Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 7925–7932

polymer

www.elsevier.com/locate/polymer

Interfacial tension of compatibilized blends of LDPE and PA6: the breaking thread method

L. Minkova[a,*], Hr. Yordanov[a], S. Filippi[b], N. Grizzuti[c]

[a]*Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bontchev str. bl.103A, 1113 Sofia, Bulgaria*
[b]*Dipartimento di Ingegneria Chimica, Università di Pisa, via Diotisalvi 2, 56126 Pisa, Italy*
[c]*Dipartimento di Ingegneria Chimica, Università di Napoli, piazzale V. Tecchio 80, 80125 Napoli, Italy*

Received 9 April 2003; accepted 19 September 2003

Abstract

The interfacial tension of the uncompatibilized and compatibilized blends of low density polyethylene (LDPE) and polyamide 6 (PA6) has been measured by the breaking thread method. Different types of compatibilizer precursors have been used: poly(ethylene-co-acrylic acid) (Escor 5001, by Exxon) having 6 wt% concentration of acrylic acid; an ethylene-acrylic acid zinc ionomer (Iotek 4200); a triblock copolymer with polystyrene end blocks and a rubbery poly(ethylene–butylene mid block (SEBS) (Kraton G 1652); and SEBS-g-MA (Kraton FG 1901X) with 2 wt% maleic anhydride. The compatibilizing efficiency of the different types of the compatibilizer precursors towards the blends has been evaluated quantitatively by the values of the interfacial tension obtained. It has been shown that Iotek and SEBS-g-MA posses the highest compatibilizing efficiency, demonstrated by the strongest decrease of the interfacial tension and the dimension of the droplets of the dispersed phase. Contrary, SEBS almost does not influence the interfacial tension and the size of the particles. Hence, it possesses the lowest compatibilizing activity towards the blends. The compatibilizer Escor displays an activity lower than that of Iotek and SEBS-g-MA, but it is higher than that of SEBS.

Keywords: Compatibilized LDPE/PA6 blends; Interfacial tension; Breaking thread method

1. Introduction

The interface has a crucial role in controlling the morphology and final properties of an immiscible polymer blend. The interfacial tension is the most basic parameter, which characterizes the interface between polymers. The values of the interfacial tension for various homopolymer pairs, using different techniques, have been reported [1–3]. The quantification of the properties of the interface is even more important when an interfacial modifier is added to the blend. The literature data about values of the interfacial tension of polyethylene/polyamide system are scarce. They concern mainly the blends of high density polyethylene (HDPE) with polyamide 6 (PA6) [4–7]. The values obtained vary from 13.5 mN/m [4,7] to 14.6 mN/m [5,6] and to 18.3 mN/m depending on the experimental temperature and the molecular mass of the homopolymers [5,6]. The systems linear low density polyethylene/PA6 and low density polyethylene/PA6 have the interfacial tension values of 12.5 mN/m [7] and 8.9 [3], correspondingly. Adding a compatibilizer to a blend of two incompatible polymers, results into a reduction of the interfacial tension [8]. The addition of compatibilizing agents to HDPE/PA6 systems leads to a strong reduction of the interfacial tension [5,9]. Values of 2 and 1.5 mN/m are obtained for such compatibilized systems [9]. The values for the system HDPE/PA6 in the presence of 2–10 wt% ionomer (Surlyn) are in the range of 7–11 mN/m, depending on the HDPE molecular mass and the sample preparation method [5].

There is a variety of methods for determining the interfacial tension. The pendant drop [1,10,11] and spinning drop [12,13] are the techniques mostly used. The above methods are equilibrium methods and normally require long experimental time and involve complicated experimental procedures. A simpler and more expeditious technique is the breaking thread method based on an analysis developed by Tomotika [14]. The interfacial tension can be obtained by

---

[*] Corresponding author. Tel.: +359-2-9712964; fax: +359-2-8707523. *E-mail address:* minkova@polymer.bas.bg (L. Minkova).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.09.054

studying the break-up of a molten polymer fibre embedded into another polymer via a mechanism known as capillary instabilities. The analysis quantifies the disintegration of an elongated thread, which is subjected to a sinusoidal distortion. Careful annealing of the experimental materials is required to eliminate the elastic components from the disintegration process. Once the thread and the matrix have melted totally and relaxed, distortions start to grow and the change in the amplitude is recorded with time. The theoretical background of the method is described elsewhere [4,5,15–18]. According to Lord Raleigh, the amplitude α grows exponentially with time t at a growth rate q:

$$\alpha = \alpha_0 \exp(qt),$$

where α_0 is the initial distortion amplitude.

The growth rate is then given by:

$$q = \sigma\Omega(\lambda_m, p)/2\eta_c R_0,$$

where σ is the interfacial tension, $\Omega(\lambda_m, p)$ is a tabulated function [14] related to the viscosity ratio $p(p = \eta_d/\eta_c)$, λ_m is the dominant wave length, η_c is the zero-shear viscosity of the continuous phase (matrix) and η_d is the zero-shear viscosity of the dispersed (thread) phase, R_0 is the initial radius of the thread.

At a given position of the thread the distortion is photographed at regular intervals of time. The amplitude α can be obtained from the expression:

$$\alpha = (b - a)/4,$$

where b is the largest diameter and a is the smallest diameter. The growth rate of the distortion q can be calculated from the slope of the line, obtained by plotting $\log(2\alpha/D_o)$ against time, where D_o is the original thread diameter. The time $t = 0$ may just coincide with the first measurement. The interfacial tension σ can be calculated as:

$$\sigma = q\eta_c D_o/\Omega(\lambda_m, p)$$

The applicability of the breaking thread method requires certain conditions [4,5,15–18].

In the previous papers the compatibilizing efficiency of three types of compatibilizer precursors (CP) towards blends of low density polyethylene (LDPE) with PA6 have been studied: (i) poly(ethylene-co-acrylic acid) (Escor 5000, 5001 and 5010, by Exxon) having different concentration of acrylic acid (from 6 to 11 wt%) [19]; (ii) ethylene-glycidylmethacrylate copolymer (Lotader GMA AX8840) [20]; (iii) triblock copolymer with polystyrene end blocks and a rubbery poly(ethylene–butylene mid block (SEBS) (Kraton G 1652) and SEBS-g-MA (Kraton FG 1901X) with 2 wt% maleic anhydride [21]. The effectiveness of the CP has been evaluated by an investigation of the thermal properties and the morphology of binary (LDPE/CP and PA6/CP) and ternary (LDPE/PA6/CP) blends, as well as by solvent fractionation experiments. It has been demonstrated that during melt blending the reactive groups of the CP react quite easily, with the reactive groups of PA6 to give CP-*g*-PA6 copolymers. The composition of the graft copolymers has been approximately determined by gravimetric and calorimetric measurements. The compatibilizing efficiency of the ethylene-glycidylmethacrylate copolymer has been found to be comparable to that of the ethylene-acrylic acid copolymers, and lower than that of a maleic anhydride-functionalized SEBS.

In this work the interfacial tension of uncompatibilized and compatibilized blends of LDPE and PA6 has been measured by the method of breaking thread. The aim has been to evaluate quantitatively the compatibilizing efficiency of different types of CP towards the blends.

2. Experimental part

2.1. Materials

The LDPE kindly provided by Polimeri Europa, was Riblene FF20 with a melt flow index (MFI) to 0.8 g/10 min. Polyamide-6 (PA6) was a commercial sample, kindly supplied by Snia Tecnopolimeri, with an intrinsic viscosity of 1.45 dL/g (measured at 25 °C in 85% formic acid) and contents of amine and carboxyl end groups of 34 and 35 meq/kg, respectively. The CP were: (i) an acrylic acid functionalized polyethylene, Escor 5001, produced by Exxon. Escor 5001 contains 6% w/w acrylic acid (AA) branches and its MFI is 2.0 g/10 min; (ii) an ethylene-acrylic acid zinc ionomer (Iotek 4200) with MFI = 3.0 g/10 min and $d = 946$ kg/m^3, provided by Exxon-Mobil Chemical Mediterranea; (iii) a triblock copolymer with polystyrene end blocks and a rubbery poly(ethylene–butylene mid block (SEBS) (Kraton G 1652), provided by Shell Chemical Company; (iv) SEBS-g-MA (Kraton FG 1901X) with 2 wt% maleic anhydride, provided by Shell Chemical Company.

Before use, all the polymers were accurately dried under vacuum for 12 h at 80 °C. The blends LDPE/compatibilizer were prepared with a batch mixer (Brabender Plasticorder) of 40 ml capacity, at 235 °C and 60 rpm for 4 min. The composition of the blends LDPE/compatibilizer was 99.5/0.5 and 98/2 w/w.

2.2. Microscopic observation and image analysis

Threads of PA6 polymer are spun from a molten granule on a hot plate. A typical thread has a diameter of 20–50 μm and a length of 10 mm. Before use the fibres were stored to relax at 80 °C for 24 h in order to eliminate the residual stresses. The LDPE polymer or LDPE/CP blend were compression moulded in thin films to serve as a matrix component. Before use the materials had been cleaned with alcohol. Great care was taken to avoid contamination in further actions. The thread is placed (at room temperature) between two films of the second polymer (LDPE or blend of LDPE with a compatibilizer), each with dimensions 10 × 10 × 0.6 mm. The system is enclosed between two glass sheets, placed under an optical microscope Ortholux Leitz in a Linkam hot stage. Care is taken that no pressure is exerted on the system to avoid deformation of the thread. In each experiment the sample is at first slowly heated to the melting temperature of the matrix in order to avoid air bubble formation at the interface. Then the temperature is increased almost up to the melting temperature of the thread. The system is allowed to anneal for 5 min. Finally, the sample is rapidly heated to the test temperature. The temperature profile was: heating up to 120 °C at a rate 5 °C/min, held at this temperature 1 min; heating from 120 to 220 °C at a rate 10 °C/min and held at this temperature 5 min; finally heating from 220 to 235 °C at a rate 10 °C/min. Then, in the molten state, distortions start to grow at the interface of the thread. Digitized images of the developing oscillations were captured. An image processing system (Scion Image) was used to measure the amplitude (α) and the wavelength (λ) of the growing distortions. The amplitude was calculated by measuring the evolution of the minimum and maximum diameters of one oscillation. Each value of interfacial tension is obtained from an average of at least five experiments. The typical error in the interfacial tension observed was ± 5%.

2.3. Measurement of the zero shear rate viscosity of the components

The zero shear viscosities of the polymers were obtained by measuring the viscosity at different shear rates and by extrapolating the Newtonian plateau value with a Carreau model [22]. Disk of polymers were pressed from preblended resins (LDPE, PA6, blends LDPE/compatibilizer) between two metal plates in a mould at 200 °C for the LDPE and LDPE/compatibilizer blends and at 235 °C for the PA6. Rheological measurements were performed on a constant stress rheometer in oscillation mode (Rheolab MC20, Physica Messtechnik GmbH). The rheometer had a plate–plate geometry and a plateau diameter of 25 mm; the gaps were in the range of 1.2–1.8 mm. All experiments were performed at 235 °C. At low shear rates, the tanδ was sufficiently near 90° to consider the polymers as Newtonian non-viscoelastic fluids.

2.4. SEM observations

Electron microscopic microphotographs were made on the fracture surfaces of the blend LDPE/PA6 75/25 w/w, compatibilized with 0.5 and 2 phr of the different compatibilizers. The preparation of the compatibilized blends is described elsewhere [19,21]. The blends were fractured under liquid nitrogen and the surfaces were covered with gold. A Scion Image processing system was used to measure the dimensions of the droplets of PA6 dispersed phase.

3. Results and discussion

Fig. 1 presents the typical rheological behaviour at 235 °C of some of the samples. Although the method is based on liquids exhibiting Newtonian behaviour, it is believed that this analysis is adequate for viscoelastic polymers, if the break-up process occurs at very low shear rates. In this case, the molten polymers essentially behave like Newtonian fluids and the zero shear viscosities can be used in the calculations. This technique is applicable, only if the polymers exhibit zero-shear viscosities and therefore the loss angle should be close to 90°. The zero shear viscosities of the different samples obtained by the Carreau model are given in Table 1. The addition of the compatibilizer to the LDPE matrixes almost does not change or increases the viscosities as predicted by the emulsion models [23]. The only exception is the blend LDPE/Escor 98/2 w/w.

Typical examples of the break-up behaviour of a PA6 thread in a LDPE and LDPE/compatibilizer matrixes are illustrated in Fig. 2(a) and (b). A reasonably regular sinusoidal distortion develops after which the thread breaks up into droplets separated by one wavelength. As seen small satellite droplets are formed in between the larger ones. A linear relationship between the logarithm of the dimensionless distortion ($2\alpha/D_o$) versus time was obtained (Fig. 3(a) and (b)). The slope of this line is equal to the growth rate (q) of the distortion. The measurements at the last stage of break up, i.e. where bead strings and satellite droplets are formed, are not taken into account [18]. Moreover, the measurements of the amplitude are started only from $\alpha_0/R_0 \geq 0.1$ since smaller amplitudes are not visible (α_0 is the initial distortion amplitude).

The experimental values are collected in Table 2. It should be mentioned that the evaluation of the tabulated function Ω_m is only possible if thread break-up is generated by a distortion having a dominant wavelength close to the theoretical one [13,14]. So, the experimental wave number ($X_{\exp}$) must be compared to the theoretical one (X_m) to provide control over the quality of the experiment. For a given viscosity ratio p, there will be one dominant wavelength λ_m at which the amplitude grow is the fastest;

Table 1
Zero shear viscosity for LDPE, PA6 and the blends LDPE/compatibilizer

Sample	η^* at 235 °C, Pa s
LDPE	4760
PA6	3490
LDPE/Escor 99.5/0.5 w/w	4730
LDPE/Escor 98/2 w/w	3480
LDPE/Iotek 99.5/0.5 w/w	4720
LDPE/Iotek 98/2 w/w	5200
LDPE/SEBS 99.5/0.5 w/w	5140
LDPE/SEBS 98/2 w/w	5200
LDPE/SEBS-g-MA 99.5/0.5 w/w	5140
LDPE/SEBS-g-MA 98/2 w/w	5400

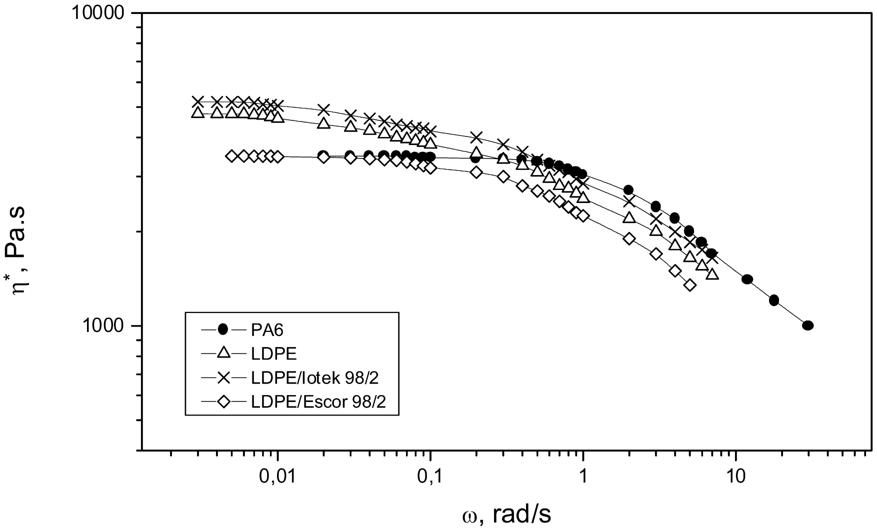

Fig. 1. Typical rheological behaviour of some of the polymers used.

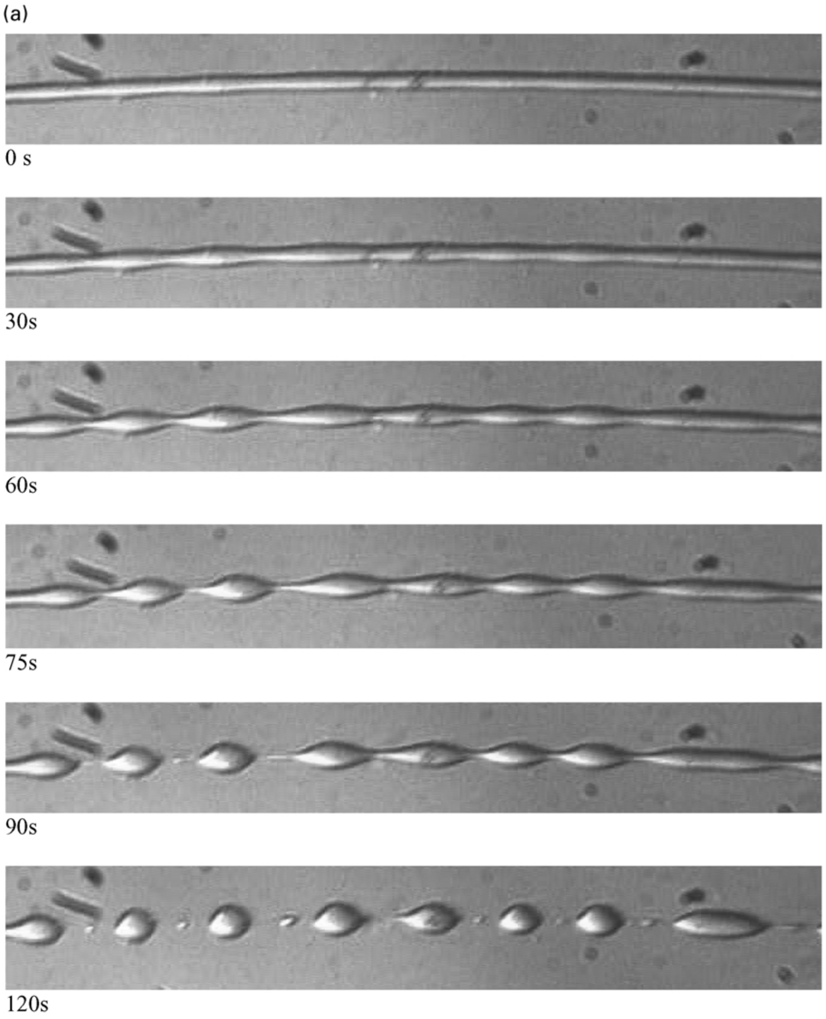

Fig. 2. Sinusoidal distortions of a PA6 thread embedded in a LDPE (a) and in a LDPE/Escor 99.5/0.5 w/w (b) matrixes at 235 °C.

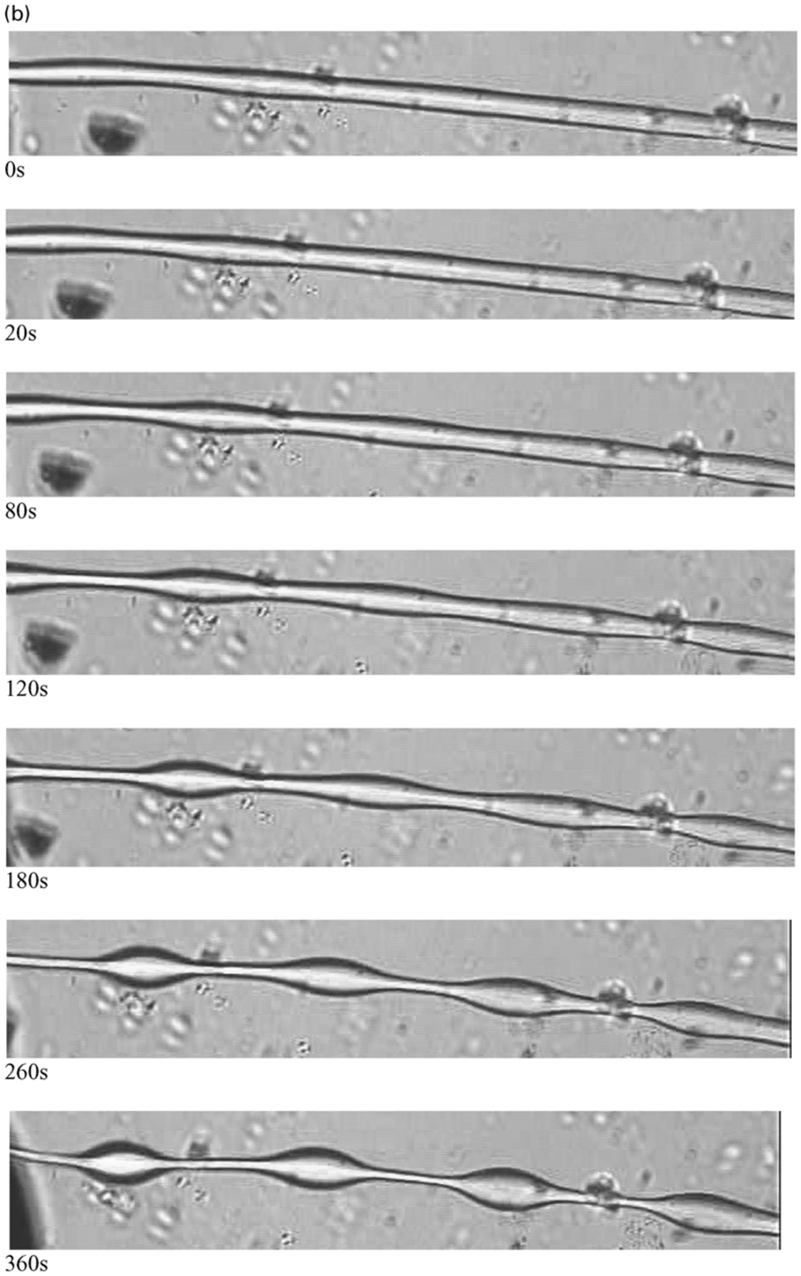

Fig. 2 (*continued*)

Table 2
Measured interfacial tension at 235 °C

Matrix	Viscosity ratio, p	X_m (theor)	X_{exp} (exp.)	Ωm	$qD_o \times 10^6$ (μm/s)	σ (mN/m)
LDPE	0.73	0.58	0.57	0.090	0.2357	12.5
LDPE/Escor 99.5/0.5	0.73	0.58	0.57	0.09	0.1485	7.8
LDPE/Escor 98/2	1.00	0.56	0.57	0.067	0.119	6.2
LDPE/Iotek 99.5/0.5	0.73	0.58	0.58	0.09	0.0779	4.0
LDPE/Iotek 98/2	0.73	0.58	0.57	0.09	0.0531	3.0
LDPE/SEBS 99.5/0.5	0.81	0.57	0.56	0.075	0.184	10.5
LDPE/SEBS 98/2	0.73	0.56	0.54	0.09	0.1561	9.0
LDPE/SEBS-g-MA 99.5/0.5	0.68	0.58	0.56	0.092	0.0937	5.2
LDPE/SEBS-g-MA 98/2	0.65	0.57	0.56	0.1	0.0697	3.8

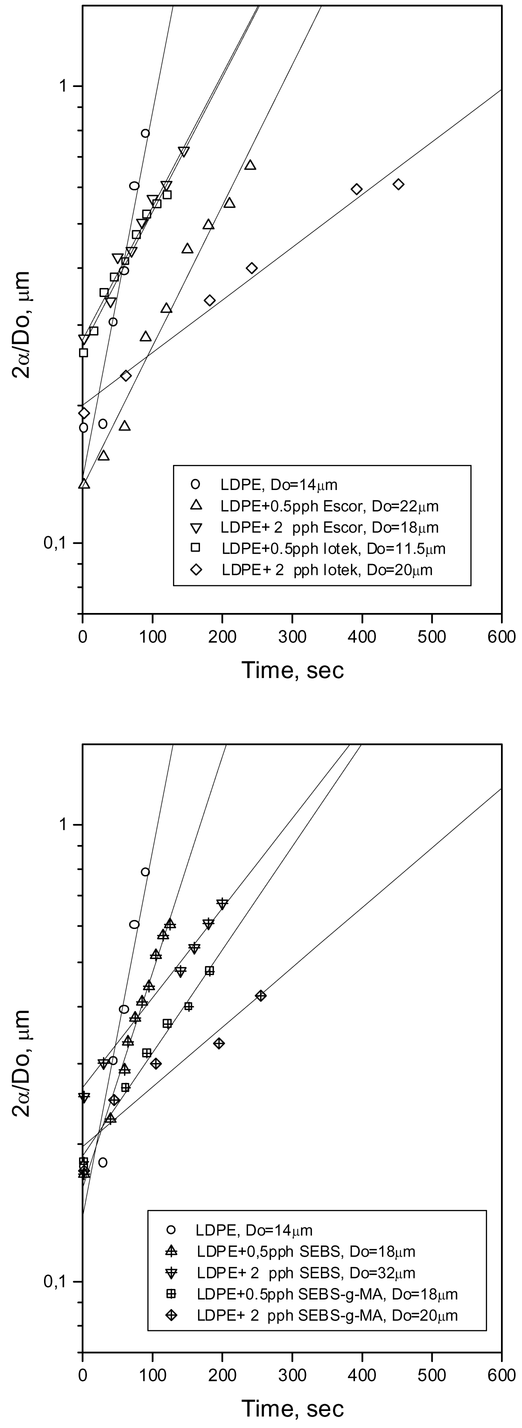

Fig. 3. Relative amplitude vs. time for LDPE, LDPE/Escor, LDPE/Iotek (a) and for LDPE, LDPE/SEBS, LDPE/SEBS-g-MA (b) at 235 °C.

the distortion having this wavelength consequently causes the thread to break up into droplets. The dominant wave number $X_m (= 2\pi R_0/\lambda_m)$ and its corresponding value Ω_m are graphically presented as a function of the viscosity ratio elsewhere [13]. The data for X_{exp} and X_m, presented in Table 2, demonstrate that the dominant wavelength is close to the theoretical one for all samples. It should be mentioned that if X_{exp} does not coincide perfectly with X_m that could be due to the fact that the break-up of the fibre occurs at wavelength λ smaller than the dominant wavelength λ_m. In this case the graphical representation of $\Omega(\lambda, p)$, covering a range of $10^{-3} < p < 10^2$ and $0.1 < X < 0.9$ should be used [4].

In this work the breaking thread method was used for measuring the effect of adding different compatibilizers to the system LDPE/PA6. In a typical blending process, the shear and elongation forces favour the migration of the compatibilizer to the interface and lowering of the interfacial tension can occur. However, in the breaking thread method the experiments are carried out under almost ‘static’ conditions and the migration of the interfacial modifier is more difficult since the modifier must be added to either the matrix or dispersed phase. Different interfacial tension values can be obtained determined by the fact to which of the components the interfacial agent is added [11]. So, it should be emphasized that in all experiments the compatibilizer is added always to a matrix polyethylene phase. Moreover, for small amount of the compatibilizer, it was possible to perform the experiment, while for high amounts, the matrix became opaque and the experiments were no longer possible. The thermal stability in air atmosphere of the polymers also is taken into consideration. Due to their molecular structure all compatibilizers investigated possess lower thermal stability than that of polyethylene. Therefore at high temperature the addition of a high amount of compatibilizer to LDPE leads to degradation processes in the compatibilized matrix. On that reason an appropriate amount of compatibilizer (0.5 phr; 2 phr) has been used for all the experiments.

In general all experiments including a compatibilized polyethylene matrix have shown the following peculiarities: (i) the wavelengths are less uniformly distributed along the thread than in the case of neat homopolymers [4]. That is why only the measurements with the best agreement between X_{exp} and X_m have been taken into account; (ii) for systems with compatibilizers, there might be a yield stress in the zero shear rate range, which counteracts the driving force for break-up [4]. That is why very thin threads have been used [4].

The values of the interfacial tension measured (Table 2) are plotted versus the content of a compatibilizer (Fig. 4(a)). The value for the interfacial tension of the uncompatibilized system is in a good agreement with the literature data [3]. The addition of SEBS almost does not change the interfacial tension, while a strong decrease of the interfacial tension could be observed with the addition of only 0.5 phr Iotek or SEBS-g-MA compatibilizers to the matrix LDPE phase. The further increase of the content of these compatibilizers up to 2 phr leads to a slight decrease of the interfacial tension. The obtained values for the latter compatibilized systems are in a perfect agreement with the values for similar compatibilized systems [9]. Considering the decrease of the interfacial tension as a measure of the

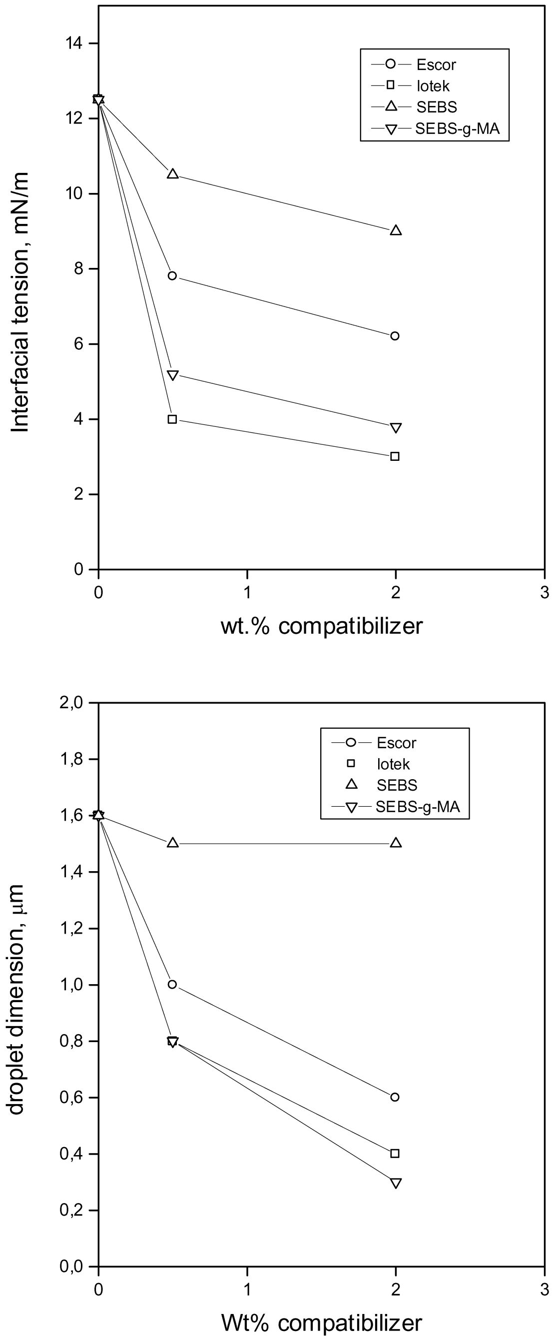

Fig. 4. Dependence of the interfacial tension (a) and of the droplet dimension (b) on the wt% compatibilizer for the different systems. The droplet dimension has been measured for the compatibilized blend LDPE/PA6 at 75/25 w/w.

effectiveness of a certain compatibilizer it could be stated that Iotek and SEBS-g-MA demonstrate the strongest activity towards LDPE/PA6 blends. Escor 5001 decreases the interfacial tension between the components with about 50%, while the SEBS compatibilizer posses the lowest activity. These results are in agreement with the reduction of the dimensions of the dispersed particles caused by the addition of a compatibilizer to the blend LDPE/PA6 75/25 w/w (Fig. 4(b)).

4. Conclusion

The determination of the interfacial tension of uncompatibilized and compatibilized LDPE/PA6 blends by means of the breaking thread method leads to the following conclusions: the addition of a compatibilizer to the blend reduces the interfacial tension. The degree of the interfacial tension decrease depends strongly on the type and concentration of the compatibilizer. The compatibilizing activity of the different compatibilizers has been evaluated quantitatively by the value of the interfacial tension. The compatibilizers Iotek and SEBS-g-MA demonstrate the strongest activity towards the blends; these compatibilizers reduce substantially the interfacial tension, which in turns leads to the drastic decrease of the dimension of the dispersed particles. Contrary, the compatibilizer SEBS almost does not reduce the interfacial tension and the dispersed particles dimension. The compatibilizer Escor posses an activity lower than that of Iotek and SEBS-g-MA, but higher than that of SEBS.

Acknowledgements

This work was financially supported by the Italian Ministry of University and Scientific and Technological Research (Contract MM09244737) and by the Bulgarian Science Research Foundation (Contract X-1104).

References

[1] Roe RJ. J Coll Interf Sci 1969;31:228.
[2] Elmendorp JJ. PhD Thesis, Delft University of Technology, The Netherlands, 1986 Elmendorp JJ. Polym Engng Sci 1986; 26:418.
[3] Luciani A, Champagne MF, Utracki LA. Polym Netw Blends 1996;6: 41. Luciani A, Champagne MF, Utracki LA. Polym Netw Blends 1996;6:51.
[4] Elemans PHM, Jansen JMH, Meijer HEH. J Rheol 1990;34:1311.
[5] Chapleau N, Favis BD, Carreau PJ. J Polym Sci B 1998;36:1947.
[6] Chapleau N, Favis BD, Carreau PJ. Polymer 2000;41:6695.
[7] Liang H, Xu R, Favis BD, Schreiber HP. J Polym Sci B 2000; 38:2096.
[8] Wu S. Polymer interface and adhesion. New York: Dekker; 1979.
[9] Chen CC, White JL. Polym Engng Sci 1993;33:923.
[10] Kamal MR, Lai-Fook R, Demarquette NR. Polym Engng Sci 1994;34: 1834.
[11] Hu W, Koberstein JT, Lingelser JP, Gallot Y. Macromolecules 1995; 28:5209.
[12] Patterson HT, Hu KH, Grinstaff TH. J Polym Sci Part C 1971;34: 31.
[13] Elmedorp JJ, De Vos G. Polym Engng Sci 1986;26:415.
[14] Tomotika S. Proc R Soc London (A) 1935;150:322.
[15] Mekhilef N, Favis BD, Carreau PJ. J Polym Sci B 1997;35:293.

[16] Lepers J, Favis BD, Tabar RJ. J Polym Sci B 1997;35:2271.
[17] Lepers J, Favis BD, Lacroix C. J Polym Sci B 1999;37:939.
[18] Veenstra H, Van Lent BJJ, Van Dam J, De Boer AP. Polymer 1999;40:6661.
[19] Filippi S, Chiono V, Polacco G, Paci M, Minkova L, Magagnini PL. Macromol Chem Phys 2002;203:1412.
[20] Chiono V, Filippi S, Yordanov Hr, Minkova L, Magagnini PL. Polymer 2003;44:2423.
[21] Filippi S, Yordanov Ch, Minkova L, Polacco G, Talarico M. Macromol Chem Phys, In press.
[22] Carreau PJ. Trans Soc Rheol 1972;16:99.
[23] Lacroix C, Bousmina M, Carreau PJ, Favis BD, Michel A. Polymer 1996;37:2939.