

Influence of Chemical and Mechanical Compatibilization on Structure and Properties of Polyethylene/Polyamide Blends

B. JURKOWSKI, K. KELAR, D. CIESIELSKA

Division of Plastics and Rubber Processing, Institute of Material Technology, Poznań University of Technology, 61-138 Poznan, Piotrowo 3, Poland

Received 10 June 1997; accepted 14 November 1997

ABSTRACT: LDPE/PA6 binary blends and LDPE/PA6/compatibilizer ternary blends were prepared in a Brabender extruder, equipped with a prototype static mixer. Compatibility of the components was estimated by rheological properties (viscosity and a melt flow index), and observations of the structure were made with the help of scanning electron microscopy and tensile strength. It was found that the blends' structure and properties are dependent on the recipe content of the polymer blends and the conditions of their manufacturing. Uniformity of the blends of the thermodynamically immiscible polymers was improved by using a prototype static mixer giving mechanical compatibilization and a compatibilizer giving chemical compatibilization. LDPE grafted with a maleic anhydride (LDPE-*g*-MAH) was used as a compatibilizer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 719–727, 1998

Key words: mechanochemical modification; grafting; compatibilizer; mechanical compatibilization; PA6; LDPE; static mixer; melt mixing

INTRODUCTION

Properties of polymer blends depend on many factors, especially blend composition, interphase interactions, size and shape of the particles of the dispersed phase, and the rheological characteristics of the blend's components. In blends of immiscible polymers or with limited miscibility, obtaining a good dispersion of the dispersed phase in the polymer matrix is difficult.^{1,2} The so far undertaken attempts to solve this problem were based on the application of mixing rotors or mixing elements in screws of internal mixers or extruders. Static mixers are also used during polymer coextrusion, whose effect was additionally strengthened by using dynamic mixers (usually disc-head or

cavity-transfer mixer types). However, this solution implies significant investment and does not ensure the desired effect always. Introducing additional components having a chemical structure similar to that of the components to be mixed, known as compatibilizers, reduce the interfacial tension between phases. As a result, the size of the dispersed phase is reduced, and the phase structure in the polymer blend is stabilized.^{1–6} Most frequently, they are block or graft copolymers.

The aim of this work was to compare the effectiveness of the mechanical compatibilization by use of a prototype static mixer and chemical compatibilization (introduction to the blend of a third-phase compatibilizer). For this purpose, the structure and properties of the blends of low-density polyethylene (LDPE) and polyamide six (PA 6) were evaluated.

EXPERIMENTAL

Materials

The components used in the study were LDPE (Malen E) made by the Petrochemical Plant

Correspondence to: B. Jurkowski (jurkowsk@sol.put.poznan.pl).

Contract grant sponsor: Polish Committee of Scientific Research; contract grant number: 7.T08E.014.11.

Journal of Applied Polymer Science, Vol. 69, 719–727 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/040719-09

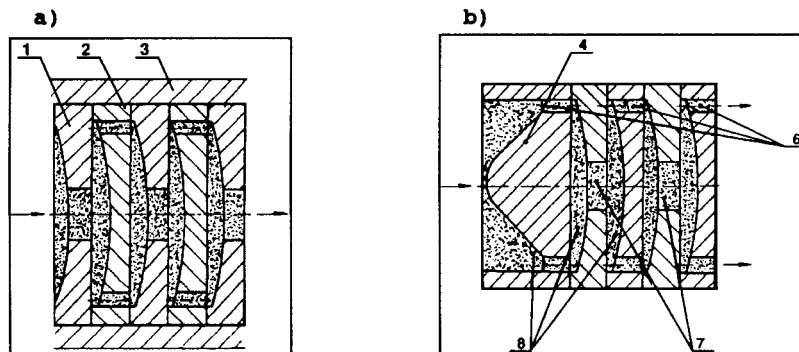


Figure 1 Design of static mixers: (1) insert with a lenticular cavity and the channel passing the trough centrally; (2) insert with a lenticular cavity and passing through holes set on the circumference; (3) barrel; (4) insert with conic lug and passing through holes on the circumference; (6) passing through holes; (7) central hole; (8) wedged material.

(Płock, Poland) and PA6 (Tarnamid T-27) made by the Nitrogen Chemistry Plant (Tarnów, Poland). Before use, PA6 was dried in a vacuum chamber at 80°C for 48 h. Polyethylene grafted with a maleic anhydride (LDPE-*g*-MAH) obtained by the method described elsewhere⁷ was used as a compatibilizer.

Procedures

The blends to be studied were produced using a Brabender plasticorder (type FOD 234) with a tested static mixer of a special design and an extrusion head (Fig. 1).⁸⁻¹⁴ Between the extruder's cylinder and head, a set of different mixing elements was assembled. These elements divide the stream of the extruded material into streamlets. These streamlets are converged into another configuration and mutually infiltrate, creating a new stream. This considerably homogenizes the blend composition and stabilizes the temperature pressure of the batch coming to the die. This process also helps to bring the macroradicals generated in dispersive mixing closer together and to recombine. It is a necessary condition for mechanochemical (reactive) processing. This design allows one

to mix components in controlled conditions as well. The length of the mixer, in which inserts Nos. 1 and 2 were alternated, is 120 mm. The rates at which the molten batch is moving through the static mixer were selected so that the residence time of the material was about 2 min in the regions during which it was heated up to 235°C.

In the first stage, our objective was to determine the shearing stress appearing during the extrusion of LDPE and PA 6. The studies were done with three similar homogenizing inserts having different diameter holes and at different rotational speeds (20–110 min⁻¹) of the plasticorder screw. Shear rates were determined from the output during the extrusion of LDPE and PA6. This output depends not only on the screw speed and geometry of the channels through which the polymer is flowing, but also on the coefficient of friction.¹⁵

In the second stage, the binary LDPE/PA 6 blends and ternary LDPE/PA 6/LDPE-*g*-MAH blends were extruded. The rotational speed of the screw was 50 min⁻¹. Holes in the homogenizing inserts of $d = 1.4$ mm in diameter (shearing stress τ was $2.4 \cdot 10^5$ Pa) were used. The recipes of polymer blends used in this investigation are given in Table I.

Table I Recipes of Polymer Blends Studied

Compatibilizer	Compatibilizer Contribution (wt %)	Concentration of Individual Components in the Blend LDPE/PA6 (wt %)			
		90/10	80/20	70/30	60/40
No compatibilizer	—	90/10	80/20	70/30	60/40
LDPE- <i>g</i> -MAH	5	85/10	75/20	65/30	55/40

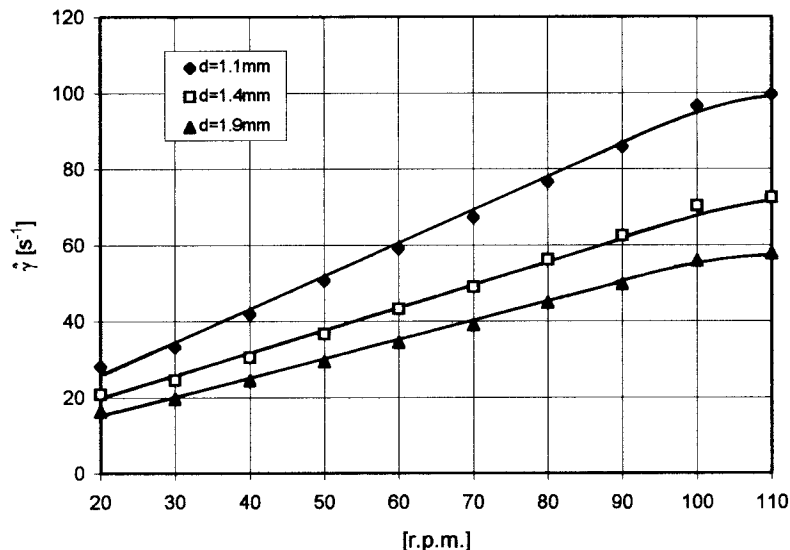


Figure 2 Shearing rate versus the rotational speed of the screw during extrusion of LDPE for different diameters of holes in the homogenizing inserts.

The rheological properties of the extrudates were determined by a capillary rheometer made by Instron. Measurements were done at 235°C using a capillary tube of $L/D = 34.2$ at the following shear rates: $\dot{\gamma} = 7.3, 18.25, \text{ and } 36.5 \text{ s}^{-1}$. The mean error of the viscosity measurement expressed as the geometrical mean of the viscosity measurements of individual polymer components, taking into account their percent concentration in the blend, was 7.5%.

The melt flow index (MFI, 235°C; 21.1N) of the

blends was determined by an MP-IIRT-M plastometer made in the USSR. The strength of the samples made of these blends was measured by use of a computer-operated Instron tensile testing machine Model 1115 (UK).

Samples for the structural tests were cooled down in liquid nitrogen and fractured. The fracture surface was coated with gold for the SEM studies. The morphology of the blends was tested on a scanning electron microscope JOEL type JMS-50A (Japan).

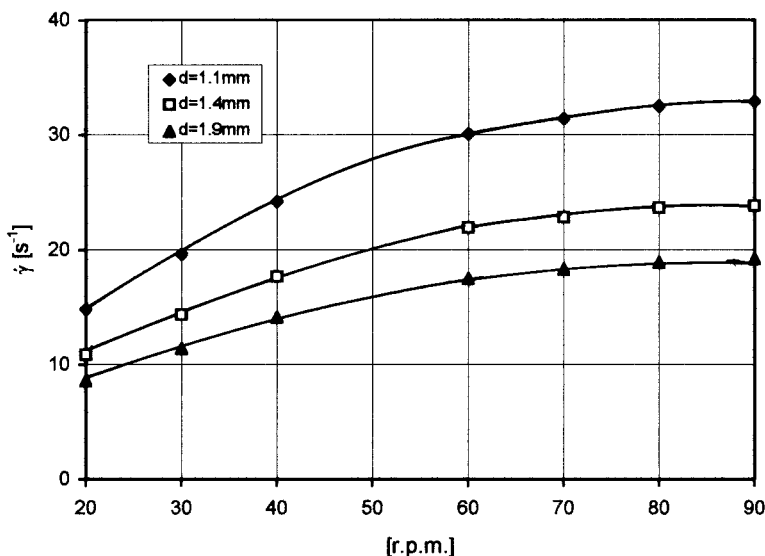


Figure 3 Shearing rate versus the rotational speed of the screw during extrusion of PA 6 for different diameters of holes in the homogenizing inserts.

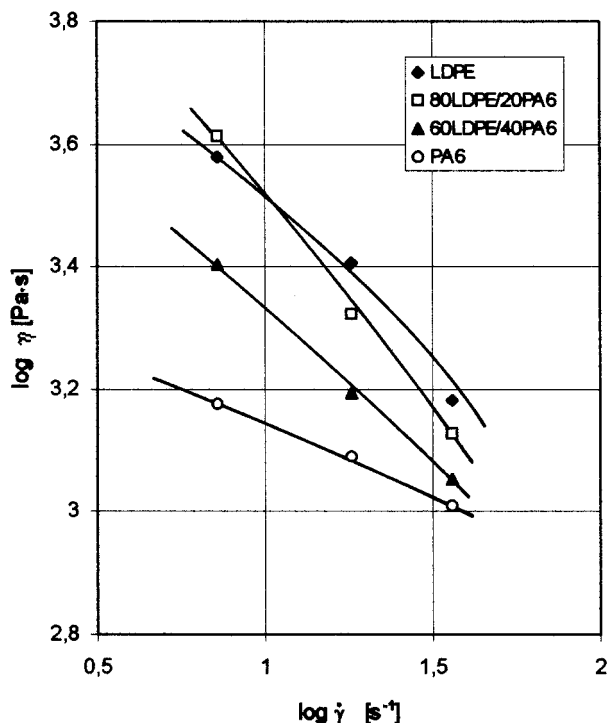


Figure 4 The rheological dependency viscosity η versus shearing rate $\dot{\gamma}$ for the binary LDPE/PA6 blends.

RESULTS AND DISCUSSION

Figure 2 presents the shearing rates versus the rotational speed of the screw during the extrusion of LDPE for different diameters of holes in the homogenizing inserts. It can be seen that with increasing the rotational speed of the screw and diminishing the diameter of holes in the homogenizing inserts the shearing rate increases.

Figure 3 presents an analogous dependence for PA 6. A comparison of the two dependencies reveals that when extruding PA 6 the shearing rate is much lower as compared with that of LDPE for the same rotational speed of the screw and the same diameter of holes in the homogenizing inserts. This is a consequence of a lower flow resistance during PA6 extrusion.

The rheological properties of the polymer blends strongly depend on their morphology.^{16–18} The phase structure of the polymer blends is essentially determined by the temperature and shearing rate.¹⁹ Polymer blends of limited miscibility are usually characterized by significantly reduced viscosity in comparison to that approximated by use of the additivity rule, which evidences that an increase in the viscosity of a polymer blend is

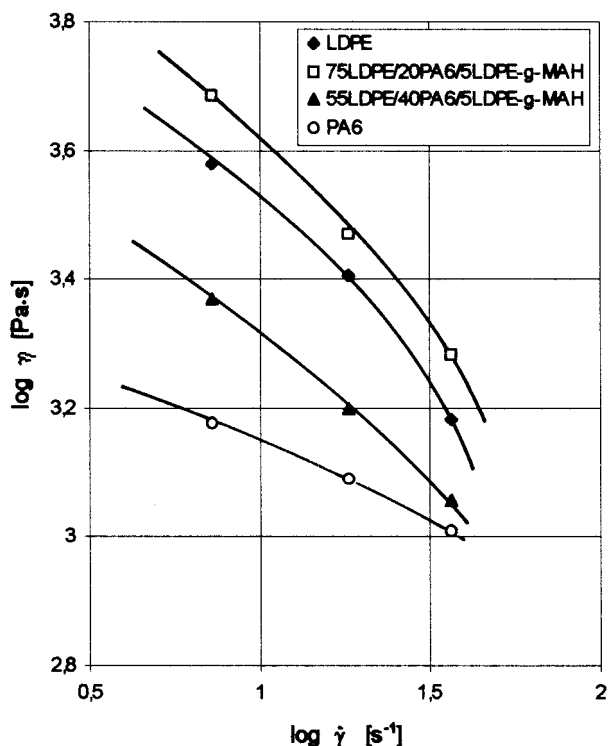


Figure 5 The rheological dependency viscosity η versus shearing rate $\dot{\gamma}$ for the ternary LDPE/PA6/LDPE-g-MAH blends.

an indication of increased interphase interactions.

Figures 4 and 5 present the rheological depend-

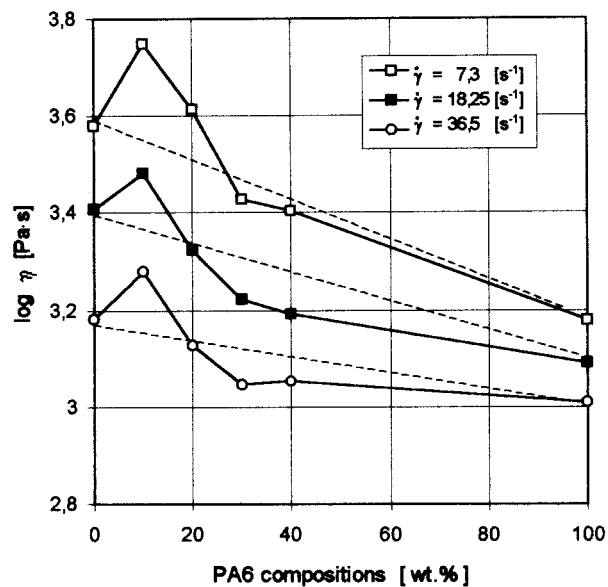


Figure 6 Viscosity of LDPE/PA6 blends as a function of PA6 concentration in the blend.

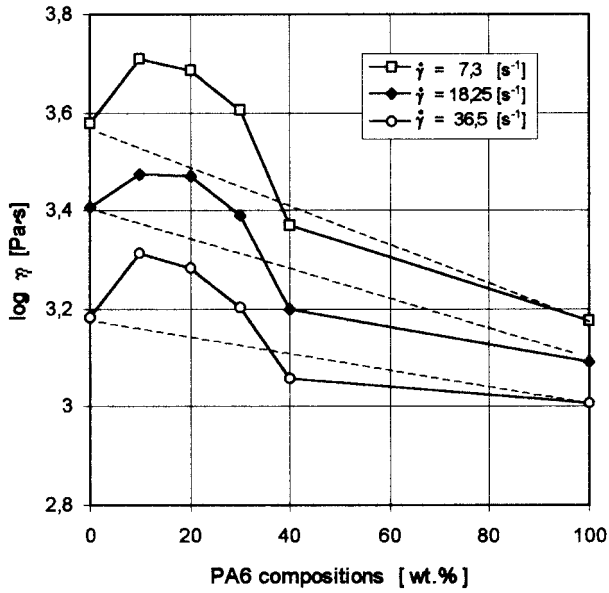


Figure 7 Viscosity of LDPE/PA6/LDPE-*g*-MAH blends as a function of PA 6 concentration in the blend.

encies $\eta = f(\dot{\gamma})$ for the studied binary LDPE/PA6 and ternary LDPE/PA6/LDPE-*g*-MAH blends recorded at 235°C. It was found that the flow of the melts of the studied blends is non-Newtonian in character. The rheological characteristics of the blends permit an analysis of the relationship be-

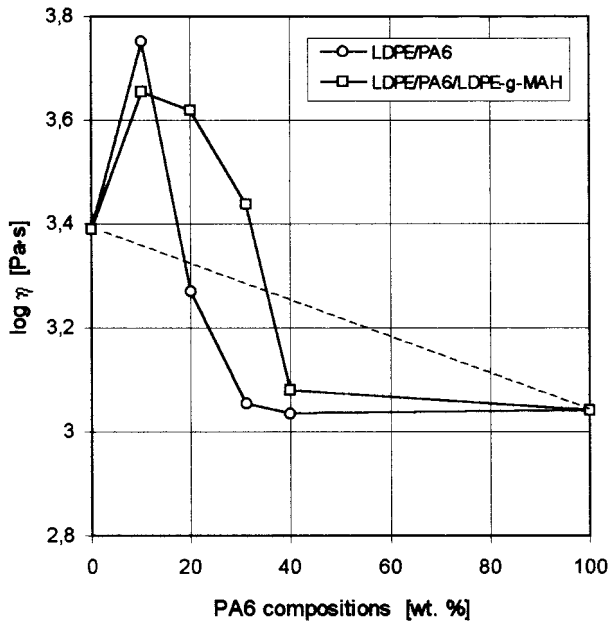


Figure 8 Viscosity of LDPE/PA6 blends as a function of PA 6 concentration for shearing stress $\tau = 41$ kPa.

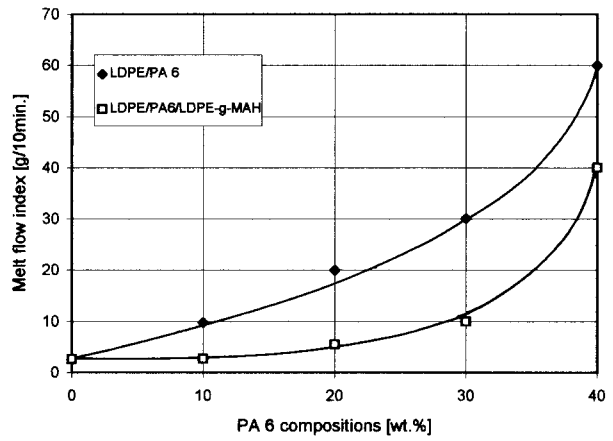


Figure 9 MFI as a function of the blend recipe.

tween their viscosity and content (see Figs. 6 and 7). In Figure 8, the viscosity of the LDPE/PA6 and LDPE/PA6/LDPE-*g*-MAH blends is shown as a function of PA6 concentration for $\tau = \text{const} = 41$ kPa.

The relation between the recipe composition of a given polyethylene–polyamide blend and its viscosity has been studied by many authors.^{2,20,21} So far, no decisive answer has been given to the question of whether the viscosity of such blends follows

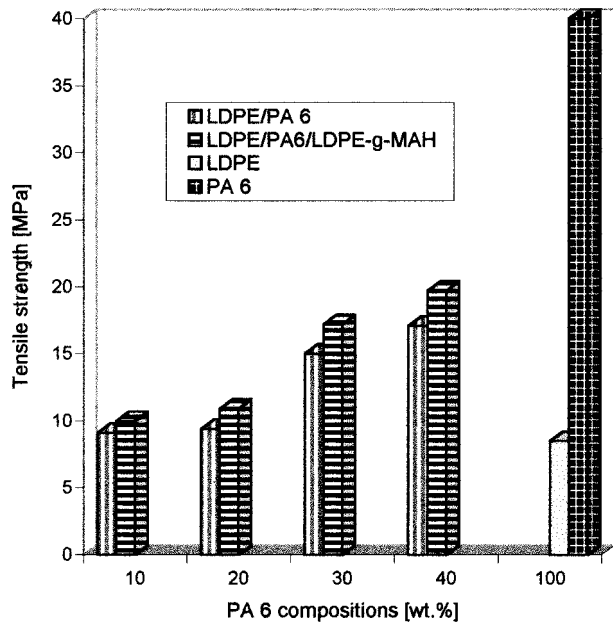


Figure 10 Tensile strength of LDPE/PA6 and LDPE/PA6/LDPE-*g*-MAH blends as a function of PA 6 concentration in the blend.

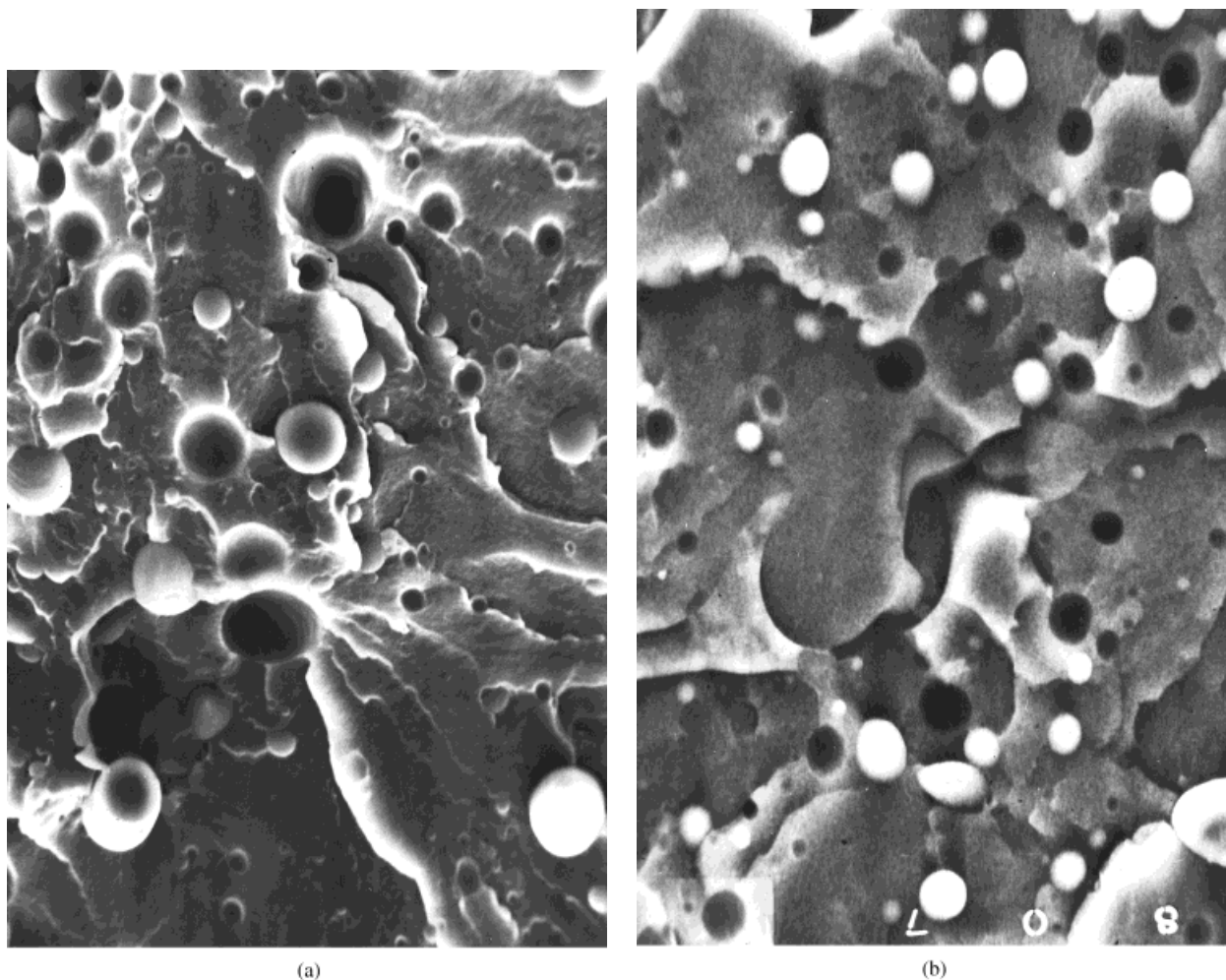


Figure 11 SEM micrographs of cryogenically fractured surfaces for blends: (a) 70LDPE/30PA6 blend; (b) 70LDPE/30PA6 blend extruded with a static mixer; (c) 65LDPE/30PA6/5LDPE-*g*-MAH blend extruded with a static mixer; (d) 65LDPE/30PA6/5LDPE-*g*-MAH blend extruded with a static mixer and processed a second time at a temperature of 230°C. Magnification 1000 \times .

linearly the changes in their content, according to the additivity rule, or whether there are negative or positive deviations from this rule. Our studies prove that the deviations from the additivity rule can be either positive or negative depending on the conditions of the blend production.^{7,22} It could be accepted that that kind of deviation from the additivity rule is related to the miscibility (total or limited) of the blend components in certain conditions, that is, in the melt and under the effect of certain shearing stress. The positive deviations from the additivity rule are frequently observed in the blends whose phases strongly interact with each other or whose components have functional groups that act chemically.^{1,2} Our supposition is

that the positive deviations from the additivity rule are a consequence of two factors: a beneficial effect of the static mixer (mechanical compatibilization) and the applied compatibilizer (chemical compatibilization). This conclusion is confirmed by the results of our article,²³ where it was shown that the tested static mixer sometimes gives a pseudomolecular distribution of immiscible polymeric components. Now, this mechanical compatibilization is visible for binary LDPA/PA6 blends containing up to 25 wt % of PA6. Here, a good dispersion of the components gives a large border surface area between phases, which should promote segmental diffusion during the processing of molten polymers. This segmental diffusion is

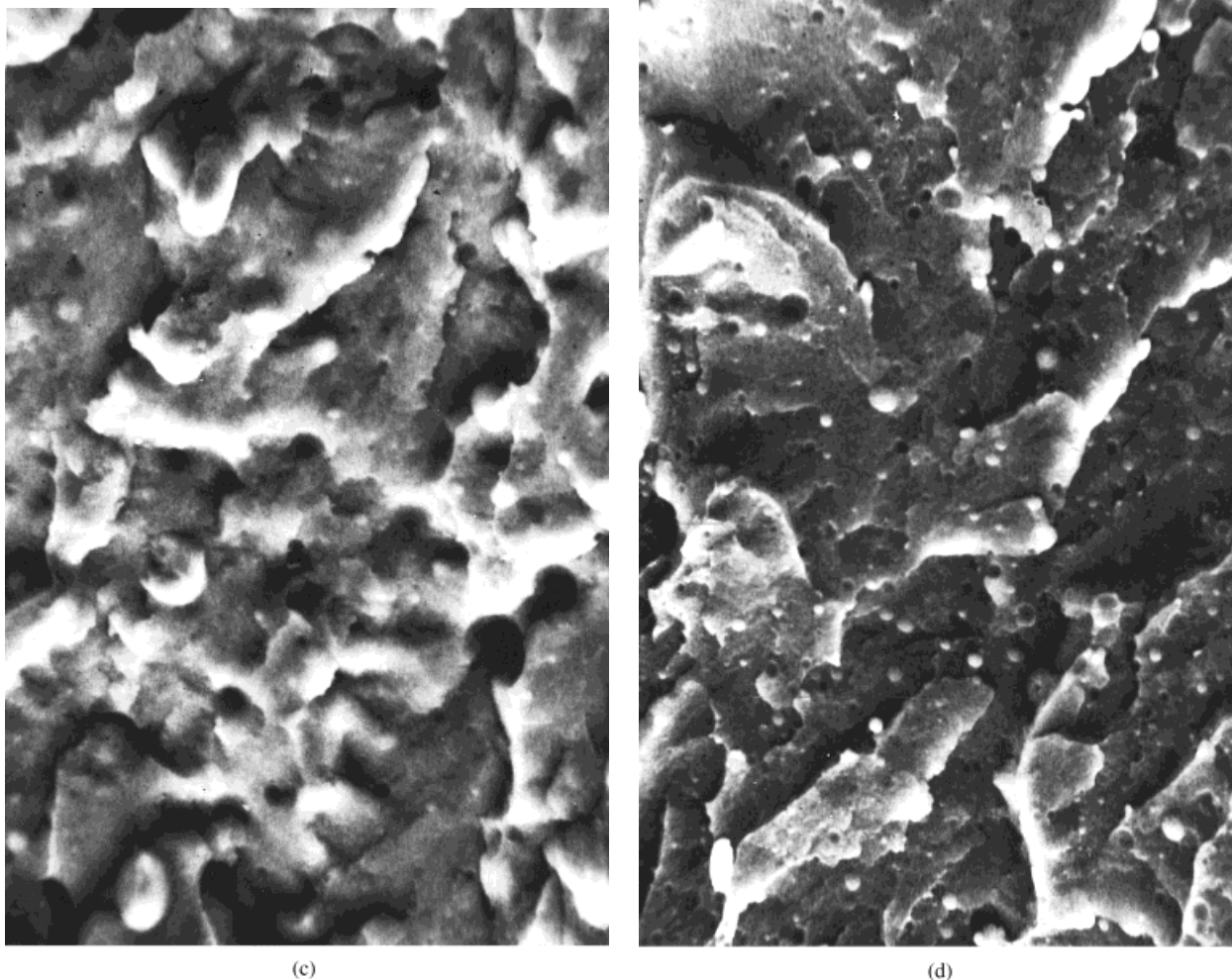


Figure 11 (Continued from the previous page)

beneficial for the stabilization of small drops of immiscible components distributed in a viscous matrix, especially after the cooling down of this matrix. This, probably, is the reason for mechanical compatibilization. For PA6, a concentration over 25 wt % is a different morphology of such a blend giving different properties, which is the subject of further investigations.

Some confirmations of the increased interaction between the blend components are the observed changes in the melt flow index (MFI) accompanying the changes in the blend content (Fig. 9). The MFI of the polymer blends whose phases do not interact or show only weak interactions change linearly with the composition content.^{24,25} For the blends whose phases have strong interactions, this dependence reveals a characteristic deviation from linearity. The dependencies

of MFI on the polymer blend content, similar to the ones that we obtained, were reported for blends of polypropylene with PA 6 in the presence of polypropylene grafted with maleic anhydride.²⁴

The mechanical properties of polymer blends depend mainly on the dispersion degree of the components and the interaction between or among them. Lack of miscibility is a reason that impact and tensile strength are reduced. Additivity and synergism evidence the miscibility of the components and positive interaction between the phases.²⁵ In Figure 10 is shown the dependence of the tensile strength on the PA6 content in a composition. In all tested samples, an increase in the PA6 content is followed by the growth of tensile strength. All ternary LDPE/PA6/LDPE-*g*-MAH blends are characterized by a higher strength than that of the binary LDPE/PA6

blends. This shows the positive effect of chemical compatibilization.

In Figure 11(a) is shown an SEM microphotograph of a fracture surface of a 70LDPE/30PA6 blend, extruded with the use of a typical extruding die. A large difference in the chemical structure of both polymers is the reason for a visible separation of the spherulitic particles in a polyethylene matrix. Poor adhesion between the phases is the reason for considerable pulling out of the dispersed phase during fracture. In Figure 11(b) is shown an SEM microphotograph of a fracture surface of a blend of the same content, but processed with a static mixer assembled on the extruder. The effect of mechanical compatibilization is visible in the relatively smaller-size particles of a dispersed phase. The morphology of the 65LDPE/30PA6/5LDPE-*g*-MAH blend extruded with a static mixer is shown in Figure 11(c), which shows a uniform morphology without spherulites, which is attributed to the effect of the chemical compatibilization of the phases by LDPE-*g*-MAH. The aim of the compatibilization of the polymeric components of the blend is phase-structure stabilization.²⁶

To study the effect of recycling on the phase stability, a 65LDPE/30PA6/5LDPE-*g*-MAH blend was extruded, first, with the static mixer and, next, after cooling, extruded again at a temperature of 230°C using a typical extruding die. Figure 11(d) shows an SEM microphotograph of a fracture surface of this system. In this figure fine polyamide domains dispersed in a polyethylene matrix are visible. This could be the result of a small coalescence during the second processing. From this, it is concluded that mechanical compatibilization could be reversible when the viscosity of a polymer matrix is reduced during the next stages of the processing of the polymer blends containing immiscible components. Studying this phenomenon further in detail will be reasonable, especially with an increased share of the compatibilizer and use of static mixers applying higher shear forces or use of dynamic mixers.

CONCLUSIONS

1. The viscosity of the studied polymer blends reveals positive or negative deviations from the additivity rule depending on the blend content. The deviations are similar for different shear rates.
2. The dependence of the MFI on PA6 concentra-

tion obtained for the blend of LDPE/PA6 reveals a characteristic deviation from linearity, which suggests that the interphase interactions have increased due to the effect of both the compatibilizer and the applied static mixer.

3. Mechanical and chemical compatibilization affects the improvement of uniformity of the phase structure of polymer blends.
4. Second processing the blends, earlier being compatibilized mechanically or chemically, might cause a small coalescence.

The authors thank the Polish Committee of Scientific Research (Grant No. 7.TO8E.014.11) for financial support.

REFERENCES

1. S. J. Park, B. K. Kim, and H. H. Jeong, *Eur. Polym. J.*, **26**, 131 (1990).
2. B. K. Kim, S. Y. Park, and S. J. Park, *Eur. Polym. J.*, **27**, 349 (1991).
3. W. J. Macknight, *Polym. Eng. Sci.*, **25**, 349 (1985).
4. D. Heikens and W. Barentsen, *Polymer*, **18**, 1124 (1985).
5. H. Raval, S. Devi, Y. P. Singh, and M. H. Mehta, *Polymer*, **32**, 493 (1991).
6. A. J. Oshinski, H. Keskkula, and D. R. Paul, *Polymer*, **33**, 269 (1992).
7. B. Jurkowski, K. Kelar, D. Ciesielska, and R. Urbanowicz, *Kautsch. Gummi Kunstst.*, **47**, 642 (1994).
8. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 168,449 B1 (Sept. 4, 1992).
9. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 168,416 B1 (June 17, 1992).
10. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 168,864 B1 (Aug. 19, 1992).
11. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 168,856 B1 (Aug. 19, 1992).
12. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 168,869 B1 (Aug. 21, 1992).
13. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 168,854 B1 (Aug. 19, 1992).
14. B. Jurkowski, R. Urbanowicz, and M. Szostak, Pol. Pat. 169,185 B1 (Aug. 19, 1992).
15. E. G. Fisher, *Extrusion of Plastics*, Iliffe, London; Interscience, New York, 1964, p. 30.
16. L. A. Utracki and M. R. Kamal, *Polym. Eng. Sci.*, **22**, 69 (1982).
17. L. A. Utracki, *J. Elast. Plast.*, **18**, 177 (1986).
18. L. A. Utracki, A. M. Catani, G. L. Bata, M. R. Ka-

- mal, and V. Tan, *J. Appl. Polym. Sci.*, **27**, 1913 (1982).
19. S. Thomas, B. R. Gupta, and S. K. De, *J. Appl. Polym. Sci.*, **24**, 2053 (1987).
20. B. R. Liang, *J. Appl. Polym. Sci.*, **28**, 2011 (1983).
21. F. P. La Mantia and A. Valenza, *Eur. Polym. J.*, **24**, 825 (1988).
22. K. Kellar, D. Ciesielska, and B. Jurkowski, *Polymer*, **40**, 302 (1995).
23. B. Jurkowski and Y. A. Olkhov, *J. Appl. Polym. Sci.*, **65**, 1807 (1997).
24. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.*, **18**, 963 (1974).
25. R. J. M. Borggreve and R. J. Gaymans, *Polymer*, **29**, 1441 (1988).
26. A. Nakayama, T. Inoue, and A. Hirao, in *The 12th Annual Meeting, The Polymer Processing Society, Sorrento, Italy, May 27–31, 1996*, p. 179.