropylene matrix, induced by the dibutyltin oxide.

Yield strain slightly increases with increasing the amount of EVA-EMA phase in the blend. However, the crosslinking of the dispersed phase does not modify the yield strain behavior of the blend. Accordingly to these results, yield properties of the PP/EVA-EMA blends change monotonously with composition of the blend, but are less sensitive to the chemical modification of the EVA-EMA phase. Similarly, an identical trend was observed for the variations of the Young modulus, as shown in Figure 4. These results prove that the modulus of heterogeneous polymer systems depends mostly on the components and on the composition, and is less sensitive to eventual interfacial interactions and morphological changes, as previously observed by Pukanszky et al.^{25,26}

Ultimate Tensile Strength

Contrarily to Young modulus, mechanical characteristics measured at large deformations, especially failure properties, show much stronger dependence on crosslinking of the EVA-EMA phase [Fig. 5(a)-(b)]. Figure 5(a) shows that the tensile stresses at break of the reactive blends are considerably higher than those of nonreactive blends. These results qualitatively agree with works on vulcanization of rubber phase in polyolefin blends.^{27,28}

On the other hand, *in situ* crosslinking of the elastomeric phase results in an increase in the

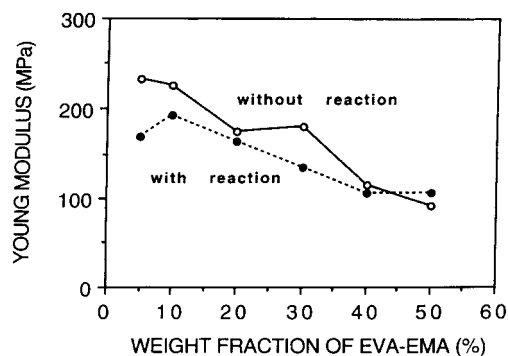


Figure 4 Young modulus at room temperature as a function of blend composition.

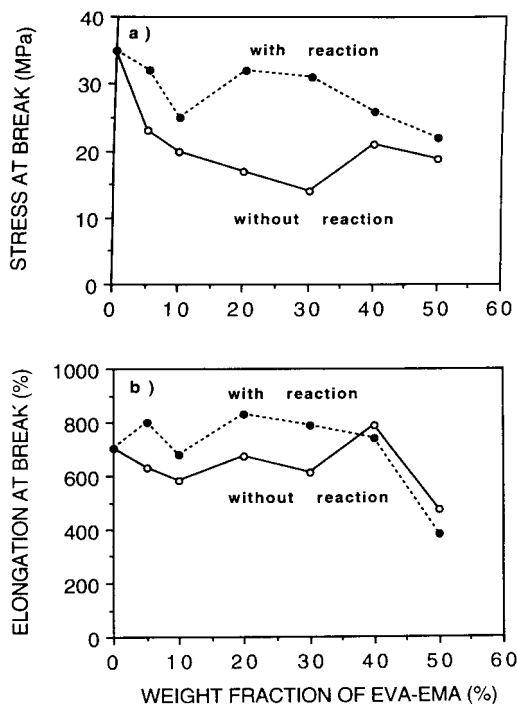


Figure 5 Ultimate tensile properties as a function of blend composition: (a) tensile stress and (b) elongation at break.

elongation at break. A significant improvement was observed for the compositions lower than 30% of EVA–EMA phase. For these compositions, both tensile strength and elongation at break increase with crosslinking of the dispersed phase. Further increase of the EVA–EMA fraction, with or without crosslinking, leads to a dramatic drop of the mechanical properties.

The improvement of the elongational properties of the reactive system suggests that a good transfer across the interface is ensured by a network structure at the interface, as already observed by Legros et al. on PET/EVA blends.²⁹ In order to explain the network structure, some experiments were carried out on a mechanical spectrometer (Rheometrics RMS 800) using a parallel plate geometry. Furthermore, a previous result¹⁵ on rheological behavior of these reactive blends had already put into evidence the existence of high interactions at the interface. From this idea, a reactive blend constituted by 80% PP and 20% EVA–EMA dispersed phase was cured 1 h at the temperature of 216°C. Then, Figure 6 shows the viscoelastic behavior of this sample at the temperature of 160°C. At low frequencies, a secondary plateau is clearly observed. This plateau could be

attributed to an agglomeration of the EVA–EMA particles. Actually, SEM observations refuted this assumption. Therefore, the origine of this plateau can provide from the presence of an interphase matrix particle, which could induce a modification of long relaxation time mechanisms by trapping physical entanglements of the matrix chains. Indeed, on SEM pictures of the Figure 2(b), it may be observed that the outline of the droplets was very different between the reactive blend and the nonreactive blend. The shapes were more irregular and the picture suggests the presence of an interphase PP-(EVA–EMA), which has been swollen by the solvent during the extraction step of the EVA–EMA phase. On the other hand, viscoelastic behavior³⁰ of (EVA–EMA)/PP constituted in weight of 80% EVA–EMA matrix and 20% PP dispersed phase, showed that interactions other than hydrodynamic ones can exist in the interfacial region. On the other hand, from the theoretical evaluation of the thickness of the interphase and the radius giration of macromolecular chain a concept of an interfacial volume was defined. From this concept point of view and assuming that a direct interaction among dispersed droplets cannot be unambiguously excluded because the percolation threshold for the system of monodisperse spheres is $\varphi = 0.156$, we can imagine an interconnectivity between EVA–EMA droplets through the physical entanglements of the matrix trapped by the EVA–EMA network in the interfacial volume.

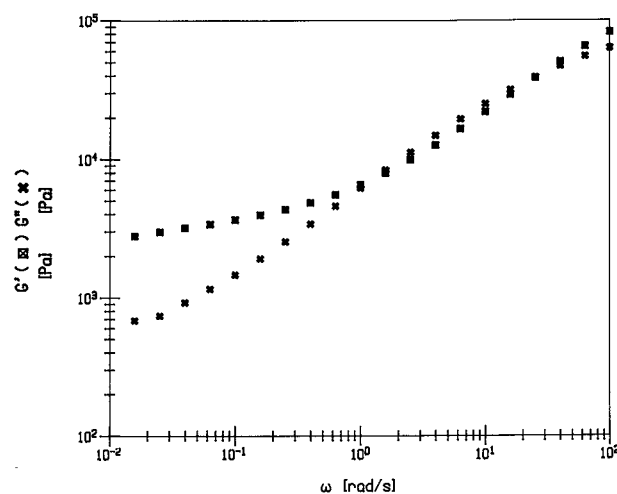


Figure 6 Viscoelastic behavior of a reactive blend (80/20) after curing (1 h) at $T = 216^\circ\text{C}$.

CONCLUSIONS

In this work, significant evidence has been found to support the *in situ* crosslinking of the elastomeric phase of a PP/EVA–EMA blend, for improving its mechanical properties. Improvement of the impact strength and ultimate tensile strain properties of the reactive system suggests that a network-type structure develops at the interphase, ensuring a good adhesion between the two phases. Same assumption was proposed previously on the base of rheological experiments¹⁵ and confirmed in this study.

Mechanical properties drastically drop with the development of a cocontinuous system when the composition of the EVA–EMA phase is higher than 30%. A 70 PP/30 EVA–EMA composition seems to be optimal in terms of mechanical behavior.

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