

Relationship Between Interfacial Tension and Dispersed-Phase Particle Size in Polymer Blends. II. PP/PA6

H. Shariatpanahi,^{1,2} H. Nazokdast,¹ M. Hemmati^{1,2}

¹Department of Polymer Engineering, Amir Kabir University, P.O. Box No. 15875, 4413 Tehran, Iran

²Department of Polymer Science and Technology, Research Institute of Petroleum Industry, P.O. Box No. 18745, 4163 Tehran, Iran

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ABSTRACT: Simple blends with different viscosity ratios of the components as well as compatibilized blends varying both in type and content of the compatibilizers were used to study the relation between the interfacial tension and the dispersed-phase particle size for PP/PA6 (80/20 wt %) blends in this work. Four compatibilizing systems including poly(ethylene-*co*-methacrylic acid) ionomers, a maleic anhydride-grafted propylene copolymer, maleic anhydride-grafted polypropylene, and a maleic anhydride-grafted styrene ethylene butylene copolymer were used. For blends

prepared in an internal mixer, a power-law relation was found between the capillary number and the torque ratio of the blends' components. This relation was used to estimate the interfacial tension for the compatibilized blends. The relation between the steady-state torque of the blends as a measure of viscosity and the estimated values of interfacial tension were also investigated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 54–63, 2003

Key words: morphology; compatibilization; viscosity

INTRODUCTION

Most of the polymer pairs exhibit weak interfacial interaction, which leads to an unstable course morphology and poor mechanical properties when compounded in the form of immiscible blends. To improve the interfacial interaction, a compatibilizing agent is usually added, which can promote a stable fine distribution of the dispersed phase by reducing the interfacial tension between blend components. Such a compatibilizer may be either (a) a graft or block copolymer or ionomer having segments that may separately interact with each of the incompatible polymers or (b) a functionalized polymer or copolymer which reacts with one or both of the polymers, forming a compatibilizing polymer. The latter procedure is often referred to as *in situ* compatibilization, to emphasize that the compatibilizer is formed during the mixing process.^{1,2}

Blends of isotactic polypropylene (iPP) and polyamide (PA) have received much attention over recent years, since they combine the environmental stability and ease of processing of the former with the thermomechanical characteristics of the latter.^{3–12} However, the compatibility of PP with PA6 is poor due to the lack of polar groups. In an attempt to increase the compatibility be-

tween these polymers, different compatibilizers were employed. These compatibilizers are generally based on homopolymers and copolymers functionalized with a polar monomer such as maleic anhydride (MA), especially MA-functionalized PP,^{3,8,11} an MA-functionalized ethylene propylene elastomer,^{6,7} and MA-functionalized styrene block copolymers.^{3–7,9,10,12} Some authors also used ionomers as a compatibilizing agent for the PP/PA system.^{13–15} They reported that poly(ethylene-*co*-methacrylic acid) ionomers (EMA-I), usually partially neutralized in the Na or Zn salt form, can be used as effective compatibilizers for PP/PA blends.

In our previous work,¹⁶ theories concerning the relation between the dispersed-phase particle size of a two-phase blend and the affecting parameter were reviewed. It was shown that there is a relationship among the dispersed-phase particle size, the viscosity ratio of the components, and the interfacial tension between the phases of PP/EPDM (80/20 wt %) blends prepared in an internal mixer. In the present work, an attempt was made to obtain a similar relation for PP/PA6 (80/20 wt %) blends. This relation was then applied to estimate the interfacial tension of these blends, compatibilized with different compatibilizers.

EXPERIMENTAL

Materials

Three types of PP, varying in melt-flow indexes (MFIs), and three PA6's with different melt viscosities

Correspondence to: H. Nazokdast (Nazdast@aku.ac.ir).

TABLE I
Properties and Suppliers of Materials Used

Material	Properties	Supplier
PP1	MFI ^a = 3, $T_m = 165\text{ }^\circ\text{C}$, $\rho = 0.9$	Iran Petrochemical, MOPLEN I-30
PP2	MFI ^a = 7, $T_m = 165\text{ }^\circ\text{C}$, $\rho = 0.9$	Iran Petrochemical, MOPLEN C-30
PP3	MFI ^a = 1.5, $T_m = 165\text{ }^\circ\text{C}$, $\rho = 0.9$	Iran Petrochemical, MOPLEN S-30
PA1	$M_n = 22,000$, $T_m = 210\text{ }^\circ\text{C}$	Allied Singnal Inc., Capron 8207F
PA2	$M_n = 17,500$, $T_m = 210\text{ }^\circ\text{C}$	BASF Corp., Ultramid B3
PA3	$M_n = 29,300$, $T_m = 210\text{ }^\circ\text{C}$	Allied Signal Inc., Capron 8209F
EMA-I	Na-neutralized, % neutralization = 50% Ethylene/methacrylic acid = 91/9, sp gr = 0.94, MFI ^b = 1	DuPont, Surlyn 8528
PP-MA	MFI ^a = 120, functionality = 1 wt %	DuPont Fusabond MZ-109D
EPR-MA	Functionality = 1 wt %	DuPont, Fusabond MF-416D
SEBS-MA	Functionality = 1.8 wt %	Shell Chemical Co. Kraton G 1901 X

^a 250 °C/2.160 kg.

^b 190 °C/2.160 kg.

were used for blending. The compatibilizers used were the poly(ethylene-co-acrylic acid) ionomer (EMA-I), MA-grafted PP (PP-MA), the MA-grafted ethylene/propylene elastomer (EPR-MA), and the MA-grafted styrene-butadiene-styrene block copolymer (SEBS-MA). The main characteristics of the used materials and their suppliers are listed in Table I.

Blend preparation

The first set of the blend samples, PP1, PP2, and PP3, were blended with each of PA1, PA2, and PA3 in the proportion of PP/PA 80/20 wt % without an interfacial agent (Table II). The second set of the blend samples were prepared using different types of interfacial agent systems in PP1/PA1 (80/20 wt %) blends as described in Table III.

All the blends were prepared using a Brabender internal mixer, equipped with roller-type (W50) blades at 220°C and 60 rpm. Blending was carried out by first feeding PP into the mixer, and after 3-min mixing, dried PA was charged into the mixer, and 3 min later, compatibilizing agents were added. Mixing was continued for 10 min, after which the mixture was

discharged. The steady-state torque (SST) of each component as well as of the blends, recorded at 10 min of mixing, was used as a measure of the viscosity.

Morphology studies

The morphology of the blends was studied using a scanning electron microscopy technique (SEM S360, Cambridge, Instruments) in conjunction with automatic image analysis. SEM studies were performed on cryogenically fractured surfaces of blend specimens which were etched for 24 h at room temperature by formic acid. The surfaces were sputtered with gold before viewing. For each blend sample, three micrographs were analyzed and the number-average diameter of the particles was calculated.

RESULTS AND DISCUSSION

Simple blends

To analyze our experimental results, a relation similar to that suggested by Wu¹⁷ for a twin-screw extruder

TABLE II
Characterization of Simple Blends

Sample Code	Matrix	Dispersed phase	TR ^a	η_d^a (Pa s)	η_m^a (Pa s)	d (μm)
1	PP1	PA1	2.4	440	280	5.6
2	PP2	PA1	1.09	440	470	2.3
3	PP3	PA1	6.4	440	210	11
4	PP1	PA2	3.17	520	280	6.8
5	PP2	PA2	1.4	520	470	2.6
6	PP3	PA2	8.4	520	210	14
7	PP1	PA3	4.66	650	280	7.5
8	PP2	PA3	2.11	650	470	3.5
9	PP3	PA3	12.47	650	210	16

^a Ratio of SST of PA6 to PP at 10 min of mixing, 60 rpm, 220°C.

^b Shear viscosity at 200 S⁻¹, 220°C.

TABLE III
Characterization of Compatibilized Blends

Sample code	Compatibilizing agent composition (wt %)				d (μm)	Interfacial tension (mN/m)
	PP-MA	EMA-I	EPR-MA	SEBS-MA		
10	2	—	—	—	4	9.74
11	4	—	—	—	2.5	6.08
12	6	—	—	—	1.3	3.16
13	8	—	—	—	0.99	2.4
14	10	—	—	—	0.92	2.23
15	—	2	—	—	3.4	8.27
16	—	4	—	—	2.2	5.35
17	—	6	—	—	1.3	3.16
18	—	8	—	—	0.82	1.99
19	—	10	—	—	0.75	1.82
20	—	—	2	—	3.3	8.03
21	—	—	4	—	2.1	5.1
22	—	—	6	—	1.2	2.92
23	—	—	8	—	0.88	2.14
24	—	—	10	—	0.73	1.78
25	—	—	—	2	2.3	5.6
26	—	—	—	4	1.4	3.4
27	—	—	—	6	0.66	1.61
28	—	—	—	8	0.53	1.29
29	—	—	—	10	0.36	0.88

was used for the samples blended in the internal mixer in the following form:

$$\frac{d\eta_m \dot{\gamma}}{\gamma_{12}} \approx (\eta_d / \eta_m)^n \quad (1)$$

It has been reported that^{16,18,19}, the SST ratio in an internal mixer can be correlated to the viscosity ratio. To examine this relation for the simple blends under study, η_m and η_d , PP and PA samples were measured using a capillary rheometer (Instron 3211) at the same temperature (220°C) and shear rate as those used for blending of the blends in the internal mixer. A simple relation based on the rotor geometry and the speed was used to calculate the mixing shear rate as²⁰

$$\dot{\gamma} = \frac{2\pi N}{\ln(R_e/R_i)} \quad (2)$$

where N is the rotor speed while R_i and R_e are the rotor radius (bob radius) and the external radius (cup radius), respectively. A linear relation between the viscosity ratio (η_m / η_d) and the torque ratio (TR) (Table II) shown in Figure 1 for the simple blends indicates that η_m / η_d in eq. (1) can be replaced by the TR, leading to the following form:

$$\frac{d\eta_m \dot{\gamma}}{\gamma_{12}} \approx (\text{TR})^n \quad (3)$$

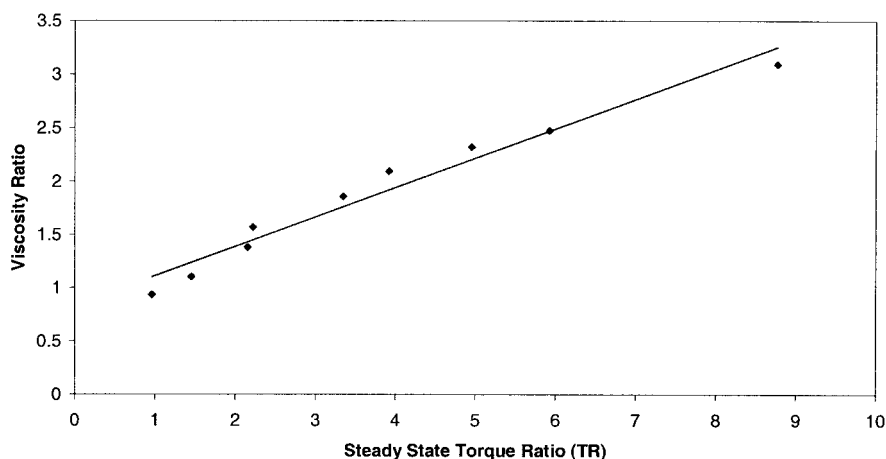


Figure 1 Viscosity ratio η_d / η_m versus TR.

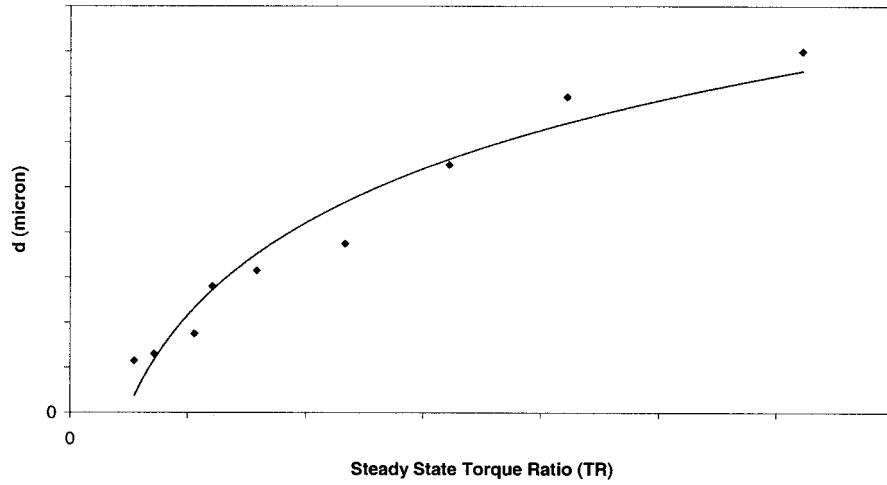


Figure 2 Number-average diameter of PA6-dispersed phase (micron) versus TR.

As $\dot{\gamma}$ and γ_{12} are the same for all the simple blends, a plot of $d \eta_m$ versus the TR can be used to calculate the exponent n in eq. (3).

Figures (2) and (3) represent the number-average particle diameter (d) and $d \eta_m$ versus the TR, respectively. The results shown in Figure 2 indicate that the PA particle size increased from 2.3 to 16 μm when the TR increased from 0.96 to 8.7. Figure 3 shows an exponential relation between $d \eta_m$ and TR; from the curve fitting of the experimental data, the exponent n was found to be about 0.522. By substituting the $n = 0.522$, eq. (1) can be rewritten in the following form:

$$\frac{d \eta_m \dot{\gamma}}{\gamma_{12}} \approx (\text{TR})^{0.522} \quad (4)$$

This results were compared with results reported in our previous work¹⁶ on PP/EPDM (80/20 wt %) blend systems, which showed a relation in the following form:

$$\frac{d \eta_m \dot{\gamma}}{\gamma_{12}} \approx (\text{TR})^{0.5141} \quad (5)$$

From comparing the results presented in Figure 4 for both systems, one may notice that the dispersed-phase particle size expressed in terms of $d \eta_m$ is larger for PP/PA6 blends than for PP/EPDM at a given steady-state TR. This can be related to a larger interfacial tension of PP/PA6 blends.

If all phase-size/steady-state TR data generated for both blend systems are considered together, it is

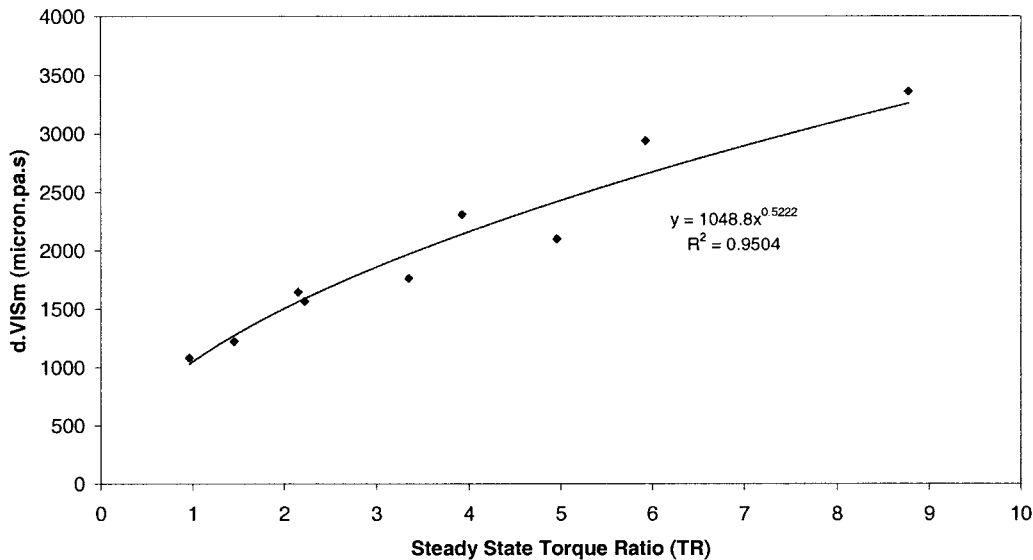


Figure 3 $d \eta_m$ versus TR.

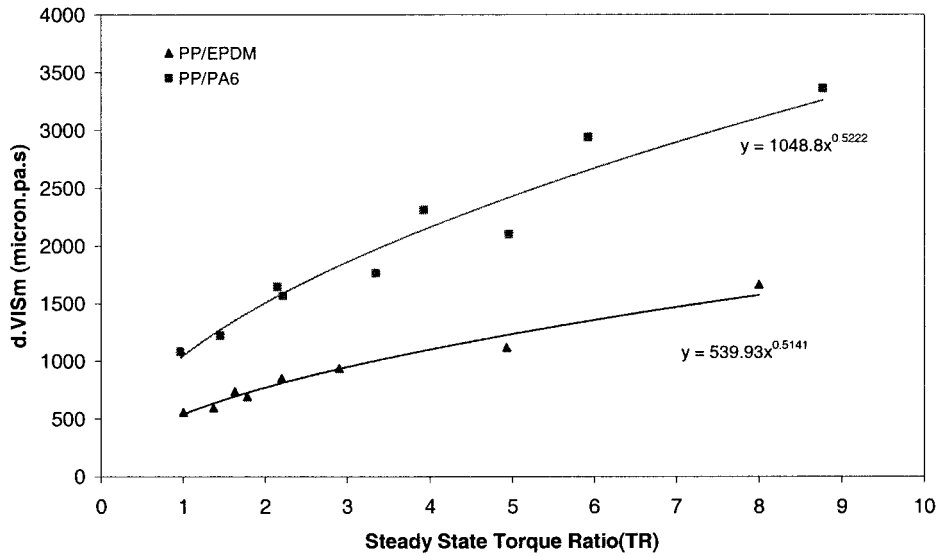


Figure 4 $d \eta_m$ versus TR for PP/EPDM and PP/PA6 blends.

found to superimpose very well when the data for the PP/PA6 blends shifted along the x (steady-state TR) axis with a shift factor of 0.49 relative to PP/EPDM. The data presented in Figure 5 show an exponential master curve of $d \eta_m$ versus the TR with $n = 0.5155$. Thus, a relation in the form of $d \eta_m \dot{\gamma} / \gamma_{12} = (\text{TR})^{0.5155}$ can be used for both systems with a narrow deviation. As this master curve is obtained for two polymeric systems with a widely varying dispersed-phase size, it may also be employed for other polymer blends with 20 wt % of a minor phase prepared in the internal mixer.

Compatibilized blends

The number-average diameter (d) of the PA phase in the PP/PA/compatibilizer blends as a function of the compatibilizer content are shown in Figures 6–10. As can be seen, for all the compatibilized blends, the dispersed particle size (d) decreases sharply with an increasing compatibilizer content until reaching a minimum and then remains nearly unchanged. These figures show that the minimum dispersed-phase particle size is 0.36, 0.73, 0.75, and 0.92 μ for SEBS–MA, EPR–MA, the ionomer, and PP–MA, respectively, indicat-

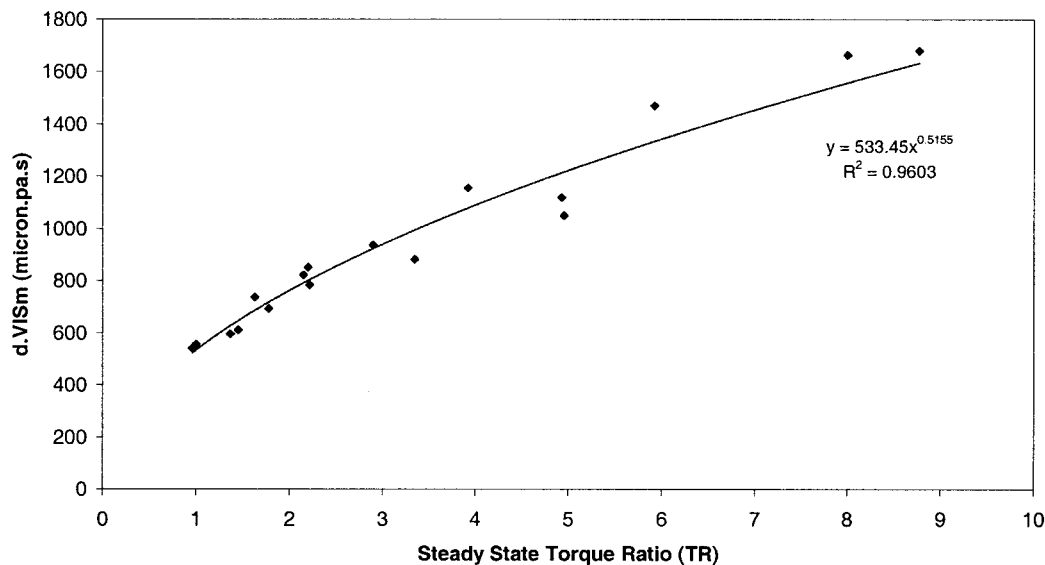


Figure 5 Master curve of $d \eta_m$ versus TR.

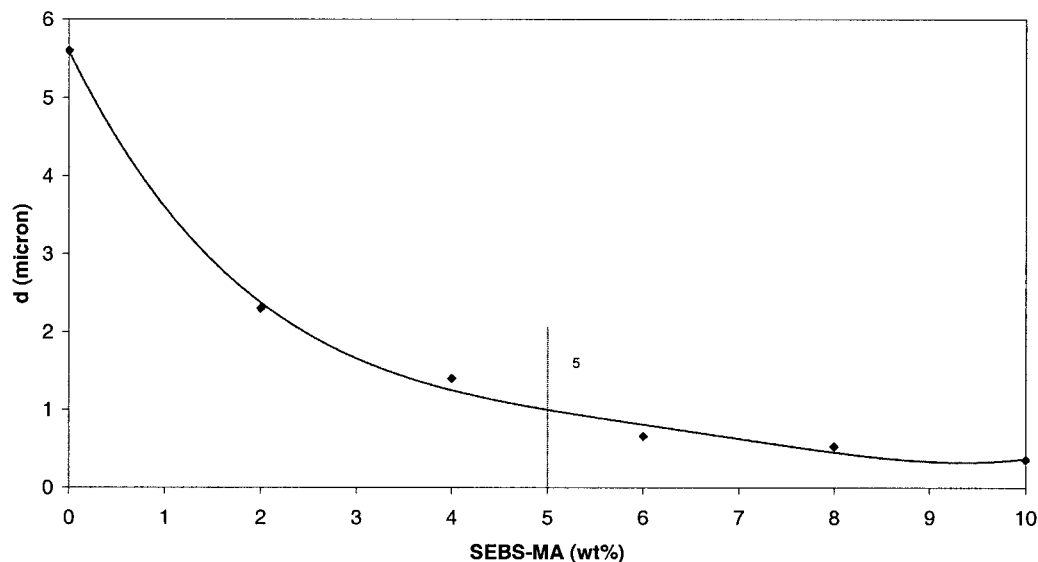


Figure 6 Number-average diameter of PA6-dispersed phase (micron) versus SEBS-MA (wt %).

ing that the number-average particle size is the smallest for the SEBS-MA compatibilized blends.

To compare the effectiveness of the different compatibilizers used, an effective content of the compatibilizer at which d reduces to $1 \mu\text{m}$ was considered as a reference. From Figures 6–9, this value was found to be 5, 7, 7.2, and 7.3 wt % for SEBS-MA, the ionomer, EPR-MA, and PP-MA, respectively.

It is generally believed that anhydride units of MA-grafted compounds such as SEBS-MA, EPR-MA, and PP-MA can react readily with the amine end groups of the PA to form a block or graft copolymer which can act as an interfacial agent between two phases.²¹ Some authors^{14–16} also believed that EMA-I's can in-

duce strong chemical and physical interaction with both phases of PP/PA6 blends through their carbonyl group. They suggested an amidation reaction between NH_2 terminal groups of PA6 and COOH groups of a copolymer in addition to possible physical interlocking with the PP phase.

Our results indicate that all the compatibilizers used are capable of acting as interfacial agents for PP1/PA4 blends and reducing the dispersed-phase particle size with respect to the simple blend no 1. SEBS-MA was found to be a more effective compatibilizer than were the others, which can be attributed to a higher functionality (about 1.8 wt %) of this compatibilizer compared to the others.

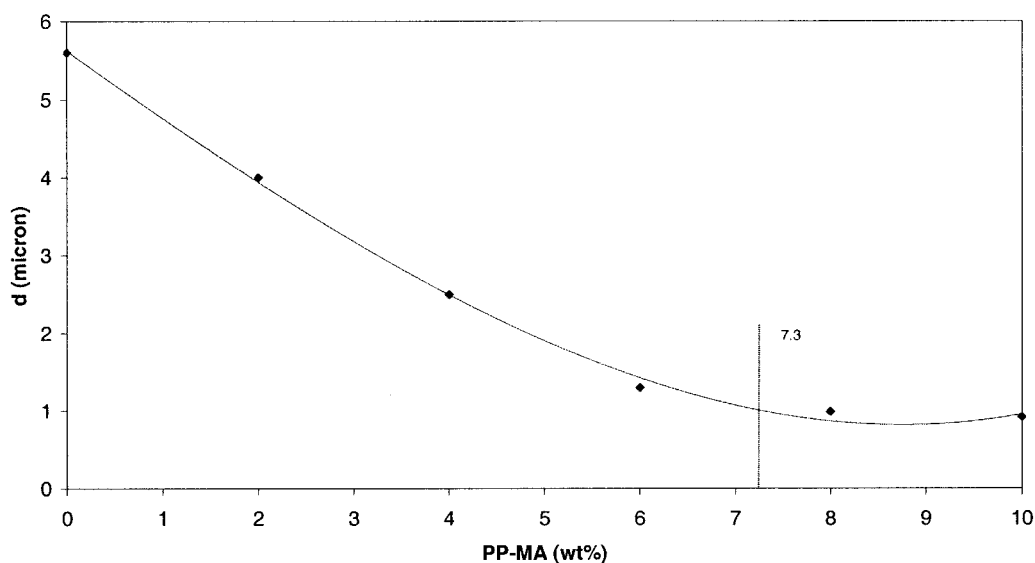


Figure 7 Number-average diameter of PA6-dispersed phase (micron) versus PP-MA (wt %).

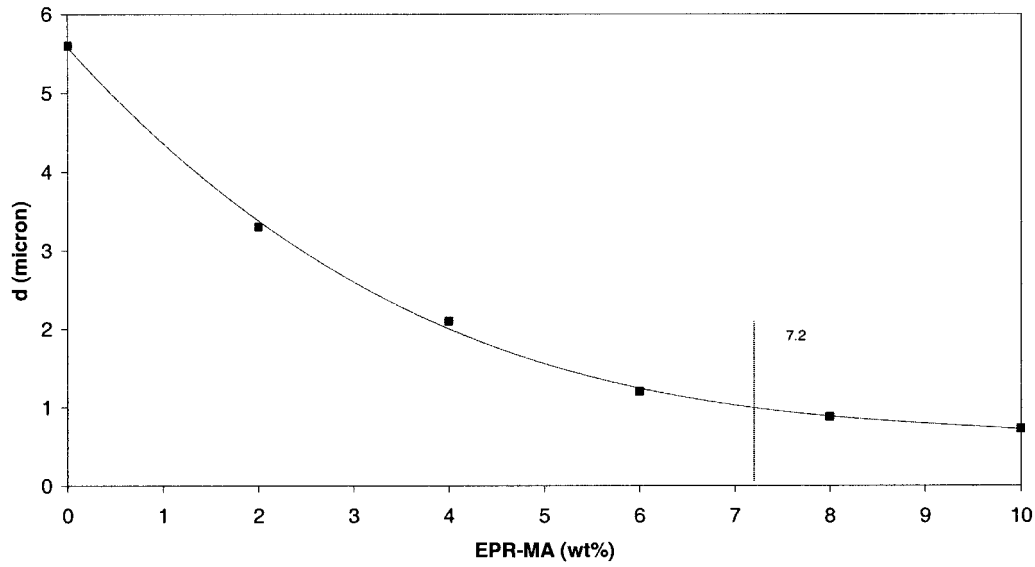


Figure 8 Number-average diameter of PA6-dispersed phase (micron) versus EPR-MA (wt %).

Surface tension estimation of compatibilized blends

If we assume that eq. (4) is applicable for the PP/PA compatibilized blends, we can rewrite this equation for the simple blend no. 1 as a reference in the following form:

$$\frac{d_1 \eta_{m1} \dot{\gamma}}{(\gamma_{12})_1} \approx (\text{TR})^{0.522} \quad (6)$$

By dividing eq. (4) into eq. (6), eq. (7) can be derived, which can be used to estimate γ_{12} of the compatibilized blends:

$$\gamma_{12} = (\gamma_{12})_1 \times \frac{d}{d_1} \times \frac{\eta_m}{\eta_{m1}} \quad (7)$$

where index 1 denotes the simple blend characteristic data. Thus, if $(\gamma_{12})_1$ is known, then γ_{12} can be calculated from eq. (7) using η_m and d given in Table III for compatibilized blends and η_{m1} and d_1 given in Table II for simple blends.

To calculate $(\gamma_{12})_1$, the surface tensions of PP and PA6 at 220°C were calculated using the surface tension values reported²² for other temperatures in conjunction with the variation of the surface tension with the temperature ($d\gamma/dT$) and polarities ($\chi_p = \gamma_p/\gamma$), which

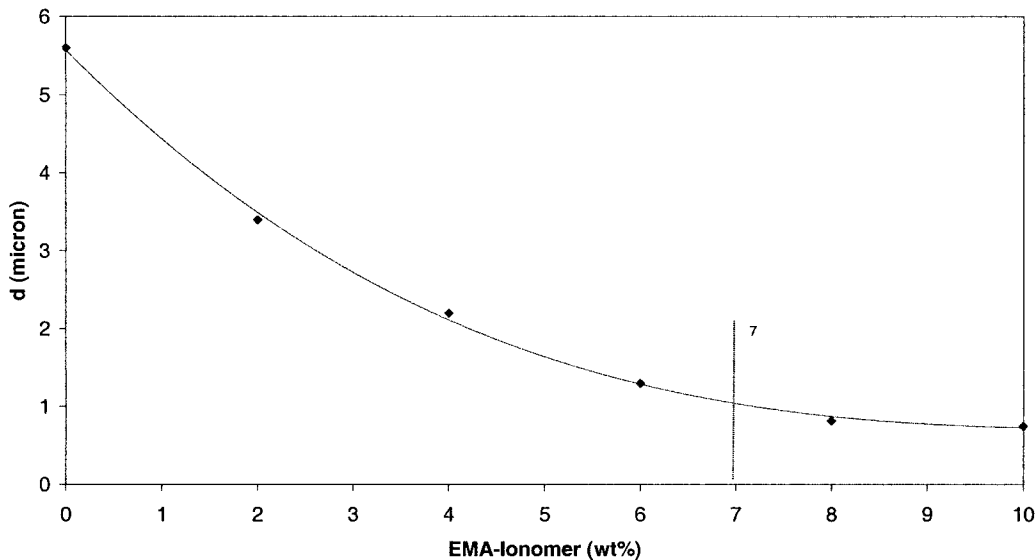


Figure 9 Number-average diameter of PA6-dispersed phase (micron) versus EMA-I (wt %).

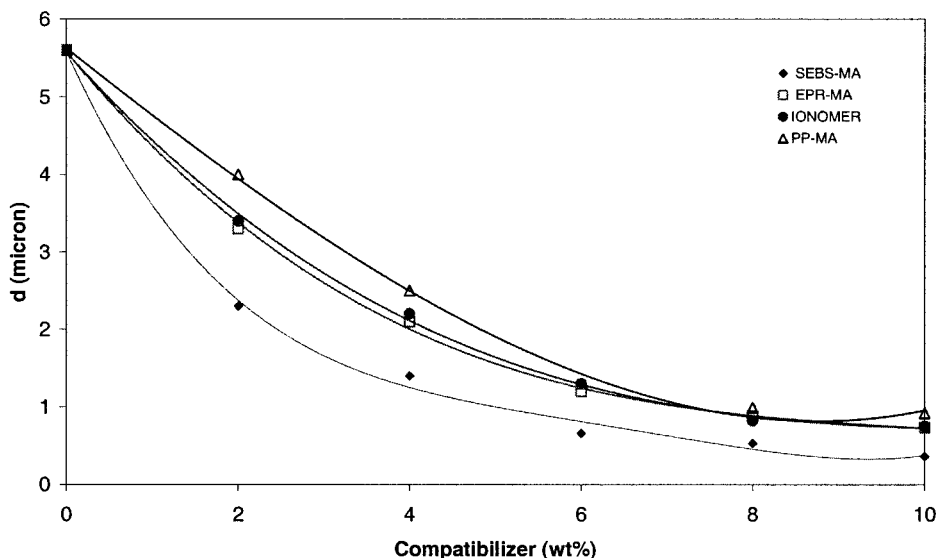


Figure 10 Number-average diameter of PA6-dispersed phase (micron) versus compatibilizer content (wt %).

is the ratio of the polar contribution of its dispersive contribution of the γ_d surface tension γ_p to γ . The surface tension γ , its dispersive contribution γ_d , and its polar contribution γ_p at 220°C for PP and PA are listed in Table IV.

Thus, the interfacial tension between PP1 and PA1 in simple blends can be calculated from the well-known harmonic mean equation²² as

$$(\gamma_{12})_1 = \gamma_1 + \gamma_2 - \frac{4\gamma_{1p}\gamma_{2p}}{\gamma_{1p} + \gamma_{2p}} - \frac{4\gamma_{1d}\gamma_{2d}}{\gamma_{1d} + \gamma_{2d}} \quad (8)$$

The value of $(\gamma_{12})_1$ at 220°C obtained from eq. (8) was found to be about 13.56 mN/m. By substituting the value of $(\gamma_{12})_1$ in eq. (7), the interfacial tension (γ_{12}) of the compatibilized blends can be estimated, which are listed in Table III.

Relationship between viscosity and interfacial tension of the blends

The SST values measured as a function of the interfacial agent content for all the compatibilized blends are shown in Figure 11. As can be seen, the SST of the blends increases with an increasing compatibilizing

content. However, the extent of the variation in the SST of the blends varies depending upon the compatibilizer type. The maximum SST is obtained for the blend containing 10 wt % SEBS-MA while the minimum SST is for the blend containing 0 wt % of EMA-I.

The SST of a blend is a measure of the viscosity^{13,15} and thus can be related to the interfacial interaction between the phases. When there is a strong interfacial interaction, that is, a low interfacial tension between phases, a positive deviation from the mixture low is expected for the blend viscosity.^{13,15} Thus, it was expected that the viscosity of the PP/PA blends increases with a decreasing interfacial tension.

As shown in Figure 12, the SST of the blends increases with a decreasing interfacial tension. However, the SST of the blends can be affected by interfacial interaction between two phases as well as by the viscosity of the compatibilizer used. To take into account the effect of the viscosity of the compatibilizers, the SST of the blends (SSTM) was calculated by the mixture law using the measured values of the SST of PP, PA, and the compatibilizer. Thus, a plot of the difference between the value of SSTM and the measured SST of the blends against the estimated interfacial tension shown in Figure 13 can be used to consider the relationship between the viscosity of the blends and the interfacial interaction more correctly. No major difference was found between these results and the results shown in Figure 12, which indicates that the viscosity of the compatibilizers have no appreciable effect on the blends' viscosity due to their low concentrations. In other words, an increase in blend viscosity with an increasing compatibilizer content is only due to interfacial interaction enhancement.

TABLE IV
Estimated Surface Tension of Polymers at the Mixing Temperature (220°C)

Polymer	γ (220°C) (mN/m)	γ_p (220°C) (mN/m)	γ_d (220°C) (mN/m)
PP	18.84	0.37	18.11
PA6	39.02	13.42	25.6

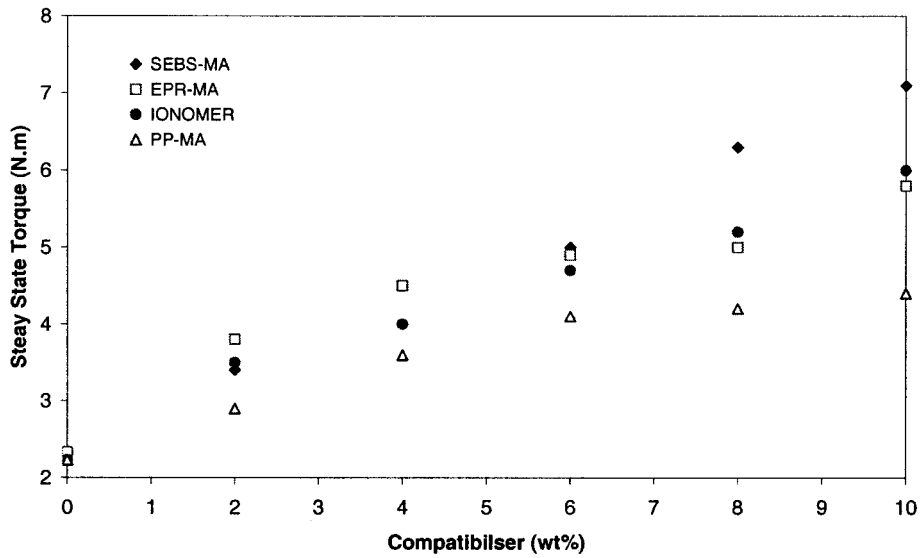


Figure 11 Steady-state TR of the blends versus compatibilizer content (wt %).

CONCLUSIONS

A power-law relation between the measured rubber particle size and the TR was obtained for the PP/PA6 (80/20) simple blends in an internal mixer. It was demonstrated that such relationship can be utilized to estimate the interfacial tension between the two phases.

It was shown that a master curve of $d \eta_m d$ versus TR can be generated on the basis of the experimental data obtained for PP/PA6 (80/20) and PP/EPDM (80/20) blends with widely different dispersed-phase sizes, by shifting along the steady-state TR axis. It was pro-

posed that this master curve may also be employed for other polymer blends with 20 wt % of the minor phase prepared in the internal mixer.

The experimental results showed that for different compatibilizing systems used in this study there is an optimum concentration of interfacial agents above which they can no longer enhance the interfacial interaction between two phases. The results show that SEBS-MA is more effective than are the others and can reduce the particle size from 5.6 ηm (for simple blends) to 0.36 ηm for 10 wt % of SEBS-MA. It may be referred to as high functionality (1.8 wt %) of this

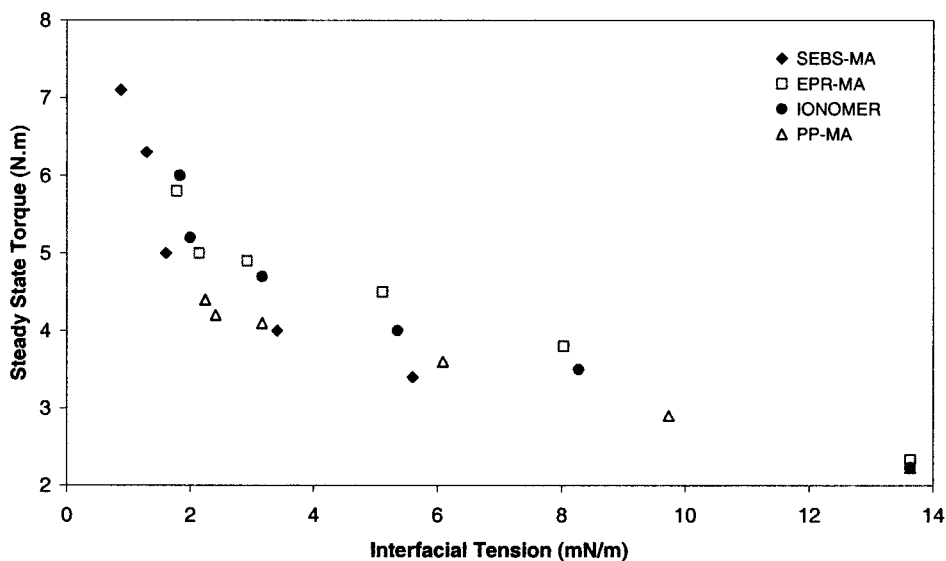


Figure 12 SSTs of the blends (N M) versus estimated surface tension (N/M).

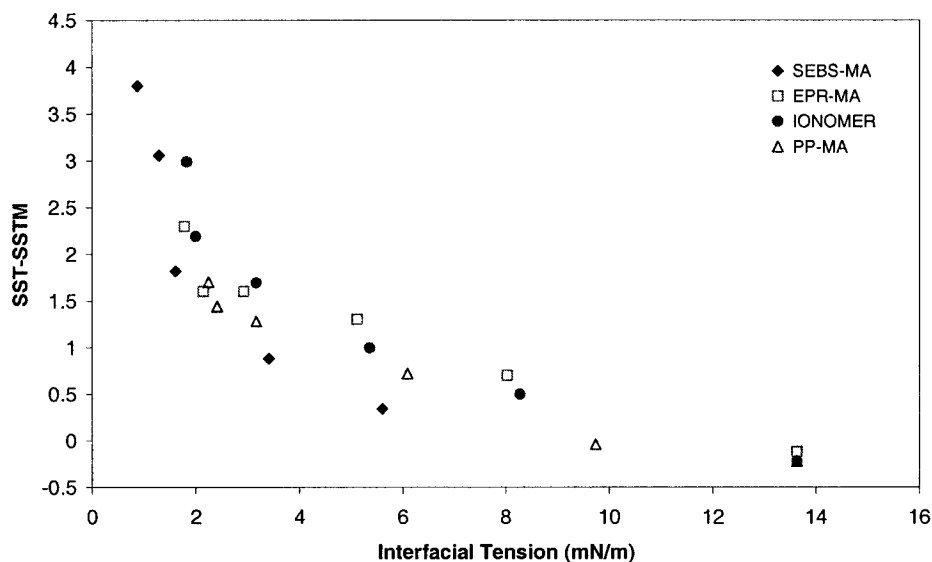


Figure 13 Difference between SST of the blends and SST from the mixture law ($N M$) versus estimated surface tension (MN/M).

compatibilizer. Finally, a sharp increase in the extent of positive deviation of the blends' viscosity was found when the amount of interfacial interaction exceeds a certain value.

References

- Xanthas, M.; Young, M. W.; Biesenberger, J. A. *Polym Eng Sci* 1990, 30, 355.
- Xanthos, M.; Dagli, S. S. *Polym Eng Sci* 1991, 31, 929.
- Holsti, R.; Seppala, J. *Polym Eng Sci* 1992, 32, 868.
- Modic, M. J.; Pottick, L. *Polym Eng Sci* 1993, 33, 13.
- Fritz, Q.; Gagiao, M. E. *J Mater Sci* 1995, 30, 3300.
- Rosch, J. *Polym Eng Sci* 1995, 35, 1917.
- Gonzalez, A.; Keskkula, H.; Paul, D. R. *Polymer* 1995, 36, 4587.
- Lee, J.; Yang, S. *Polym Eng Sci* 1995, 35, 1821.
- Ohlsson, B.; Hassander, H.; Tornell, B. *Polymer* 1998, 39, 4715.
- Ohlsson, B.; Hassander, H.; Tornell, B. *Polymer* 1998, 39, 6705.
- Li, H.; Hu, G.; Sousa, J. *J Appl Polym Sci* 1999, 37, 3368.
- Wilkinson, A. N.; Laugel, L.; Clemenens, M. *Polymer* 1999, 40, 4971.
- Favis, B. D.; Willis, J. M. *Polym Sci Part B Polym Phys* 1990, 28, 2259.
- Kim, Y.; Cho, W.; Ha, C. *Polym Eng Sci* 1995, 35, 1529.
- Favis, B. D.; Chalifoux, J. P. *Macromol Chem Macromol Symp* 1992, 56, 143.
- Shariatpanahi, H.; Nazokdast, H.; Hemmati, M.; Dabir, B.; Sadaghiani, K. *J Appl Polym Sci* 2002, 86, 3148.
- Wu, S. *Polym Eng Sci* 1987, 27, 335.
- Macknight, W. J.; Lenz, R. W.; Musto, P. V.; Somani, R. J. *Polym Eng Sci* 1985, 25, 1124.
- Purgett, M. D.; Macknight, W. J.; Vogl, O. *Polym Eng Sci* 1987, 27, 1461.
- Bousmina, M.; Alt-Kadi, A.; Faisant, J. B. *J Rheol* 1999, 43, 415.
- Marco, C.; Ellis, G.; Gomez, M. A.; Fatou, J. G.; Arribas, J. M.; Campoy, I.; Fontecha, A. *J Appl Polym Sci* 1997, 65, 2665.
- Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.