Macromol. Symp. **2012**, 321-322, 179–185 DOI: 10.1002/masy.201251132

Microstructural Evolutions of Polymer Blends by Statistical Analysis: Influence of Compatibilizer on Break-up and Coalescence Processes

V. V. Zuev, S. Bronnikov*

Summary: Statistical analysis of the size distribution of a polymer minor phase droplets was successfully applied for the characterization of morphology in a LDPE/PA6 blend (75/25 wt/wt) obtained after mixing with adding SEBS-g-MA(S) compatibilizer and/or organoclay 20A. It was shown that the developed approach provided detailed analysis of the morphology development in the polymer blends, including the primary droplets formation of the minor polymer phase and their break-up and coalescence. The introduction of organoclay increased the break-up of primary droplets and completely suppressed their coalescence. The addition of compatibilizer S, in contrast to nanoclay, did not suppress coalescence but the mean size of the primary droplets as well the droplets formed at coalescence strongly reduced. The combined addition of compatibilizer S and nanoclay did not change the morphology development of the LDPE/PA6 blend. Both processes of the droplet transformation were accelerated, similar to the system with addition of compatibilizer S only. However, the increase of nanoclay amount disturbed break-up of the primary droplets, and the mean size of these droplets increases. Thereafter, the mean size of droplets formed at coalescence also increased. The results of statistical analysis of phase morphology were found to correlate with the mechanical properties of the polymer blends. The fine dispersion of the minor polymer phase improved the stiffness of the polymer blends. For enhanced impact properties, the presence of relatively broad distribution of the minor polymer phase is necessary.

Keywords: blends; compatibilization; organoclay; polyamides; statistical analysis

Introduction

Polymer blends are widely used in plastic products for a variety of reasons, such as improved physical properties, increased service life, easier processing, complex demand for their performance and reduced product cost.[1] It is well known that the phase structure of immiscible polymer blends affects their properties in a decisive manner. The phase structure is determined by the composition and component properties of the blends, and the condition of mixing. The formation of the phase structure is a complex process. Its course is determined by the competition between the break-up and coalescence of dispersed droplets.[2,3] To influence these processes, the addition of compatibilizers, clays and other filers are used. Several studies of polymer blend/clay systems indicated that a compatibilizing effect of clay in heterogeneous blends does exist.[4–6] The droplet size of the dispersed phase in acrylonitrile butadiene rubber/styrene butadiene rubber,[7] high density polyethylene/polyamide 6 (PA6),[8] polystyrene/polyvinyl methyl ether[9] and many other immiscible blends[10] were drastically reduced by addition of clay. An other way of improving the polymers miscibility is addition of compatibilizers.

Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr.31 199004 Sankt Petersburg, Russian Federation
Fax: +7 812 3286869; E-mail: Zuev@hq.macro.ru

Their increasing concentration is known to correlate to reduction of the droplet size.[11]

Regarding the complexity of the morphology development of nanoclay/compatibilizers filled polymer blends, the goal of the present work was to quantify the factors influencing the dispersion in a low density polyethylene (LDPE)/PA6 (75/25 wt/wt) polymer blend. As additives to this polymer blend, organoclay (Cloisite 20A) and/or a compatibilizer/toughener polystyrene-*b*-poly(ethylene-*co*-butene-1)-b-polystyrene grafted with maleic anhydride (SEBS-g-MA) were used. The preparation, morphology and properties of these blends have already been described.[12]

We characterized the polymer blends morphology using statistical analysis of the minor polymer phase droplet size. The statistical size distributions were afterwards described with the model of reversible aggregation proposed by Kilian et al.[13–15] Universality of the model has been shown by its application to statistical ensembles of carbon-black particles,[13] spherolites in poly(methylmethacrylate),[13,14] micro-domains of polyamic acids in the course of their transformation to polyimides,[15] defects of metallographic samples at loading,[14] bacteria and yeast in the course of their growth,[13] and the ordered phase droplets in liquid crystalline systems.[16,17] This has given us hope for successfully describing the minor phase droplets size distribution during phase separation in polymer blends using this model.

Experimental Part

The LDPE sample was Riblene FC20 by Polimeri Europe. PA6 was provided by Rhodia, it had a relatively viscosity equal to 3.66 in 95.7% sulfuric acid at 25 °C. SEBS-g-MA was Kraton FG 1901X, by Kraton Polymers. The organoclay was Cloisite™ 20A, purchased from Southern Clay Products. It was prepared from the sodium montmorrilonite having a cation exchange capacity of 0.926 meq g^{-1} by treatment with 0.95 meq g^{-1} of $Me_2(HT)_2NCl$ (dimethyl dihydrogenated tallow ammonium chloride). Hydrogenated tallow (HT) is a blend of saturated n-alkyl groups with approximate composition: 65% C_{18}; 30% C_{16}; 5% C_{14}. The organic content of 20A was 38.5 wt % as determined by thermogravimetric analysis.

The blend and composites were prepared by melt-compounding in a Brabender Plasticorder static mixer. The blending time, after completing the addition of all components, was 10 min at 235 °C.

Scanning electron microscopy (SEM) observations of cryofractured composite samples coated with gold were made with a JEOL JSM-5600LV microscope. 85% formic acid was used to etch the samples to remove the PA6 dispersed phase. The specimens were soaked in the selected solvent at room temperature for about 48 h and were then washed repeatedly with fresh solvent. All the SEM images were recorded at Dip. di Ingegneria Chimica, Università di Pisa (Italy).

The LDPE/PA6 blend (75/25 wt/wt) and blends with additives of organoclay (5 and 10 $^{0}/_{00}$ of 20A), compatibilizer (2 $^{0}/_{00}$ of SEBS-g-MA), and mixture of organoclay and compatibilizer (2 $^{0}/_{00}$ SEBS-g-MA and 0.22 $^{0}/_{00}$ and 1.33 $^{0}/_{00}$ of 20A) were chosen as the samples for investigation.

The SEM images obtained were subsequently segmented and subjected to digital analysis using the ImageTool 3.0 software elaborated at the Health Science Center, the University of Texas, San Antonio, USA, to elucidate the statistical size distributions of the dispersed phase droplets. To analyze the resulting histograms, we used the model of reversible aggregation.

Model

The model of reversible aggregation[13–15] was inspired by application of irreversible equilibrium thermodynamics. It gives a generalized characterization of micro-structure in different liquids. According to the model, a stationary micro-structure is developed by linking the energy-equivalent units in metastable clusters called the aggregates. The aggregates are perpetually composed and decomposed under thermal fluctuations: this is a condition of their reversibility.

According to the model, the stationary statistical distribution $h(s)$ of the projected diameter s of the micro-structural entities reads as follows[13–15]

$$h(s) = as^2 \exp\left(-\frac{s\Delta u_0}{kT}\right) \tag{1}$$

where a is the normalizing factor, Δu_0 is the energy of aggregation, k is the Boltzmann constant, T is the absolute temperature and kT is the energy of thermal fluctuation. In some cases, the aggregates were shown to form not a single but rather multiple statistical ensembles.[18] This may be caused by either consolidation of primary clusters into superstructure (i. e. coalescence) or by the presence of different components in a multi-component system. Following this way, Eq. (1) should be written as[18]

$$h(s) = \sum_{i=1}^{N} a_i {s_i}^2 \exp\left(-\frac{s_i \Delta u_{0i}}{kT}\right) \tag{2}$$

where N accounts for the total number of statistical ensembles of the entities. Eq. (2) allows the determination of the mean entity area $<s_i>$ related to the i-th statistical ensemble as a normalized mathematical expectation:

$$\langle s_i \rangle = \frac{\int\limits_{s_i=s_{0i}}^{\infty} {s_i}^3 \exp\left(-\frac{s_i \Delta u_{0i}}{kT}\right) ds_i}{\int\limits_{s_i=s_{0i}}^{\infty} {s_i}^2 \exp\left(-\frac{s_i \Delta u_{0i}}{kT}\right) ds_i} = \frac{3kT}{\Delta u_{0i}} \tag{3}$$

Results and Discussion

In the present work, we studied the effect of the 20A organoclay and compatibilizer S on the dynamic phase behaviour and morphology of the LDPE/PA6 blends. Two opposite processes determine the mean droplet size during a blending process: break-up and coalescence. As a method for analysis of the evolution of the droplet size distribution following addition of different components to the starting LDPE/PA6 blend the statistical analysis of the minor phase droplet size was chosen. Our analysis is based on the model of reversible aggregation proposed by Kilian et al.[13–15] which has been successfully applied for description of the stationary size distribution of the micro-structural entities in various systems. Figure 2 shows the histograms resulting from the statistical analysis of the SEM images of the LDPE/PA6 blend and LDPE/PA6 blends with additives (Figure 1). Our attempt to describe the statistical ensembles with a unimodal version of the model of reversible aggregation Eq. (1) failed. Yet, we succeeded when applied a bimodal version of the model (Eq. (2), $N = 2$) with the fitting parameters listed inside the boxes.

In Figure 2 the dashed lines represent individual distributions, whereas the solid lines represent the sum over two ensembles according to Eq. (2). A successful analytical description indicates that the PA6 droplets form two superimposed thermodynamically optimized statistical ensembles of primary and coalesced droplets all across the phase separation in the polymer blends studied. The existence of two statistical ensembles of the minor phase particles evidences two regimes of the phase separated structure formation, and allows us to analyze separately the two processes: coalescence and break-up of the droplets.

We suggest the droplets involved in the first statistical ensemble were formed during the primary mixing and resulted from the break-up process (small droplets); whereas the droplets involved in the second statistical ensemble (big droplets) resulted from the coalescence.

The mean droplet size (area $<s_i>$) of each statistical ensemble as a function of the LDPE/PA6 blend compositions is given in Figure 3. As can be seen from Figure 2, in the pristine LDPE/PA6 (75/25 wt/wt) blend the PA6 droplets formed two superimposed, thermodynamically optimized, statistical ensembles of primary and coalescent droplets, typical for this polymer

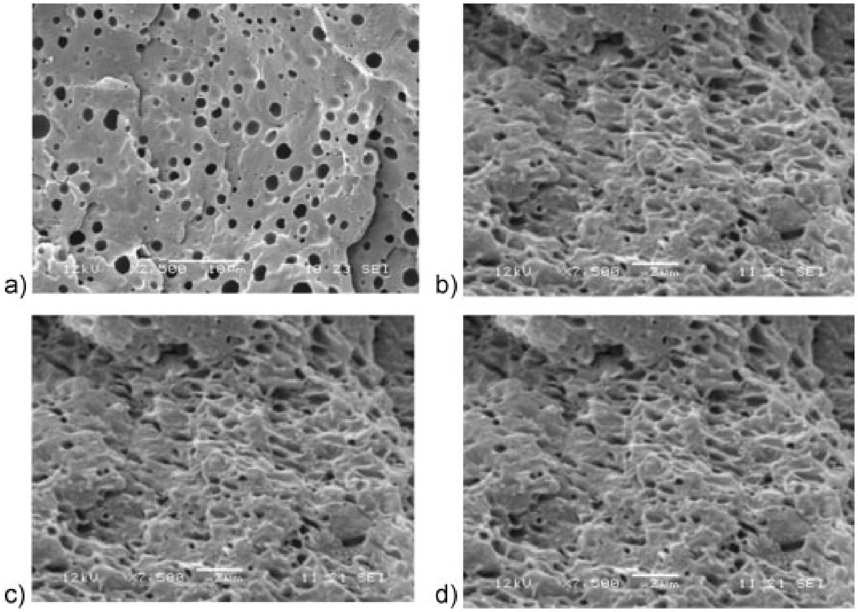

Figure 1.
SEM images of the cryofractured surfaces, etched with formic acid, of the blends: (a) HDPE(75%)/PA6(25%), (b) HDPE(75%)/PA6(25%)/20A(5‰), (c) HDPE(75%)/PA6(25%)/SEBS-g-MA(2‰) and (d) HDPE(75%)/PA6(25%)/SEBS-g-MA(2‰)/20A(0.22‰).

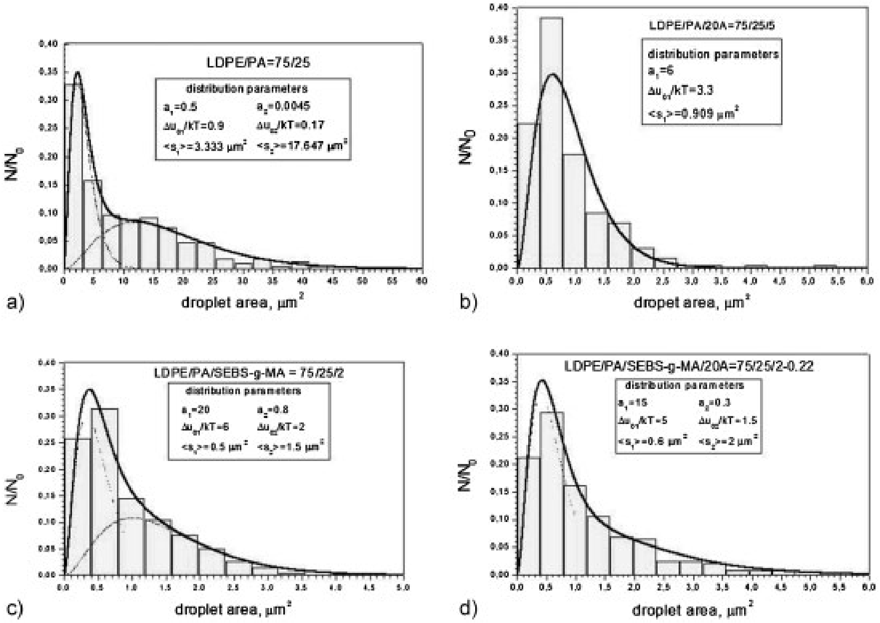

Figure 2.
Statistical area distribution of the PA6 phase droplets of the blends: (a) HDPE(75%)/PA6(25%), (b) HDPE(75%)/PA6(25%)/20A(5‰), (c) HDPE(75%)/PA6(25%)/SEBS-g-MA(2‰) and (d) HDPE(75%)/PA6(25%)/SEBS-g-MA(2‰)/20A(0.22‰) and their description using Eq. (2) with the parameters indicated within the boxes along with the mean droplet areas computed with Eq. (3).

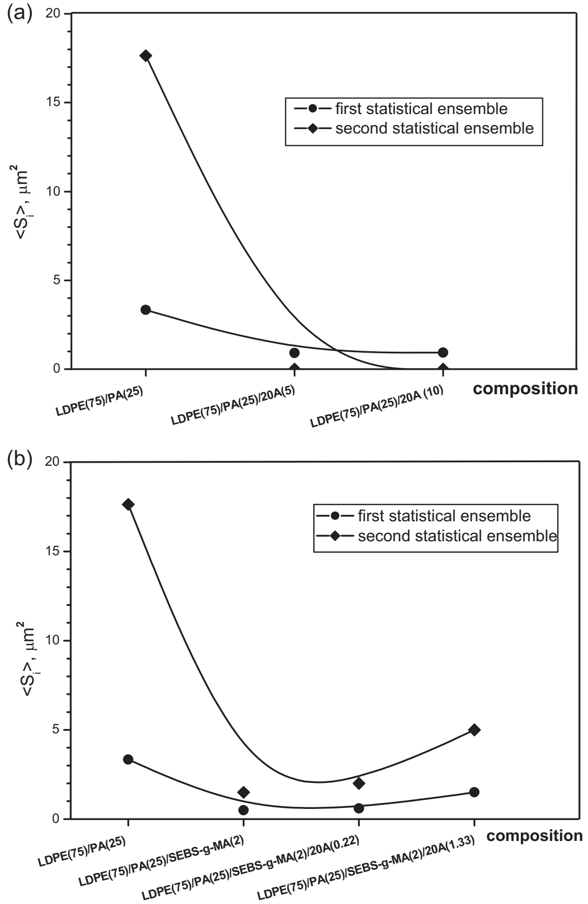

Figure 3.
The mean PA6 droplet area as a function of the blend composition (a) containing 20A and (b) containing SEBS-g-MA and 20A.

blend.[19] The mean droplet size of each statistical ensemble can be assumed as a basic value when the influence of additives on LDPE/PA6 blend morphology is analyzed. The first statistical ensemble contains not only primary droplets but also droplets after break-up processes. As Figure 3b shows, the insertion of organoclay in the polymer blend leads to significant decrease of the mean droplet size in first statistical ensemble and complete disappearance of the second statistical ensemble. Hence, organoclay stimulates the break-up of the primary droplets and completely suppresses their coalescence. Regarding the phase specific distribution in heterogeneous polymer blends, some works have shown that clay preferably resides in the blend phase with better affinity to clay.[4–8] The less polar clay Closite 20A in the polymer blends under investigation interacts similarly with both polymers and most likely resides at the interface.[10] The reduction of the PA6 domain size is a well-known resulted the compatibilization effect of nanoclay.[4–8] These investigations revealed that the addition of nanoclay in the PE/PA6 blend altered its surface tension strongly. These effects are caused by the surfactant ions, which are released from the nanoclay galleries during compounding. This accelerates the break-up process and, therefore, decreases the mean droplet size. Contrary, localization of nanoclay plates at the interface border completely suppresses the coalescence.

The effect of the compatibilizer S addition to the LDPE/PA6 blend is shown in the Figure 3b. The mean droplet size in the primary statistical ensemble strongly decreased because the compatibilizer/surfactant S reduced the interphase tension between the polymer phases. This accelerates both processes of the droplets transformation: break-up and coalescence. The acceleration of the break-up process decreases the mean droplet size of the primary ensemble, and, as a result, decreases the mean size of the droplets formed by coalescence. Hence, addition of compatibilizer S, oppositely to nanoclay, does not suppress the coalescence though the mean droplet size in both statistical ensembles strongly decreased.

The combined addition of compatibilizer S and nanoclay did not change the morphology development process in the LDPE/PA6 blend. Both processes of droplet transformation were accelerated similar to the system with compatibilizer S only. However, the increase of nanoclay content disturbs break-up of the primary droplets, and the mean droplet size in the first ensemble increased (Figure 3b). Therefore, the mean size of the droplets formed at coalescence increases too.

The phase morphology influences the mechanical properties of the polymer blends strongly. Therefore, the results obtained allow us explaine the effects of the compatibilizer S and nanoclay addition on the mechanical properties of the LDPE/PA6 blend recognized by Fillipi et al.[12] As they reported, the addition of nanoclay improved the elastic modulus but impaired the impact properties. Therefore, the fine dispersion of minor polymer phase improves the stiffness of polymer blends. To enhance the impact properties, a relatively broad distribution of the minor polymer phase is necessary.[1] But an increase of the mean droplet size in both statistical ensembles connected with the combine addition of compatibilizer S and nanoclay led to failed mechanical properties.[12]

Conclusion

A statistical analysis of the minor polymer phase droplets was successfully applied for characterization of the morphology in an LDPE/PA6 blend (75/25 wt/wt) obtained with SEBS-g-MA(S) compatibilizer and/or organoclay 20A as additives. It was found that PA6 droplets form two superimposed, thermodynamically optimized, statistical ensembles of primary and coalesced droplets all across the phase separation in the polymer blends studied. The mean droplet size of each ensemble was assumed as the basis for analysis of the influence of additives on the LDPE/PA6 blend morphology. The addition of organoclay 20A led to a significant decrease of the mean droplet size of the first statistical ensemble and full disappearance of the second statistical ensemble. Hence, introduction of organoclay increased the break-up of primary droplets and completely suppressed their coalescence. The addition of compatibilizer S, contrary to nanoclay, did not suppress coalescence but the mean droplet size in both statistical ensembles was strongly reduced. The combined addition of compatibilizer S and nanoclay did not change the morphology development process in the LDPE/PA6 blend. Both processes of droplets transformation were accelerated similar to the system with compatibilizer S only. However, an increase of the nanoclay amount disturbed the break-up of the primary droplets, and the mean droplet size in first statistical ensemble increased. As a result, the mean size of the droplets formed by coalescence increased too. The development of phase morphology influences the mechanical properties of polymer blends strongly. The results obtained allow us to explain the effects of addition of compatibilizer S and nanoclay on the mechanical properties of LDPE/PA6 blend obtained by Fillipi et al.[12] They showed that the fine dispersion of minor polymer phase improved the stiffness of the polymer blends. To enhance the impact properties, a relatively broad distribution of minor polymer phase was necessary.

Acknowledgements: The authors express their profound thanks to Drs. S. Filippi and G. Polacco, Dip. di Ingegneria Chimica, Università di Pisa, Italy, for supplying the SEM images of the blend for their statistical analysis.

[1] *Polymer blends*, D. R. Paul, C. B. Bucknall, Eds., Wiley-Interscience Publ, New York V.1-2, **2000**.

[2] L. M. Robenson, *Polymer blends: a comprehensive review*, Hanse, New York **2007**.

[3] J. J. Elmerdorp, A study polymer blending microreology, In: *Mixing in polymer processing*, C. Rauwendaal, Ed., Marcel Dekker, New York **1991**, 247–290.

[4] W. S. Chow, Z. A. Ishak, U. S. Ishiaku, J. Karger-Kocsis, A. A. Apostolov, *J. Appl. Polym. Sci.* **2004**, *91*, 175.

[5] Y. Li, H. Shimizu, *Polymer.* **2004**, *45*, 7381.

[6] B. B. Khatua, D. J. Lee, H. Y. Kim, J. K. Kin, *Macromolecules.* **2004**, *37*, 2454.

[7] H. Essawy, D. El-Nashar, *Polym. Test.* **2004**, *23*, 803.

[8] M. Mehrabzadeh, M. R. Kamal, *Can. J. Chem. Eng.* **2002**, *80*, 1083.

[9] K. Yurekli, A. Karim, E. J. Amis, R. Krishnamoorti, *Macromolecules.* **2004**, *37*, 507.

[10] J. S. Hong, Y. K. Kim, K. H. Ahn, S. J. Lee, S. Y. Kim, *Rheol. Acta* **2007**, *46*, 469.

[11] S. Hambir, N. Bulach, P. Kodgire, R. Kalganokar, J. P. Jog, *J. Polym. Sci. Polym. Phys.* **2001**, *3*, 446.

[12] S. Filippi, N. Tzankova Dintcheva, R. Scaffaro, F. P. La Mantia, G. Polacco, P. Magagnini, *Polym. Eng. Sci.* **2009**, *49*, 1187.

[13] H. G. Kilian, R. Metzler, B. Zink, *Chem. Phys.* **1997**, *107*, 8697.

[14] H. G. Kilian, M. Kopf, V. I. Vittegren, *Progr. Colloid. Polym. Sci.* **2001**, *117*, 172.

[15] H. G. Kilian, S. Bronnikov, T. Sukhanova, *J. Phys. Chem. B* **2003**, *107*, 13575.

[16] S. Bronnikov, S. Kostromin, V. V. Zuev, *Phase Trans.* **2010**, *83*, 302.

[17] V. V. Zuev, S. Bronnikov, *Liq. Cryst.* **2008**, *35*, 1293.

[18] S. Bronnikov, I. Dierking, *Phys. Chem. Chem. Phys.* **2004**, *6*, 1745.

[19] V. V. Zuev, S. Bronnikov, *J. Polym. Research.* **2010**, *17*, 731.