Interfacial Tension of Polyethylene/Polyethylene Terephthalate with Various Compatibilizing Agents

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SYNOPSIS

The effect of 12 different potential compatibilizing agents on the interfacial tension of polyethylene (PE) and polyethylene terephthalate (PET) is described. A wide range of compatibilizing agents based upon ethylene and a second comonomer were devised and used. They were divided into three categories. The first category (I) includes block polymers. The second category (II) includes random copolymers. The third category (III) includes reactive copolymers that should form graft copolymers during mixing with PET. The addition of various potential compatibilizing agents to the PE/PET binary system results in lowered interfacial tension. The efficiency of the different compatibilizing agents in reducing the interfacial tension is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The study of the interfacial tensions between different liquids and the influence of surface active additives on the interfacial tension is a subject that has long been studied. Technologies involving interfacial effects and surface active agents date to the ancients. As long ago as 1870, Quincke[1-3] reported extensive measurements of interfacial tension between organic liquids and the influence of additives on this characteristic. In the present century there have been innumerable investigations of the influence of surface active agents on interfacial phenomena and interfacial tension.[4-9] Studies of interfacial tension between polymer melts are of much more recent vintage, dating only to the 1960s.[10-23] It is well known that surface active agents can significantly reduce the interfacial tension between different liquids including oil and water in the formation of emulsions.[24,25] There have been a limited number of studies[13,20,22,26] on the influence of the addition of surface active or compatibilizing agents on the interface between two polymer melt phases.

We describe here a more extensive study of the influence of compatibilizing agents on the interfacial tension of polymer melt pairs. The basic melt pair to be studied is polyethylene (PE) and polyethylene terephthalate (PET), which are highly incompatible and are expected to have a large interfacial tension. The melt pair should also be a polymer pair that is readily compatibilized. First interfacial tension measurements for the binary system of PE and PET are described. The effect of a wide number of potential compatibilizing agents on the interfacial tension is then investigated. Twelve different compatibilizing agents that are different in chemical structure were used at varying concentrations. These have been chosen so that each of these compounds contains a significant level of ethylene units in the backbone, either in the form of blocks or randomly distributed. They also possess a second unit of higher polarity ranging from propylene to ethylene terephthalate. Several of the potential compatibilizers contain maleic anhydride (MA) that can react with chain ends in PET to form a graft copolymer that should act as a compatibilizer. The resulting group of 12 substances gives a broad range for comparison of compatibilizing agent effects on the interfacial tension of polymer pairs than has been previously discussed in the literature. We expand on this in the next section.

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EXPERIMENTAL

Materials

A thermoplastic high-density polyethylene (HDPE) and a PET were used in this study. The HDPE, which has a density of 0.97 and melt index of 8.0, was obtained from Union Carbide Company (DMDA 8007). The PET was obtained from Eastman Chemical (Kodapak PET 7352).

A series of 12 different potential surfactant compatibilizing agents were used. These fit into three categories: block copolymers, random copolymers, and reactive copolymers that form graft structures by reacting with PET.

Block copolymers in which each block is either identical or possibly miscible with one of the blend phases belong to category I. Two types of block copolymers were used. These were designated I-a for simple block copolymers (A-B) and I-b for mixed block copolymers (A-B-A). Four polybutylene terephthalate–polyethylene block copolymers (PBT-*b*-PE) as type I-a and styrene–(ethylene/butylene)–styrene triblock (SEBS) as type I-b were used, respectively.

Random copolymers containing PE and a second structural unit with varying tendencies to be miserable with PET are contained in category II. They include ethylene–vinyl acetate copolymer (EVA), hydrogenated butadiene–acrylonitrile copolymer (HNBR), and ethylene–propylene copolymer (EPR).

In category III, we include polymers that have reactive functional groups. They include MA functionalized HDPE (MA-*f*-HDPE), MA functionalized polypropylene (MA-*f*-PP), MA functionalized EVA (MA-*f*-EVA), and MA functionalized SEBS (MA-*f*-SEBS).

These various materials are summarized in Table 1 for PBT-*b*-PE block copolymers and in Table II for the other commercial compatibilizing agents.

The majority of compatibilizing agents except the PBT-*b*-PE copolymers were compounded into PET using a Werner and Pfleiderer ZSK-30 twin screw extruder at a barrel temperature of 270°C. The purpose of blending them into PET was to preform products of the PET and the various reactive maleinated polymers cited in Table I. The PBT-*b*-PE copolymers, which were only made available in small amounts, were compounded into PET using a Haake laboratory mixer at a temperature of 270°C.

Breaking Thread Experiment

Most measurements were made with a breaking thread technique. These measurements were made as follows. Fine threads of PET/compatibilizers were melt spun from a Instron capillary rheometer. The diameters of threads were in the range of 70–150 μm. Thin sheets of HDPE were prepared by a compression molding press. The thread was dried for 24 h and placed between two sheets of HDPE polymer, each with dimensions 10 × 10 × 0.5 mm. This composite was enclosed between two glass slides and placed on hot stage under a Leitz Laborex optical microscope. At the desired temperature, the distortion of the thread was photographed at regular intervals of time. The interfacial tension was obtained from Tomotika's equation[27]:

$$\kappa = \frac{\eta_m D_0 q}{\Omega(\psi, \lambda)} \qquad (1)$$

where κ is the interfacial tension, η_m is the zero shear viscosity of the matrix, D_0 is the initial thread radius, q is the growth rate, and Ω is a function of wavelength λ and viscosity ratio ψ. The growth rate q was obtained by analyzing the series of regularly taken photographs. The initial thread diameter was measured from an enlarged photograph. The function $\Omega(\psi, \lambda)$ was tabulated by Tomotika[27] and was presented graphically by Elmendorp.[28]

Table I Characteristics of PBT-*b*-PE Block Copolymers (Category I-a)

Designations	M_n of PE block	[η] of PBT-*b*-PE (g/dL)	Source
BC1	2000	0.50	R. P. Quirk[a]
BC2	14,000	0.24	R. P. Quirk[a]
BC3	20,000	0.53	R. P. Quirk[a]
BC4	50,000	0.50	R. P. Quirk[a]

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Table II Characteristics of Commercial Compatibilizing Agents

Category	Designations	Characteristics	Source
I-b	SEBS		Shell (Kraton G1652)
II	EVA	Random ethylene/vinyl acetate copolymer = 72/28	DuPont (Elvax 250)
	EPR	Random ethylene/propylene copolymer = 77/23	Exxon (Vistalon 719)
	HNBR	Random hydrogenated butadiene/acrylonitrile copolymer = 64/36	Zeon Chem (Zetpol 2020)
III	MA-f-SEBS	2% MA functionality	Shell (Kraton FG1901X
	MA-f-EVA	1% MA functionality	DuPont (Fusabond C MC-190D)
	MA-f-PP	0.5% MA functionality	Eastman Chem (Epolene E-43)
	MA-f-HDPE	1% MA functionality	BP Chem (Polybond 09440)

Pendant Drop Experiment

Interfacial tension was also measured in a pendant drop experiment at 270°C. The procedure is tedious and was only used to verify the interfacial tension value of the PE/PET binary system. Pendant drop measurements of interfacial tensions on polymer melts date back more than a quarter century.[11,12] Our apparatus consists of a modified Gaertner optical bench with a light source, a filter, a pendant drop cell, and a camera. This is the same apparatus used by Chen and White[22] and Yoon and White.[23] The rectangular cavity was filled with polymer of lower density. The drop of higher density polymer was formed by a tube that was filled with thick melt spun fiber. Photographs were taken following the change of the shape of the drop so formed with time. The enlarged prints were then analyzed.

The state of equilibrium was checked by measuring the series of diameters from the drop profile.[29,30] For each drop profile, the diameters d_e, d_8, d_{10}, and d_{12} were measured. A series of shape parameters S_8, S_{10}, and S_{12} were first determined as $S_n = d_n/d_e$. Next, a series of $1/H$ values were found from the shape parameters by using the tables of Roe et al.[30] A drop profile with a minimum variance in $1/H$ was used as a drop profile at equilibrium. An average value of $1/H$ was used. The interfacial tension κ was then calculated by eq. (2):

$$\kappa = g\Delta\rho(d_e)^2(1/H) \tag{2}$$

where g is the gravitation acceleration, $\Delta\rho$ is the difference in the densities of the two phases, and d_e is the equatorial diameter of the drop.

Subsidiary Experiments

To determine the interfacial tension between two polymer melts by the pendant drop experiment, it is necessary to know the density of each melt accurately. We carried out measurements of this type in an Instron Capillary Rheometer at low crosshead speed and 270°C. The results for PET and HDPE are listed in Table III.

Zero Shear Viscosity

Low shear rate viscosities of the PET and HDPE were investigated using a Rheometrics Spectrometer System 800. The results for PET and HDPE are listed in Table III. The viscosities of PET/compatibilizer will be discussed in a subsequent section.

RESULTS

PET/HDPE

The interfacial tension was measured for the binary blend systems of PET/HDPE. Both the breaking thread method and the pendant drop method were used to measure the interfacial tension for this system. Table IV lists the interfacial tension values measured by the breaking thread method. The av-

Table III Zero Shear Viscosities and Densities of PET and HDPE at 270°C

Material	PET	HDPE
η_0 (Pa s)	150	450
Density (g/cm³)	1.1724	0.7627

Table IV   Interfacial Tension Values Between PET and HDPE Measured by Breaking Thread Method at 270°C

	D_0 (μm)	η_t^a (Pa s)	η_m (Pa s)	Viscosity Ratio, ψ	X_m^b Exp.	X_m^b Theor.	κ (dyn/cm)
Run no.							
1	92	150	450	0.33	0.65	0.59	10.24
2	99	150	450	0.33	0.56	0.59	8.96
3	153	150	450	0.33	0.59	0.59	9.95
$\bar{x}$							9.7
σ_x							0.5

[a] η_t, viscosity of the thread phase.
[b] X_m, dominant wavenumber determined theoretically and experimentally.

erage value of the interfacial tension measured by the breaking thread method was 9.7 dyn/cm with a variance of 0.5.

The interfacial tension was also measured by the pendant drop method. Table V shows the interfacial tension data repeatedly measured by the pendant drop method. The average value of measured interfacial tension between PET and HDPE at 270°C was found to be 10.0 dyn/cm with a variance of 0.3, which is not significantly higher than the value obtained by the pendant drop method.

Block Copolymers

The influence of PBT-b-PE copolymers of Table I on the zero shear viscosity and the interfacial tension were investigated. The block copolymers lower the viscosity of the PET.

Values of interfacial tension at a concentration of 5 parts per 100 polymer matrix are shown in Table VI. It is seen that the interfacial tensions are greatly lowered to about 1.7 dyn/cm by adding PBT-b-PE copolymers.

The influence of compatibilizer level for some of these systems is shown in Table VII.

We also looked at the SEBS block copolymer. Its effect is small. The interfacial tension is only lowered to 7.5 dyn/cm randomly.

Random Copolymers

The effects of several commercially available random copolymers of Table II on interfacial tension between the PET and HDPE system were investigated. The results are in Table VI. These copolymers are EVA, HNBR, and EPR. The effects are small, with the EVA being most effective.

Reactive Copolymers

MA-g-HDPE, MA-g-PP, MA-g-EVA, and MA-g-SEBS in category III were also investigated. All of the copolymers except for the Ma-g-HDPE and Ma-g-EVA lower the zero shear viscosity of the blend with PET. The interfacial tensions with 5 parts of compatibilizing agents are summarized in Table VI. All reactive copolymers were able to lower the interfacial tension substantially. The degree of reduction was different depending on the chemical struc-

Table V   Characteristics of Pendant Drop Profile and Their Interfacial Tension Values Between PET and HDPE at 270°C

	d_e (cm)	$1/H$	$\Delta\rho$ (g/cm^3)	κ (dyn/cm)
Run no.				
1	0.220	0.4876	0.4097	9.67
2	0.250	0.3959	0.4097	9.97
3	0.240	0.4407	0.4097	10.40
Average ($\bar{x}$)				10.0
σ_x				0.30

Table VI Interfacial Tension Between PET and HDPE with Various Compatibilizers

Compatibilizer	Type of Copolymer	η_0 (HDPE) (MPa)	$\eta_0 \left(\begin{array}{c}\text{PET}\\\text{Blend}\end{array}\right)$ (MPa)	Viscosity Ratio	κ (dyn/cm)
BC1	Block		55	0.122	1.8
BC2	Block		60	0.133	1,7
BC3	Block		62	0.133	1.7
BC4	Block		65	0.144	1.7
SEBS	Block	450	170	0.378	7.5
EPR	Random	450	115	0.256	7.8
EVA	Random	450	130	0.289	6.3
HNBR	Random	450	140	0.311	7.2
MA-g-PP	Reactive	450	140	0.311	3.1
MA-g-EVA	Reactive	450	220	0.489	2.7
MA-g-HDPE	Reactive	450	260	0.578	1.9
MA-g-SEBS	Reactive	450	80	0.178	1.8

Concentration of 5 parts/100 PET measured by breaking thread method at 270°C.

ture of the copolymers. The effect of level of addition is shown in Table VII for the MA-SEBS.

DISCUSSION

Interfacial Tension Between Homopolymers

The interfacial tensions measured for PET/HDPE at 270°C are 10.0 ± 0.3 dyn/cm from the pendant drop method and 9.7 ± 0.5 dyn/cm from the breaking thread method. These values are lower that the reported value of 12 ± 1 dyn/cm at 290°C by Chappelear[10] in 1964, but matches well with the reported value of 9.9 dyn/cm at 270°C by Berger et al.[16] in 1976.

The interfacial tension also can be estimated from the surface tension of individual polymers and their polarity. Wu[31] proposed the equation:

$$\kappa = \kappa_1 + \kappa_2 - \frac{4\kappa_1^d \kappa_2^d}{\kappa_1^d + \kappa_2^d} - \frac{4\kappa_1^P \kappa_2^P}{\kappa_1^P + \kappa_2^P} \qquad (3)$$

where κ is the interfacial tension, κ_i the surface tension of polymer i, κ_i^d and κ_i^P the dispersion (nonpolar) and polar components of κ_i, respectively. The polarity values, the surface tensions and their dispersion, and polar components for the PET and the PE are listed in Table VIII. The surface tension of PET varies considerably depending on the investigators. With the surface tension values of Berger et al.[16] the estimated interfacial tension was 8.7 ± 1.2

Table VII Effect of Concentration of Compatibilizers on Interfacial Tension Between PET and HDPE by Breaking Thread Method at 270°C

Compatibilizer	Amount (phr)	η_t (MPa)	Viscosity Ratio	κ (dyn/cm)
BC1	2	113	0.251	2.8
	5	55	0.122	1.8
BC2	2	105	0.233	2.7
	5	60	0.133	1.7
BC3	2	131	0.291	2.6
	5	62	0.138	1.7
BC4	2	112	0.249	2.4
	5	65	0.144	1.7
MA-g-SEBS	1	220	0.489	3.3
	5	80	0.178	1.8

Table VIII Surface Tension, Dispersion, and Polar Components for PE and PET at 270°C for Wu's Formula

Polymer	Polarity	Surface Tension and Components (dyn/cm)			
		κ_i	κ_i^d	κ_i^p	Ref.
PE	0	21.4	21.4	0	26
PET	0.221	35.6 ± 2.7	27.7	7.9	14
		28.0 ± 3[a]	21.8	6.2	11

Values are for using in estimating interfacial tension by Wu's formula.[31]

[a] Extrapolated data from 280 to 270°C.

dyn/cm. The measured interfacial tension values of PET/HDPE in this experiment are at the upper limit of the estimated value.

Effectiveness of Different Copolymers

The efficiency of various copolymers in reducing the interfacial tension between PET and HDPE was found to be ordered as:

PBT-b-PE ≈ MA-g-SEBS ≈ MA-g-HDPE

≫ MA-g-EVA > MA-g-PP ≫ EVA

≫ HNBR > SEBS > EPR.

The copolymers that belong to category I-a and category III are the most effective compatibilizing agents in reducing the interfacial tension of immiscible polymer blends. However this is certainly very much related to the structural units in these copolymers because only I-a and the grafted products of reactive class III contain structural units with butylene or ethylene terephthalate. Among the reactive copolymers the efficiency is related to the amount of MA functional groups as well.

It must be realized that the reactive copolymers based upon maleation of PE form graft copolymers with the PET through their reactive end groups. This makes their structure similar to the PE-PBT block copolymers. It thus should not be surprising that they lower interfacial tensions as much as PE-PET block copolymers because they exhibit similar long chain segments. The same is essentially true of the maleated SEBS.

The EVA, EPR, HNBR, and SEBS have PE regions in their backbones that are very compatible with the PE homopolymers, but VA, PP, acrylonitrile, and styrene segments are immiscible in PET.

These additives are not unexpectedly much less effective. However, the level of incompatibility of this second structural unit with PET clearly has a role. Interfacial tension decreases as one varies the second structural unit from PP to styrene to VA. The later is an ester as PET is.

Effect of Compatibilizer Concentration

The effect of the extent of addition of PBT-b-PE diblock copolymers on the interfacial tension was studied for the PET/HDPE system as shown in Table VII. Interfacial tension decreases rapidly with copolymer concentration for all PBT-b-PE diblock copolymers. With the addition of 2 phr copolymer, a 75% reduction in interfacial tension took place. With an increase of the copolymer concentration of 5 phr, slightly greater reductions were observed. This trend was also observed for the addition of MA-g-SEBS as shown in Table VII. The results are similar to the previous observations by Patterson et al.[13] Anastasiadis and Koberstein,[26] and Elemans et al.[20]

Estimation of Required Amount of Compatibilizer to Saturate Interface

The amount of compatibilizer required to saturate the interface of the immiscible polymer blend can be estimated. For spherical drops of radius R, the total volume of the droplet phase V_d is given by

$$V_d = \sum \tfrac{4}{3}\pi R^3 = \tfrac{4}{3}\pi R^3 n \tag{4}$$

where n is the number of drops. When the volume fraction of the dispersed phase is ϕ_d, the total number of droplets per unit volume of the original blend is

$$n = \frac{\phi_d}{\frac{4}{3}\pi R^3}. \tag{5}$$

Then the total interfacial area, A per unit volume, becomes the product of the number of droplets and individual surface area

$$A = \frac{\phi_d}{\frac{4}{3}\pi R^3} 4\pi R^2 = \frac{3\phi_d}{R}. \tag{6}$$

If each compatibilizing agent molecule occupies an area a at the interface, then the number of compatibilizing agent molecules is given by eq. (6) divided by a. The total amount of compatibilizing agent of

molecular weight M, required to saturate the interface is

$$\text{amount compatibilizer} = \frac{3\phi_d M}{aRN} \qquad (7)$$

where N is Avogadro's number.

Paul[32] suggests a possible value of 50 Å^2 for a. If we use this value, 2% block copolymer (molecular weight 10,000) is needed to saturate all of the interface of a minor phase when it is dispersed as spherical droplets of radius 1 μm in diameter.

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