Influence of Compatibilizer Addition on Particle Size and Coalescence in TPU/PP Blends

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ABSTRACT: The effect of the addition of ethylenic copolymers with different acrylic acid contents on the morphology and coalescence of blends of thermoplastic polyurethane and polypropylene has been investigated. The blends were prepared using a twin-screw extruder. Although the copolymers were immiscible with both blend components and no chemical reaction at the interface could be found, the blend properties were improved. Copolymers that form a stable interfacial layer between the blend components lead to a stabilization of the morphology. Addition of a copolymer containing 4% acrylic acid results in a markedly reduced particle size and improved mechanical properties in addition to the stabilization against coalescence. The copolymer concentration was varied over a wide range. One percent of copolymer was enough to reduce the particle size; about 3 wt % of added copolymer was sufficient to stabilize the morphology against coalescence in quiescent melt and to achieve an optimum in mechanical properties. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2217–2226, 1997

Key words: blends; compatibilization; thermoplastic; polyurethane; polypropylene; morphology; coalescence

INTRODUCTION

Most polymer blends consist of thermodynamically immiscible components. The resulting multiphase morphology has a considerable influence on the mechanical properties[1,21] of the blend. It is well known that the morphology of a heterogenous polymer system is not only influenced by the properties of the blend components, but also to a large extent by the blending process.[2–5] This is usually done by melt mixing of the polymers in batch mixers or extruders, commonly with twin-screw extruders.

Due to the importance of the subject for the application of blends, a great deal of research is being done on the morphology development during processing in melt-mixing devices. This work can be classified into studies on dilute Newtonian systems, with rheological properties and concentrations far from practical applicability for polymer melts, viscoelastic model substances, and experimental studies on the morphology development in polymer blends using different mixing devices. Several research groups are investigating the development of the morphology in twin-screw extruders.[2,3,6] Quick sampling in pressurized zones of the extruder is difficult and, thus, a real time monitoring of the morphology in different regions of the extruder has only just recently been accomplished.[6,7]

Two counteracting processes control the evolution of the morphology during the processing of polymer blends[2,8–10]: (1) particle deformation and

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breakup, and (2) coalescence. A great deal of research has been done concerning droplet breakup and the dispersion process (e.g., ref. 11, summarized in ref. 2), whereas there are fewer publications dealing with the mechanism and kinetics of the coalescence of the dispersed particles in quiescent melt and under shear. A short summary of the articles dealing with coalescence will be given here.

The three-step mechanism of coalescence in polymer blends has been confirmed by several authors.[9,12]

First, the particles approach each other until only a thin film of matrix polymer remains at their interface. Coalescence of the two drops can only take place when the matrix polymer between them is removed. The rate of draining of the thin polymer film depends on its mobility. Theoretical models exist for immobile, partially, or completely mobile interfaces. The applicability of these models depends on the properties of the blend components. A comparison of experimental results[9,13] with theoretical predictions[14] indicates that interfaces in some uncompatibilized blends are completely mobile; other authors (e.g., ref. 15) conclude from their results that the interfaces are partially mobile. Even in uncompatibilized blends the interface may be completely immobile for the case of high viscosity ratios (>100). The second step of coalescence is widely accepted to be the rate-determining step in the kinetics of coalescence.

If the film thickness becomes smaller than the critical distance for film rupture (the values given by various authors range from 5 to 50 nm[9,14,16,17]), instabilities in the film lead to its rupture and one single particle is formed. Coalescence may be regarded as being completed at this stage or when the newly formed particle has reached a spherical shape.

The influence of compatibilizers on coalescence and the mechanism of morphology stabilization has been studied.[8,18,19] For surfactants in Newtonian systems, coalescence is suppressed by steric hindrance of the surfactant located at the interface between two liquid components.[20] A similar mechanism has been proposed by Sundararaj[13] for polymer blends with a compatibilizer that forms an interphase between the blend components.

In spite of these results, the role of coalescence in polymer blends, especially in blends containing a compatibilizer, is still not fully understood. The goal of this study was to clarify the influence of compatibilizers, which do not consist of blocks of the blend components, on the morphology and coalescence in a binary polymer blend.

EXPERIMENTAL

Materials and Their Characterization

The blend components used in this work were a polyester thermoplastic polyurethane elastomer (TPU; Elastollan™ C 64 D, ELASTOGRAN GmbH) and a polypropylene (PP; Novolen™ 1127 MX, BASF AG).

The thermoplastic polyurethane (shore hardness: 64 D) is a block copolymer consisting of hard segments and polyester soft segments. The polypropylene is a homopolypropylene (MFR 230°C/2.16 kg = 8 g/10 min) recommended for flat-sheet die extrusion.

Ethylenic copolymers with varying acrylic acid concentrations were used as compatibilizing agents. The ethylenic copolymers contained 0% (EC 0, Lucalen™ A 2710 H, BASF AG), 4% (EC 4, Lucalen™ A 3110 M, BASF AG) and 20% (EC 20, Luwax™ ES 9656, BASF AG) acrylic acid, respectively. Additionally, EC 4 contains 7%, EC 0 19% of butylacrylate.

Rheological measurements were carried out with a high-pressure capillary rheometer Rheograph 2003 (Göttfert). The capillary had a diameter of 1 mm, the length-to-diameter ratio was 30. The viscosity functions of the polymers were measured at the processing temperature of TPU ($T = 230°C$) and carreau fitted. The viscosity ratio of the blend components was determined by division of the viscosities of the dispersed phase (PP) by the matrix polymer (TPU).

The surface free energy of injection-molded samples was determined by contact angle measurements with H_2O and CH_2I_2 at room temperature. The interfacial free energy was calculated using the geometric mean equation.

Processing

Before processing, the thermoplastic polyurethane was dried for at least 3 h in vacuum at 100°C.

Blending of the components was done by melt mixing in a corotating, intermeshing twin-screw extruder ZSK 30 (L/D = 32, Werner & Pfleiderer). The screw configuration was adapted for the blend system TPU/PP. If not otherwise stated, the composition of the blend was TPU/PP = 80/20 wt %.

The melt temperature was 230°C. The output was 10 kg/h, with a residence time of about 50 s.

S2 specimens according to DIN 53504 for tensile testing and morphology analysis were injection molded using a Battenfeld BA 500/200 at a melt temperature of 230°C.

Morphology

The particle size of the blends was determined using phase contrast light microscopy (BH 2, Olympus) on 3 μm cryo-microtomed thin sections. The microscope was fitted with either a camera for photographs or a CCD camera for digitalization of the images for quantitative analysis. The pictures were acquired under comparable conditions (brightness, contrast) and analyzed with a Quantimet 970 (Leica) using a programmed algorithm. Manual corrections were minimized to assure comparability of the results.

The distribution of the equivalent circle diameter was measured. The number average mean particle diameter (d_n) and the standard deviation as a measure for the broadness of particle size distribution were used for interpretation. At least 1000 particles were analyzed.

Injection-molded S2 tension test specimens were cryofractured in their gage length. The fractures were analyzed using a low-voltage SEM (GEMINI, Zeiss) without previous sputtering at an acceleration voltage of 1 kV.

The stability of the morphology against coalescence in quiescent melt was determined by annealing of granules in a metal bath at 230°C, similar to the processing temperature. The granules were dried for 3 h in a vacuum oven and then wrapped in aluminium foil. The annealing time began with the dipping of the specimen into the metal bath. The specimens were quenched in ice water after annealing in order to freeze the morphology.

RESULTS AND DISCUSSION

Properties of the Blend Components and Unmodified Blends

The rheological behavior of the blend components and compatibilizers is shown in Figure 1. The viscosity functions of TPU and PP have a similar form, but the viscosity of TPU is about three times higher than that of PP. Consequently, the viscosity ratio between the blend components is nearly constant over the whole range of the shear rate. The ethylenic copolymers exhibit a different rheological behavior. With the exception of EC 0, the copolymers have a lower viscosity than polypropylene.

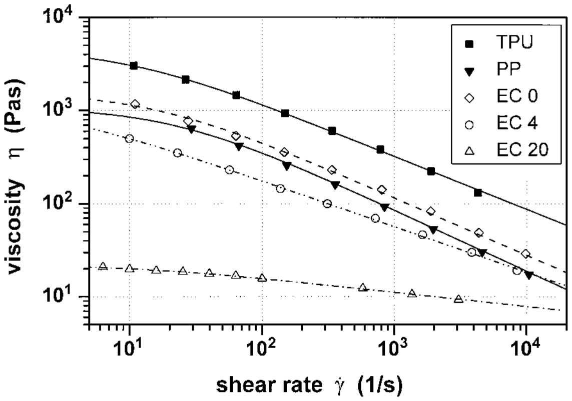


Figure 1 Viscosity functions of the blend components and the copolymers.

Thermoplastic polyurethane elastomer and polypropylene exhibit distinct differences in polarity and surface free energy (Table I). Because of the resulting large interfacial free energy of 5.3 mJ/m^2, only slight interactions in the interface of the two components in the blend can be expected.

Cryofractures of the unmodified blend confirm this assumption (Fig. 2). The distribution of the size of the dispersed particles of PP in the matrix of TPU is rather broad. The fracture passes mainly along the phase boundaries. No signs of interfacial adhesion are observed on the particles or in the remaining holes.

The lack of interactions between the blend components is also proved by dynamic mechanical analysis, differential scanning calorimetry, and the complete separation of the blend into its components from solution.[21]

Figure 3 shows the mechanical properties of blends with various PP contents. As expected, the blending of TPU and PP leads to a reduction of tensile strength and elongation at break compared to the values for the pure components. Phase inversion takes place at a PP content of about 30–40 wt %.

Ethylenic Copolymers as Compatibilizers

Morphology

SEM micrographs of cryofractures indicate that no interfacial adhesion is induced by the addition

Table I Surface Free Energy

	Surface Free Energy γ_s (mJ/m^2)			
Polymer	γ_s^d (Dispersive Component)	γ_s^p (Polar Component)	γ_s	γ_s^p/γ_s (Polarity)
TPU	30.6	8.5	39.1	0.22
PP	19.7	0.8	20.6	0.04

of 5 wt % of EC to the blend [Fig. 4(a)–(c)]. Fractures passing through particles result from the mechanical anchoring of the elongated particles obtained by injection molding.

Quantitative analysis of light micrographs shows that the addition of up to 3–5 wt % of the various ethylenic copolymers leads to a reduction of the particle size compared to the uncompatibilized blend (Fig. 5). The efficiency of the ethylenic copolymers in reducing the particle size varies, with EC 4 having the largest effect. Using EC 4 reduces the particle size up to 70% of the value for the uncompatibilized blend.

Mechanical Properties

EC 0 and EC 20 exhibit a similar effect on the tensile strength and elongation at break, with the mechanical properties showing a steady decrease with increasing compatibilizer content. Figure 6(a) shows this behavior for EC 20.

In contrast, EC 4 leads to enhanced properties [Fig. 6(b)]. The mechanical properties markedly increase up to a concentration of 3–5 wt % EC 4 and then level off.

No evidence for a chemical reaction or strong interactions between the components induced by EC 4 was found (using DMA, DSC, solubility, cryofractures). Thus, the improvement in the mechanical properties is thought to be due to the effect of the compatibilizer on particle size and stabilization of the particles against coalescence. This effect will be discussed in the following section.

COALESCENCE IN QUIESCENT MELT

Unmodified Blends

Annealing of melts of uncompatibilized blends leads to a pronounced coarsening of the morphology [Fig. 7(a)–(c)]. The corresponding quantitative analysis is given in Figure 8. A linear increase of the particle size is observed with annealing times up to about 30 min. With longer times, the particle diameter reaches a constant level. Annealing times longer than 30 min are not relevant for practical purposes and will not be further considered.

The initial particle size of the blend has no influence on the coarsening rate. The gradient of the linear portion of the plot of mean particle diameter vs. annealing time (0.44 μm/ 10 min) was not influenced in annealed blends having a larger

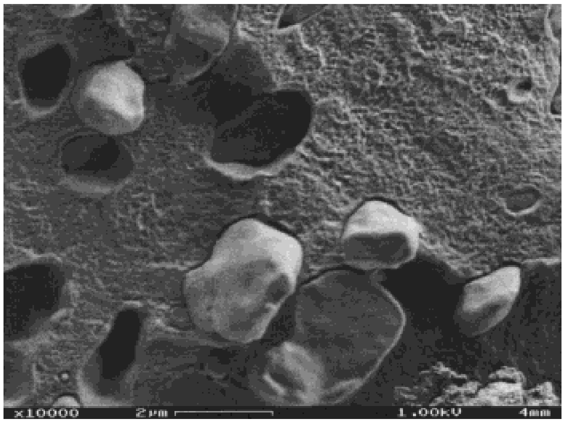


Figure 2 Cryofracture of an injection-molded specimen of the blend TPU/PP = 80/20.

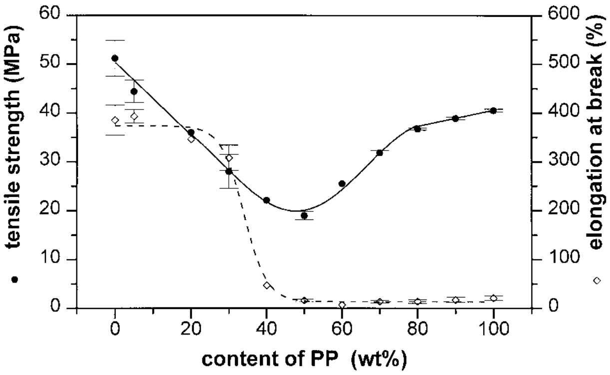
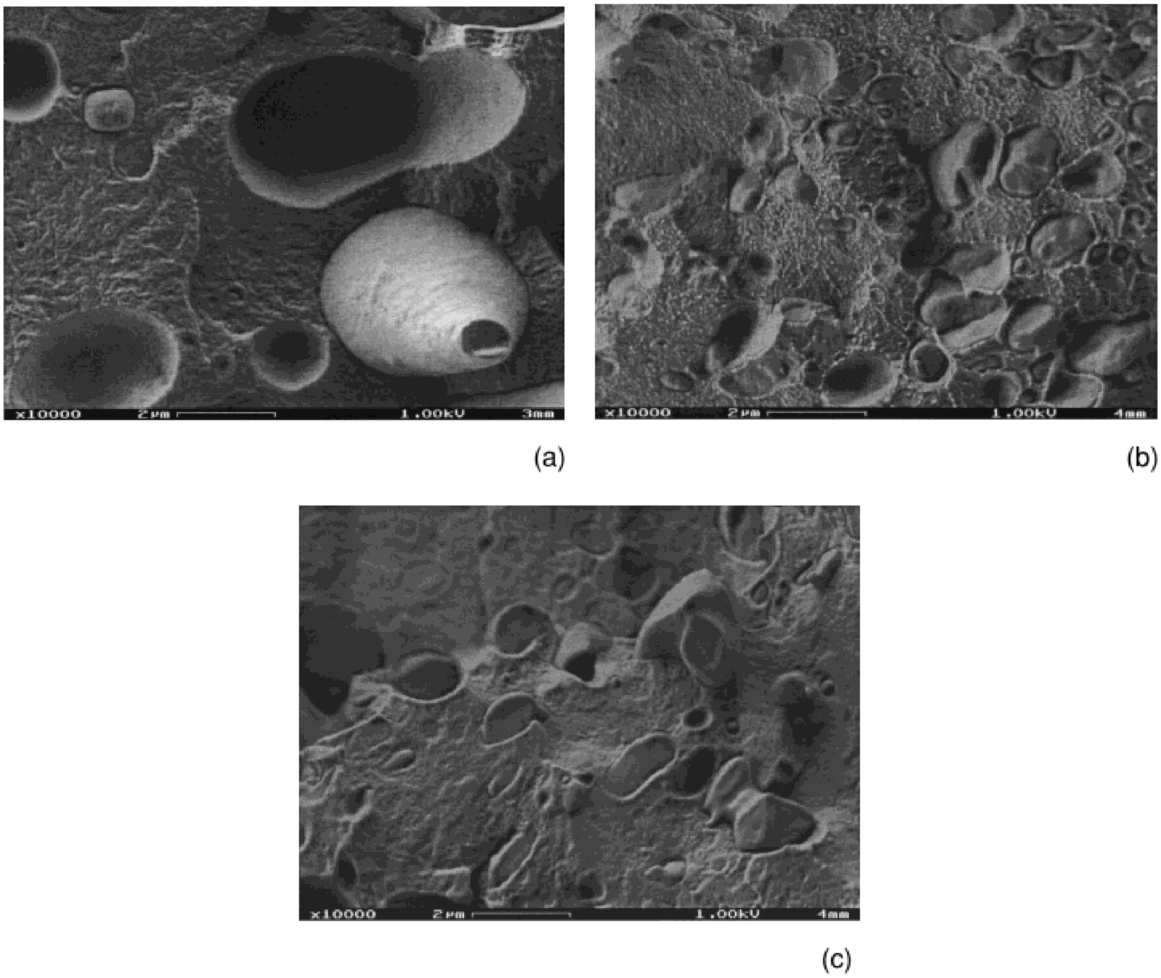


Figure 3 Tensile strength and elongation at break as a function of the blend composition.



(a) (b)

(c)

Figure 4 Cryofractures of injection-molded specimens of blends containing 5 wt % of copolymer. (a) EC 0, (b) EC 4, (c) EC 20.

mean particle diameter prepared under different processing conditions.

Measurements of the solution viscosity of TPU in DMF shows that the molecular weight of the TPU is not affected by annealing. This indicates that the change in the mean particle diameter with annealing is not due to a change in the viscosity of the TPU as a result of thermal degradation.

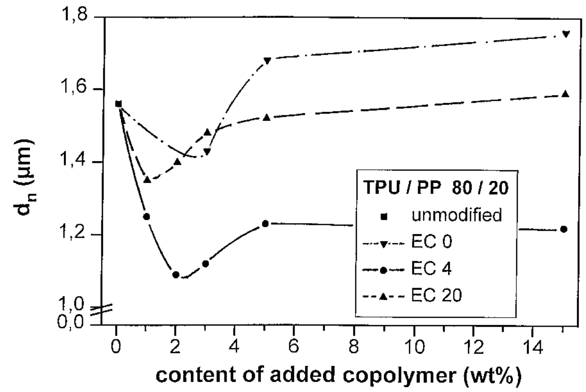


Figure 5 Number-average mean particle diameters of granules with different contents of copolymer.

Blends Compatibilized with Ethylenic Copolymers

Figure 9 shows the efficiencies of the three ethylenic copolymers in stabilizing the morphology during annealing. The addition of 5 wt % of EC 0 has no significant influence on the morphology and its stability. In contrast, EC 4 leads to complete stabilization of the granule morphology. EC 20 shows a similar stabilizing effect, but at larger mean particle diameters than EC 4.

Because no evidence for a chemical reaction between TPU and acrylic acid was found, the differences in the efficiency of the three ethylenic copol-

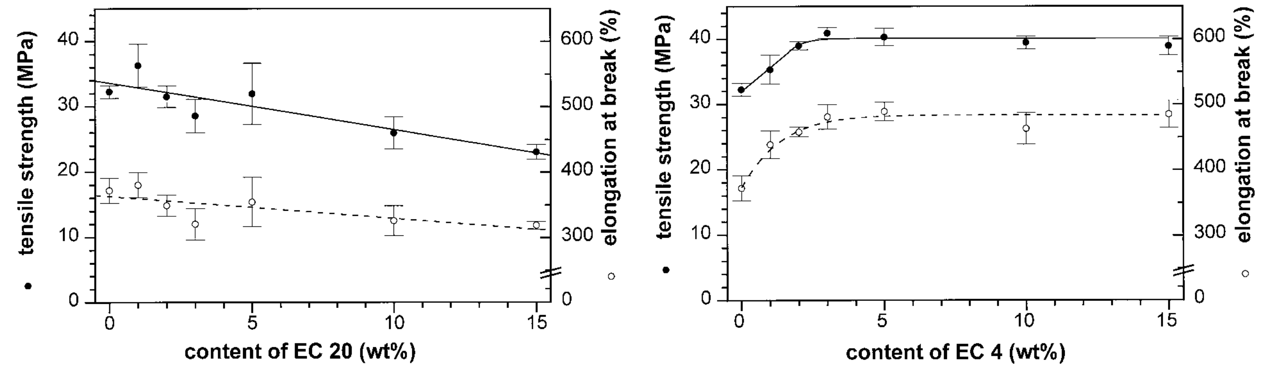


Figure 6 Tensile strength and elongation at break vs. EC content. (a) EC 20, (b) EC 4.

ymers are thought to result from differences in their tendency to form a stable interphase between TPU and PP. Such a layer, which sterically hinders coalescence by immobilizing the interface, has been postulated by several authors, for example Sundararaj.[13]

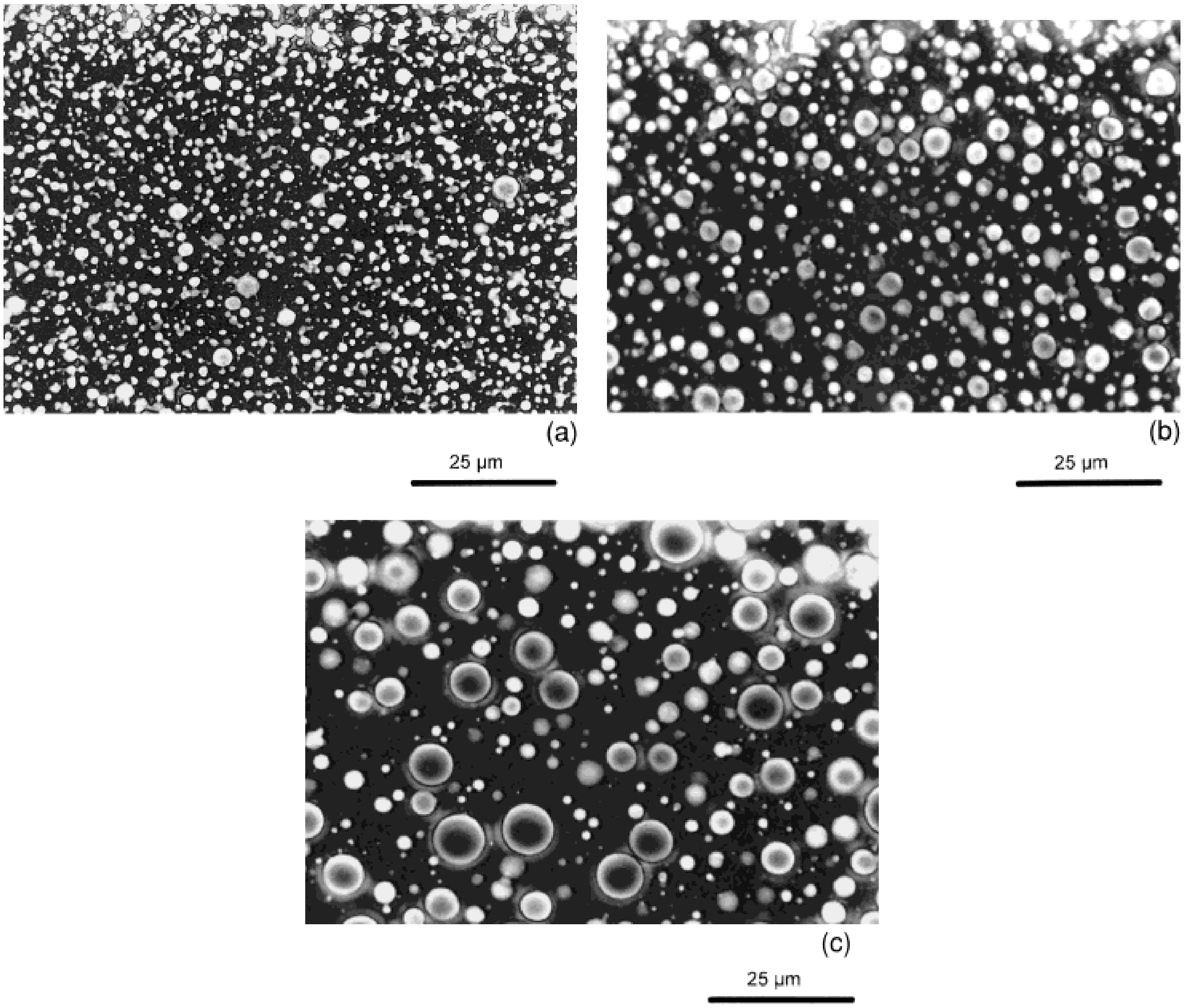


Figure 7 Morphology of TPU/PP = 80/20 granules before (a) and after 15 (b), and 30 (c) min of annealing at 230°C.

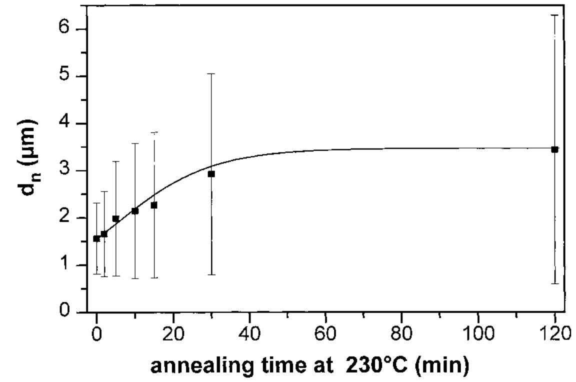


Figure 8 Number-average mean particle diameter and broadness of the particle size distribution of the unmodified blend in dependence on the annealing time.

To be able to immobilize the interface, the compatibilizer must be located at the interface. Additionally, it must have sufficient interactions with the blend components to resist against being removed from in between the droplets during their collision.

This seems to be the case with copolymers consisting of blocks of the blend components. For random copolymers or compatibilizers that are immiscible with the components, such as the ethylenic copolymers in our blend system, only little data exist.[22]

TEM showed that all three compatibilizers are situated at the interface (examplary shown for EC 4 in Fig. 10). The difference in the experimental results leads to the conclusion that the resistence to removal from the interface during coalescence is different for the three copmpatibilizers.

The ethylenic copolymers used in this study have different polarities of the constituing monomers. Therefore, EC 20 is the most and EC 0 the least polar compatibilizer. This may be the reason that EC 0 can be removed from the interface during the collision of particles, leading to coalescence.

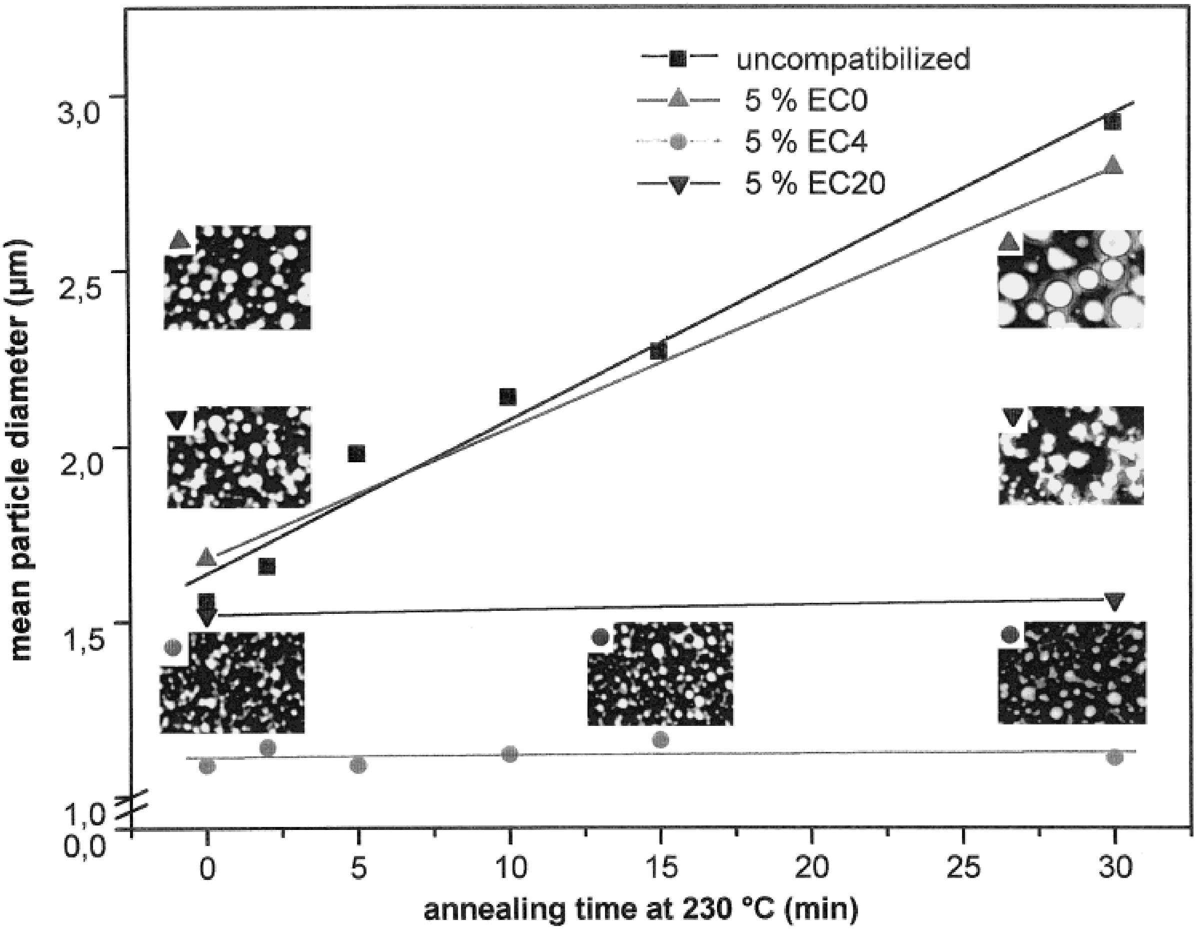


Figure 9 Particle size and morphology of TPU/PP/EC = 80/20/5 granules annealed at 230°C.

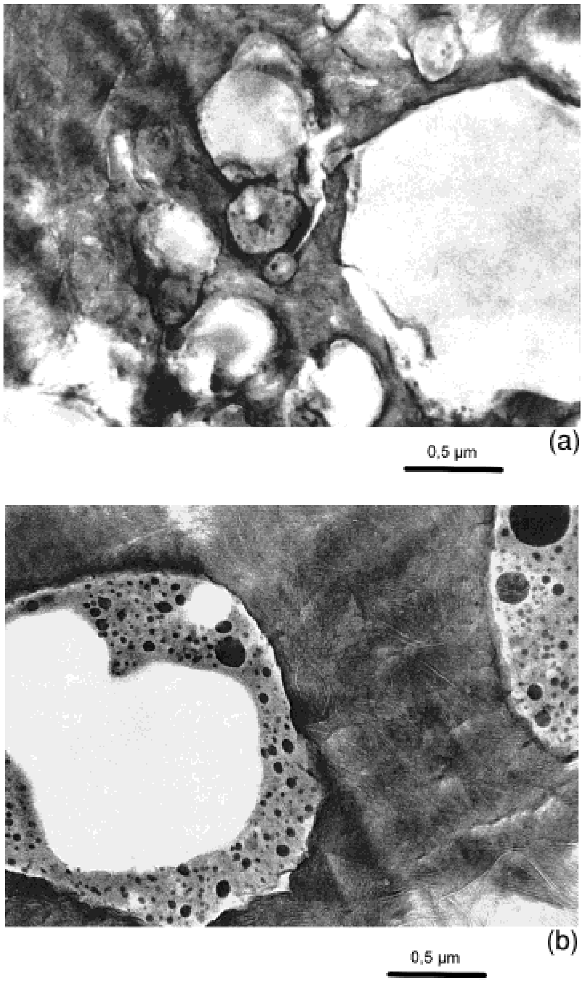


Figure 10 TEM micrographs (stained with RuO_4) of TPU/PP with 5 (a) and 30 (b) wt % of EC 4.

Influence of EC Content on the Stability of the Blend Morphology

If the suppression of coalescence is a steric effect of the interfacial layer of compatibilizer, the EC content in the blend needs to be high enough to at least partially coat the PP particles. To verify this, the influence of the compatibilizer concentration on the rate of coalescence was investigated with the three ethylenic copolymers.

Addition of EC 0 was ineffective in the suppression of coalescence in all concentrations tested, which may be explained by its inability to form a stable interfacial layer.

Figure 11 a shows that with 1 wt % EC 4 the coarsening of the morphology is suppressed compared to the unmodified blend. Larger concentrations of EC 4 completely suppress coalescence in quiescent melt for annealing times of up to 30 min. These results are in good agreement with recent work from Horák et al.,[23] whose experimental results indicate that 2.5% of a copolymer are sufficient to coat the surface of the dispersed phase in a blend of similar composition. Recently, Macosko et al.[24] showed that low contents of the copolymer ($\cong$1%), which lead to a surface coverage of less than 5%, are sufficient for particle size reduction. The prevention of static coalescence needs a surface coverage of about 20%.

EC 4 [Fig. 11(a)] and EC 20 [Fig. 11(b)] show a similar stabilization of the morphology, the major difference being the additional decrease in the initial particle size achieved with EC 4. This is thought to result from the different rheological properties of the ethylenic copolymers. The viscosity of EC 4 is much higher than that of EC 20 (Fig. 1), which allows it to transmit the shear forces from the TPU matrix to the PP particles during melt mixing.

Coarsening of Morphology by Injection Molding

The changes in the morphology of the blend caused by injection molding and the effect of compatibilization must be considered for a correlation of morphology and mechanical properties. A coarsening of the morphology takes place during injection molding of the unmodified blend [Fig. 12(a) and (c)]. Adding 5 wt % of EC 4 leads to similar particle sizes in the granules and in the injection-molded specimens [Fig. 12(b) and (d)].

These results show that the interfacial layer of EC 4 prevents coalescence in quiescent and in sheared melt.

CONCLUSIONS

The morphology of TPU-based blends with 20 wt % of PP is coarsened significantly by annealing in quiescent melt and by injection molding.

To improve the stability of the blend morphology against coalescence, ethylenic copolymers were added. The best results were achieved with a compatibilizer containing 4% of acrylic acid (EC 4), which has the most suitable rheological and surface properties for formation of a stable interfacial layer between the blend components. This interphase is believed to sterically hinder coalescence. Unlike the other compatibilizers used, the addition of EC 4 also leads to a reduced particle size of the virgin granules.

About 3 wt % of acrylic acid containing ethyl-

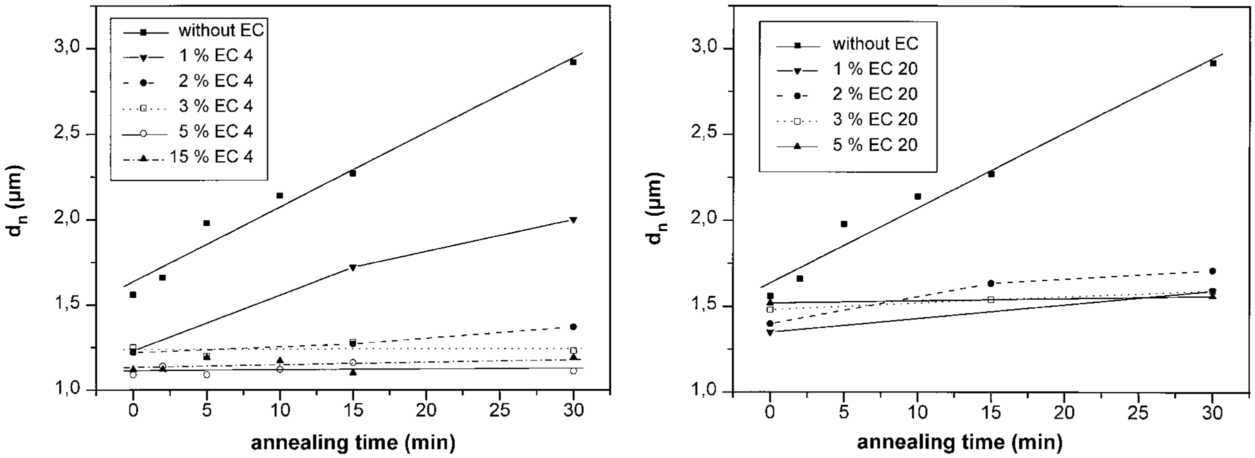


Figure 11 Influence of the content of EC on coalescence: (a) EC 4, (b) EC 20.

enic copolymers are needed to completely stabilize the morphology against coalescence. This amount forms a sufficient interfacial layer of compatibilizer.

With EC 4, the mechanical properties were also improved. Because no evidence for interfacial adhesion and chemical reactions between the components was found, the improvement is probably a

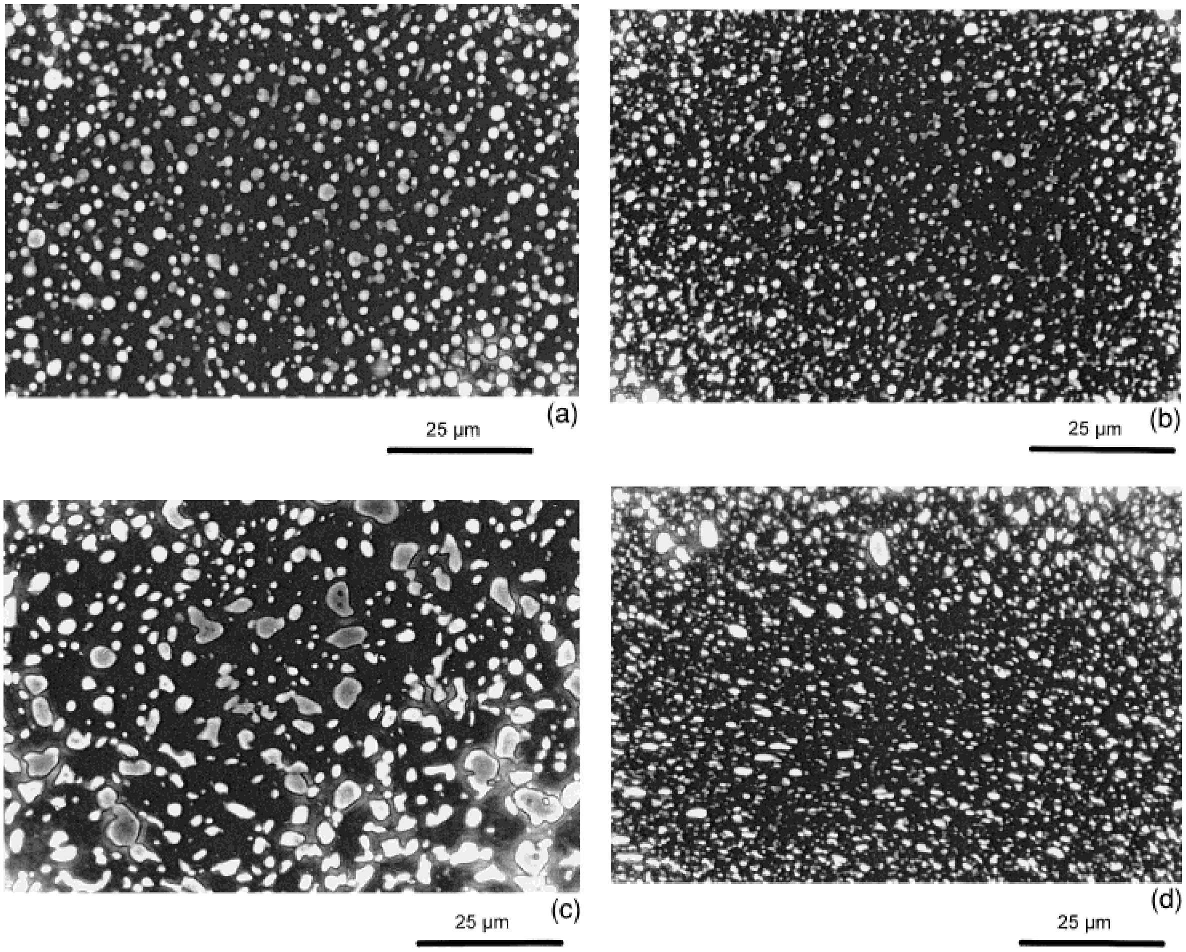


Figure 12 Morphology of granules (a, b) and injection-molded samples (c, d) without (left) and with 5 wt % of EC 4 (right).

result of the reduction of the particle size and the stabilization of the morphology during injection molding.

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