

Yield Strength of Low-Density Polyethylene–Polypropylene Blends

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ABSTRACT: Polymer waste recycling is becoming a major problem, because huge amounts of synthetic polymers are manufactured every year for many different purposes. Polymer scraps are gathered from the Municipal Solid Waste (MSW). Within those wastes there are several different polyolefins—such as polyethylene, polypropylene, and polystyrene—all incompatible with each other. In order to recycle these polymers, compatibilization of these polyolefins is needed to avoid high sorting costs and unacceptably low market-value products. In this work, the compatibilization of low-density polyethylene with polypropylene is accomplished through the addition of maleated polyethylene and maleated polypropylene. Prediction of the tensile properties of these blends is attempted, using a model based on continuity of phases in a two-components mixture of thermoplastics. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 275–281, 1997

Key words: polymer blends; yield strength; maleated polyolefins; compatibilization; phase continuity

INTRODUCTION

Blending of polymers represents one of the most cost-effective ways to upgrade material properties and, hence, has the potential to be a reliable and cheap way to recycle them.^{1,2} On the other hand, polymers are generally insoluble in each other; thus, their blends show rather poor mechanical properties.^{3–5} Compatibilization is needed in order to improve mechanical performance and make recycling favorable. The addition of small amounts of maleic anhydride-grafted polyolefins (“maleated polyolefins”) has been shown to be a successful method of compatibilization of low-density polyethylene (LDPE)–polypropylene (PP) blends.^{6,7} The moieties of maleic anhydride are grafted onto the polymers and rapidly hydrolyze to esters in the presence of moisture, thus forming

strong hydrogen bonds. This results in an improved interphase adhesion between the two immiscible polymers.

The degree of compatibilization can be evaluated in terms of the change in the mechanical properties of the blend. The prediction of mechanical properties using models for the blending of multi-component materials is important for determining the maximum potential obtainable in the mechanical properties of the blend. There are numerous models able to predict, with reasonable accuracy, the modulus^{8,9} and the yield strength^{10–12} of multi-phase systems with a given phase structure. A common method of examining the degree of compatibility is to compare a measured mechanical property of a blend to the value obtained as the weighted average of the pure components of the mixture,^{10,13} as stated by the “rule of mixtures.” For example, the yield strength of a blend may be written in terms of the properties of the constituents:

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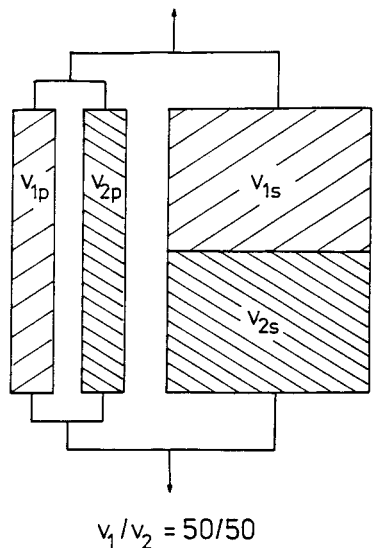


Figure 1 Equivalent box models for binary blends with composition 50/50 by volume (after ref. 14).

$$S_{ybrm} = S_{y1}v_1 + S_{y2}v_2 \quad (1)$$

where S_{y1} and S_{y2} are the yield strengths of components 1 and 2, respectively, v_1 and v_2 the volume fractions of components 1 and 2, and S_{ybrm} the yield strength of the blend. This simple rule of mixtures applies for good adhesion between the phases. There is ample experimental evidence to show that the phase structure of a polymer blend affects its elastic modulus, yield strength, and other ultimate properties. Usually, qualitative evaluation of the continuity of phases can be performed by electron microscopy, even though sometimes a quantitative measurement is rather difficult to achieve. In this article, we characterize the yield strength for blends of low-density polyethylene with polypropylene using a model proposed by Kolarik.^{14,15} These two polyolefins, usually reported as immiscible,⁴ were chosen because they represent a large percentage of the MSW. This model allows one to predict the potential bounds for the yield strength for perfect adhesion (upper bound) and no adhesion (lower bound). Two limiting cases are identified as lower (“series” coupling) and upper (“parallel” coupling) bounds (Fig. 1) that can be interpreted as

1. Very weak interfacial adhesion, so that debonding occurs between the fractions coupled in series. Thus, the series branch does

not affect the resulting yield strength, which is determined only by the parallel branch:

$$S_{yb-} = S_{y1}v_{1p} + S_{y2}v_{2p} \quad (2)$$

where v_{1p} and v_{2p} are the volume fractions of components 1 and 2, respectively, which can be considered as coupled in parallel to the acting force.

2. The interfacial adhesion is strong enough to transmit stress between the components; the series branch is to add to the parallel one.

$$S_{yb+} = (S_{y1}v_{1p} + S_{y2}v_{2p}) + \{v_s[(v_{1s}/S_{y1}) + (v_{2s}/S_{y2})]\}v_s \quad (3)$$

where v_{1s} and v_{2s} are the volume fractions of components 1 and 2, respectively, which can be considered as coupled in series, and v_s is the sum of them.

The volume fractions coupled in parallel or in series are related to each other by the phase continuity parameters C_1 and C_2 , which express the fraction of component 1 or 2 that can be considered as coupled in parallel to the acting force:

$$v_{1p} = v_1 C_1; \quad v_{2p} = v_2 C_2$$

$$v_{1s} = v_1(1 - C_1); \quad v_{2s} = v_2(1 - C_2)$$

Also, it can be shown¹⁵ that

$$v_{1p} = [(v_1 - v_{1cr})/(1 - v_{1cr})]^{T_1}, \quad \text{and}$$

$$v_{2p} = [(v_2 - v_{2cr})/(1 - v_{2cr})]^{T_2},$$

where v_{1cr} and v_{2cr} are the critical volume fractions (the percolation thresholds) for the components 1 and 2, respectively; T_1 and T_2 the critical exponent for a three dimensional lattice.¹⁶⁻¹⁸

The above relations allow the calculations of all the parameters required for the prediction of yield strengths.

This model has been applied successfully to our LDPE-PP blends, since they satisfy all the assumptions required for the model to work: i.e., blending does not affect structural characteristics of the components, such as degree of crystallinity and the spherical shape of the dispersed phase. The constants needed for the calculations of yield strength are readily available in literature.^{16,17}

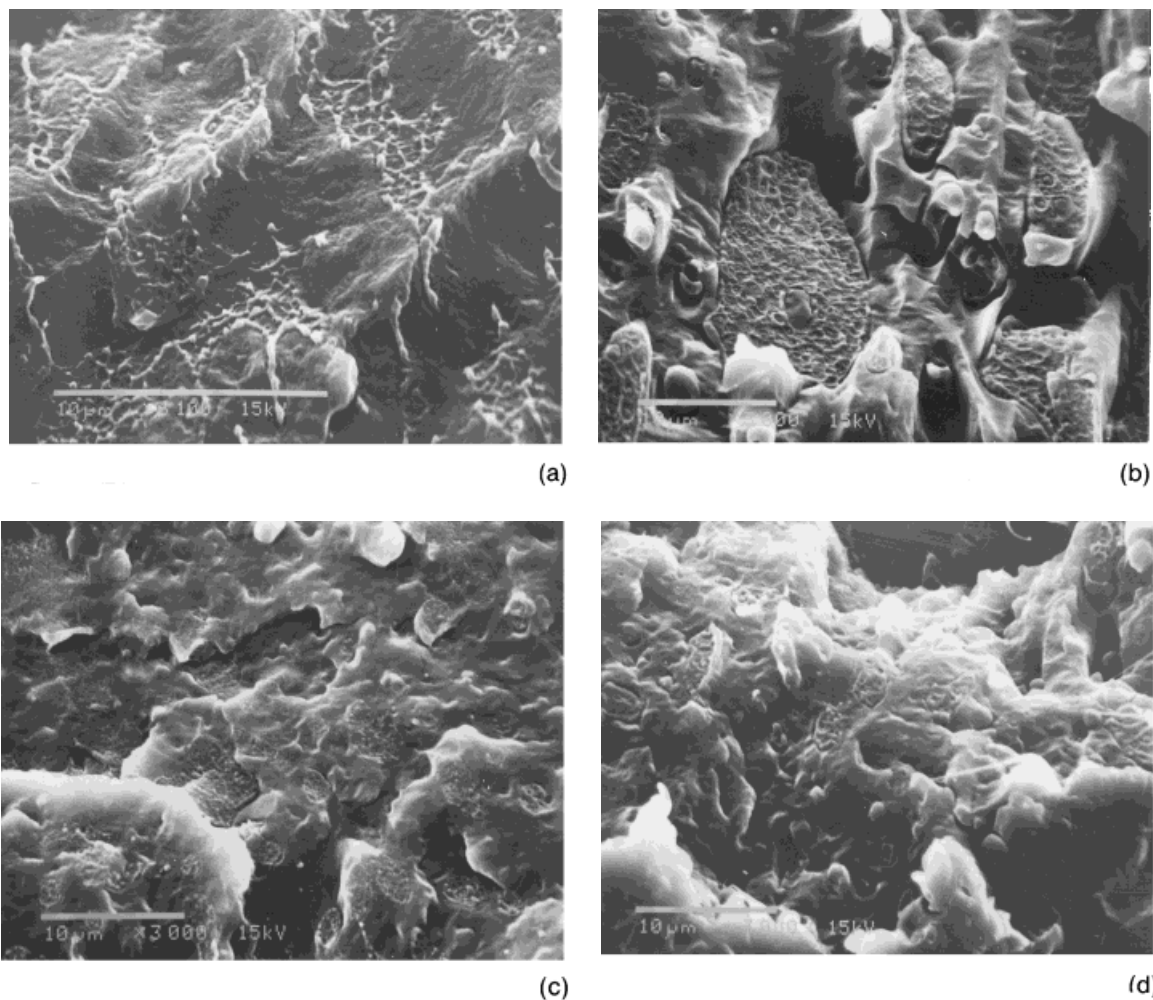


Figure 2 SEM photomicrographs of 25% maleated PE/PP 50/50 (a) and 30/70 (c), neat 50/50 (b) and 30/70 (d).

The relation of the measured values of the yield strength of the blends to the upper and lower bounds are, thus, used as a measure of the degree of adhesion between phases and, along with examination of phase size and degree of dispersion, an indication of the extent of compatibilization of the blend components.

EXPERIMENTAL

Maleated polypropylene (Polybond[™] 3001) and maleated polyethylene (Polybond[™] 3009) were obtained from Uniroyal Chemical. Low-density polyethylene and polypropylene were commercial products available in our laboratories. All the polymers were supplied in form of pellets.

Pellets of different polymers were blended in a twin-screw Brabender mixer at 190°C for 12 min at 50 r.p.m.

Three different sets of blends were prepared: (1) neat polyolefins, (2) neat polyolefins with 25% on total weight of maleated polyolefins, and (3) maleated polyolefins.

Dog-bones specimens (cross-section area: 3.9 mm², gauge length: 21.68 mm) were compression molded in a Wabash heat press at 200°C for 5 min, then water quenched under pressure.

Yield strengths were measured using an Instron 1011 tensile machine, equipped with a 100 lb load cell, with a crosshead speed of 10 mm/min.

Differential scanning calorimetry was carried out with a Perkin-Elmer DSC7 thermal analyzer under nitrogen atmosphere. Samples (11 ± 1 mg)

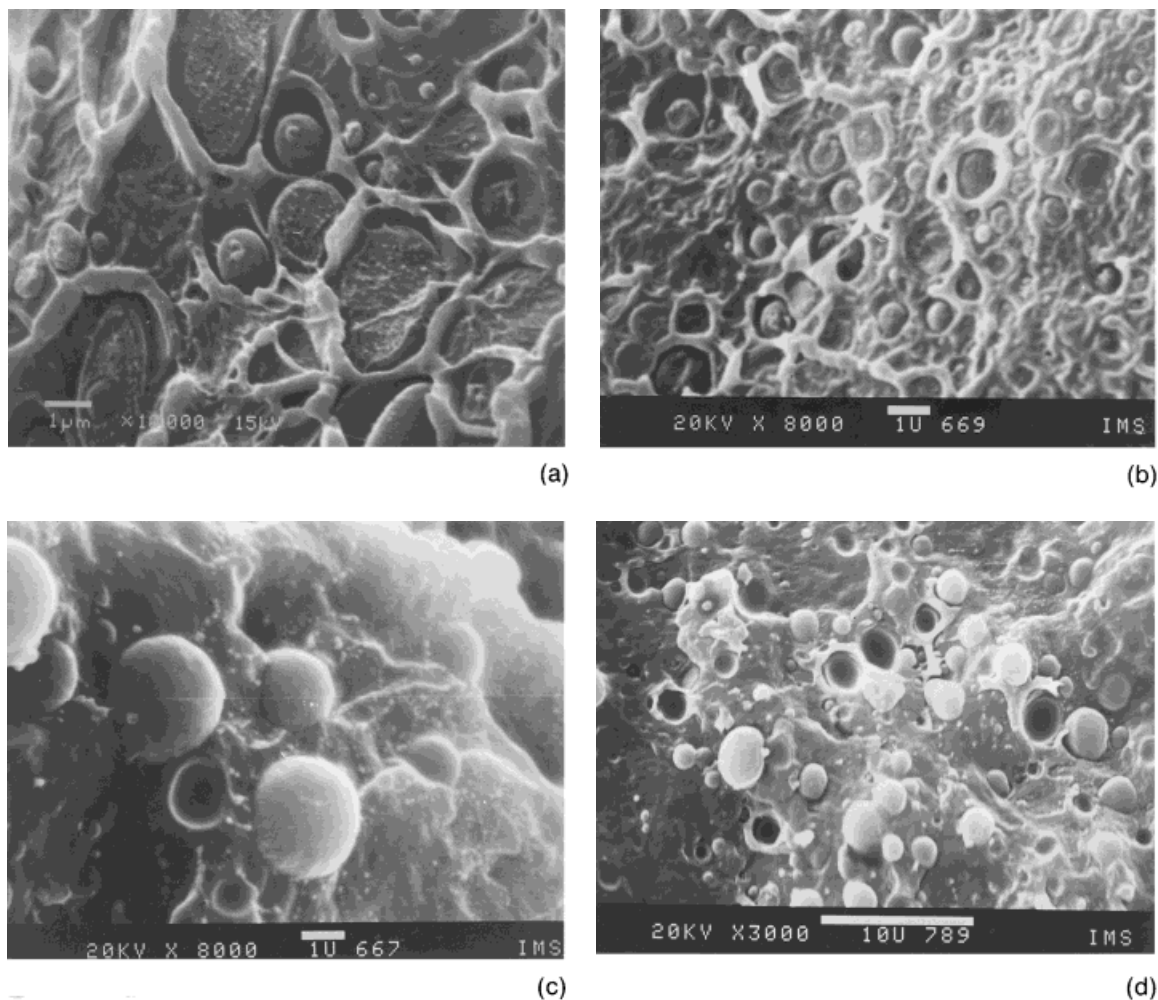


Figure 3 SEM photomicrographs of PE/PP 70/30 (a), 90/10 (b), 10/90 (c,d).

were heated from 50 to 200°C at 10°C/min and held at that temperature for 3 min to eliminate thermal history effects. They were then cooled to 50°C (10°C/min), maintained there for 3 min, and heated again up to 200°C, recording the melting behavior in that range of temperature.

Micrographs were taken with an Amray 1200 B scanning electron microscope. Samples were notched, frozen in liquid nitrogen, cryo-fractured, and then coated with an Au/Pd alloy.

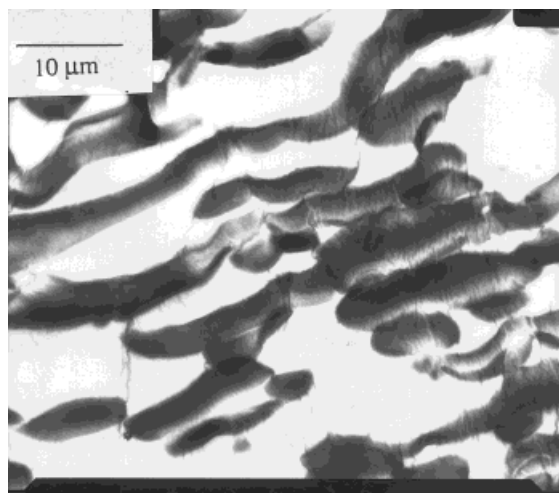
Samples were also examined using transmission electron microscopy. Thin sections were microtomed and the polyethylene phase then stained with ruthenium tetroxide.

RESULTS AND DISCUSSION

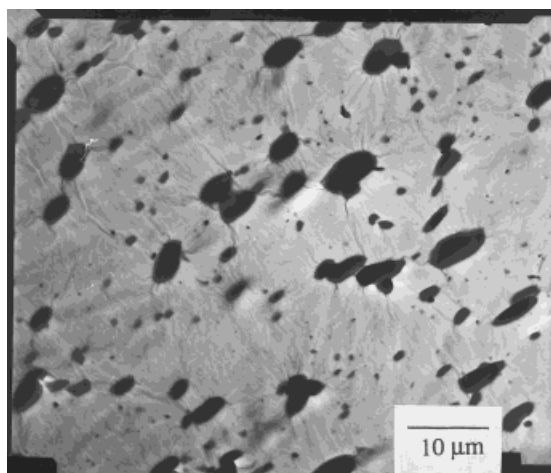
Kolarik's model has been utilized to characterize the yield strength of LDPE-PP blends, with or

without the presence of a compatibilizer. Interfacial adhesion has also been tested with the same approach.

Two basic conditions must hold in order to apply this model: Blending should not affect the properties of the pure components (e.g., crystallinity), and the blend should show a spherical phase structure. We checked the validity of both these conditions for our blends through electron microscopy and DSC. Micrographs of different compositions and different blends showed that the phase structure is the same in all the three cases (neat, partially maleated, totally maleated), namely, a dispersed phase, usually with spherical domains, in a matrix of the other component. The spherical particles are of the order of 2 to 12 μm , depending upon composition, and are better dispersed in the presence of the compatibilizer. For the neat blends, a substantial debonding between



(a)



(b)

Figure 4 TEM photomicrographs of neat PE/PP 50/50 blend (a) and 10/90 blend (b).

the phases is always observed; when the maleated polyolefins are present in the mixture a significant improvement of the interface is noted, along with the absence of cavitation, as can be seen from Figure 2. The occurrence of a phase inversion is also observed (Fig. 3). When the scanning electron microscopy technique was not powerful enough to clarify the phase structure, TEM was used. This allowed us to assign the proper phase structure for each component in each composition of the three blends. Figure 4 a shows TEM micrographs of the 50/50 (a) and 10/90 (b) LDPE/PP neat blends. Both SEM and TEM displayed an improvement in interfacial adhesion when male-

ated polyolefins are present in the blend. Melting temperatures and heats of fusion were measured using DSC for each composition of the three blends. It is clear that there is no change in crystallinity for the neat components, because both the melting temperature and the heat of fusion values remain unchanged, within experimental accuracy.

The parameters required for the calculations of the parallel and series volume fractions were found in literature^{16,17} and are

$$v_{1cr} = 0.157; \quad T_1 = 1.7$$

$$v_{2cr} = 0.03; \quad T_2 = 1.9$$

where 1 is the polyethylene phase and 2 is the polypropylene.

The lower and upper bounds for the three different blends were calculated according to eqs. (2) and (3); an "ideal" bound was also calculated using eq. (1) (Table I). Figures 5–7 show the comparison of the experimental data with the corresponding calculated values. All the experimental data, for the three kinds of blends, fit well with the predicted trend for the upper bound. The data for the totally maleated blend lay between the upper limit and the rule of mixtures results, which indicates that a strong interfacial adhesion has been achieved. The nonmaleated and the 25% maleated blends show good adhesion as well. Moreover, we should note that the observed values of the yield strengths of the partially maleated blends are about 10% higher than those of the neat PP/PE blends. This leads us to believe that the simple addition of a small percent of a compatibilizer (as maleated PP or PE) can result in a maintaining of good mechanical properties in blends of recycled polyolefins.

CONCLUSIONS

In this work a model for the prediction of yield strength of polymer blends has been tested to understand the potential of blending as a way to recycle large amounts of polymer wastes. The model has been showed to be appropriate for PE/PP blends, whose experimental yield strength values lay on the calculated upper bound. The addition of a relatively small amount of a compatibilizer (maleated PP and PE) leads to a main-

Table I Observed and Calculated Yield Strength for the Heat, 25% Maleated, 100% Maleated PE/PP Blends

| Sample PE/PP | $S_{yb,obs}$ (MPa) | S_{ybrm}^a (MPa) | S_{yb-}^b (MPa) | S_{yb+}^c (MPa) |
|---------------|--------------------|--------------------|-------------------|-------------------|
| Neat | | | | |
| 0/100 | 34.70 ± 0.03 | 34.70 | 34.70 | 34.70 |
| 10/90 | 32.48 ± 0.82 | 32.27 | 28.21 | 31.09 |
| 30/70 | 23.54 ± 1.32 | 27.40 | 17.68 | 24.58 |
| 50/50 | 20.42 ± 0.70 | 22.53 | 10.99 | 19.17 |
| 70/30 | 14.65 ± 0.44 | 17.67 | 7.96 | 14.84 |
| 90/10 | 11.45 ± 0.09 | 12.80 | 8.61 | 11.58 |
| 100/0 | 10.36 ± 0.13 | 10.36 | 10.36 | 10.36 |
| 25% Maleated | | | | |
| 0/100 | 38.38 ± 0.38 | 38.38 | 38.38 | 38.38 |
| 10/90 | 35.36 ± 0.99 | 35.90 | 31.20 | 34.82 |
| 30/70 | 27.36 ± 1.90 | 30.92 | 19.66 | 28.35 |
| 50/50 | 22.65 ± 0.78 | 25.94 | 12.60 | 22.89 |
| 70/30 | 17.75 ± 0.63 | 20.97 | 9.77 | 18.40 |
| 90/10 | 13.94 ± 0.12 | 16.00 | 11.17 | 14.89 |
| 100/0 | 13.51 ± 0.24 | 13.51 | 13.51 | 13.51 |
| 100% Maleated | | | | |
| 0/100 | 37.46 ± 0.60 | 37.46 | 37.46 | 37.46 |
| 10/90 | 36.49 ± 0.62 | 36.13 | 30.45 | 35.86 |
| 30/70 | 32.88 ± 0.67 | 33.46 | 19.72 | 32.81 |
| 50/50 | 29.39 ± 0.57 | 30.79 | 14.68 | 30.05 |
| 70/30 | 27.81 ± 0.86 | 28.13 | 14.71 | 27.50 |
| 90/10 | 25.30 ± 0.70 | 25.46 | 19.73 | 25.19 |
| 100/0 | 24.13 ± 0.15 | 24.13 | 24.13 | 24.13 |

^a From eq. (1).^b From eq. (2).^c From eq. (3).

taining of the yield strength of the blends, usually reported as immiscible, with rather low mechanical properties. The phase morphology of the

blends in the presence of compatibilizer is also improved, showing a finer dispersion and a better adhesion between the two phases.

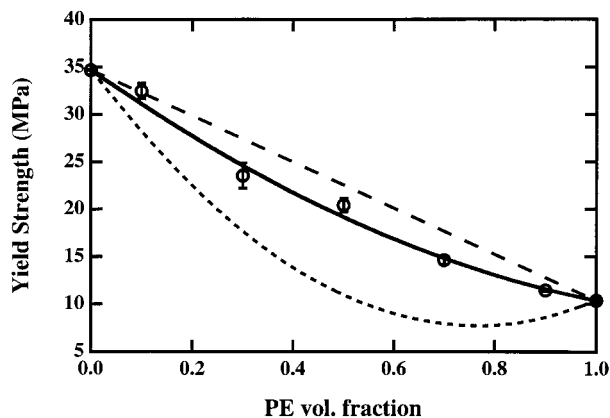


Figure 5 Comparison of calculated upper and lower bounds of yield strength with experimental data for “neat” PE/PP blends. Solid, dashed, and dotted lines represent the results obtained by eqs. (3), (1), and (2), respectively.

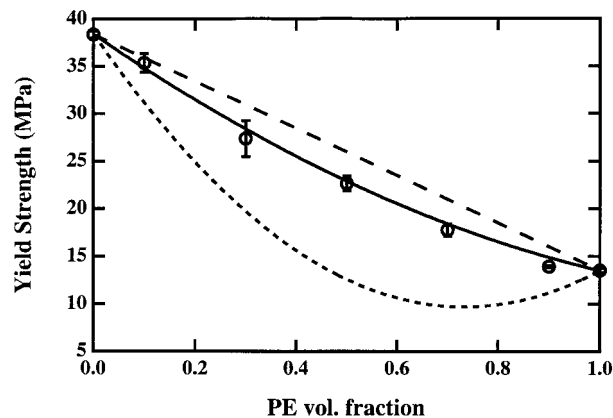


Figure 6 Comparison of calculated upper and lower bounds of yield strength with experimental data for PE/PP blends containing 25% of maleated PE and PP. Solid, dashed, and dotted lines represent the results obtained by eqs (3), (1), and (2), respectively.

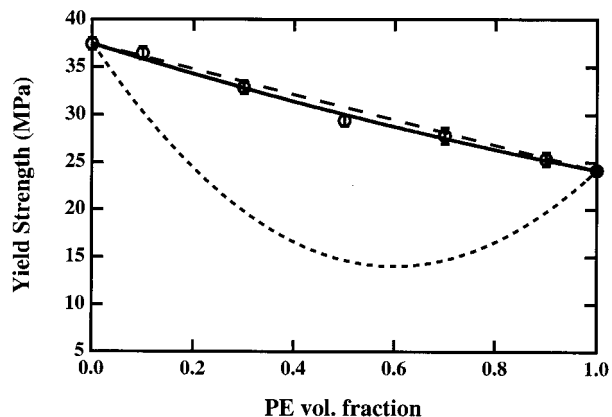


Figure 7 Comparison of calculated upper and lower bounds of yield strength with experimental data for maleated PE/maleated PP. Solid, dashed, and dotted lines represent the results obtained by eqs. (3), (1), and (2), respectively.

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