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Study on In-Situ Compatibilization of the PP/PA6 Blends in Twin Screw Extruders

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Summary: The in-situ compatibilization of PP/PA6 blend was studied in a twin screw extruder. The maleic anhydride (MA) content, peroxide concentration, shear rate and feeding order were among the variables investigated. Degree of grafting of samples collected prior to feeding of PA6 into the extruder was measured using titration combined with FTIR technique. From the SEM results it was found that the increasing of initial MA concentration led to larger PA particle size which could be related to secondary reactions between excess MA and PA. The melt linear viscoelastic measurements performed on the blend samples and the obtained relaxation time spectra showed shorter form relaxation time and interfacial relaxation time for one-step compatibilized sample compared to the sample prepared by the two-step method with the same degree of grafting. This was attributed to the stronger interfacial interaction of the one-step compatibilized blend samples which could be resulted from greater efficiency of grafting and/or compatibilization. These results were supported by SEM results which showed smaller particle size for the one-step compatibilized samples. It was demonstrated that melt linear viscoelastic measurement could provide a great insight into understanding the compatibilization process in twin screw extruder.

Keywords: blend; compatibilization; morphology; viscoelastic properties

Introduction

Most polymers are thermodynamically immiscible and their blending usually leads to formation of matrix-dispersed type morphology. The viscosity and elasticity ratio, shear rate and flow field are among the important parameters that determine the size and size distribution of the dispersed phase.[1–3] In the compatibilized blends type and concentration of the compatibilizer also play a significant role in determining the dispersed particle size.[4,5] Therefore, it is generally desirable to generate blends with well defined and reproducible morphologies. The rapid growth in the use of polymer blends and composites is undoubtedly related to the availability of methods for controlling the physical and chemical interactions at the interfaces. This can be achieved by adding to an immiscible polymer blend, appropriate interfacial agents (compatibilizer) like block and graft copolymers that locate preferentially at the interface. The compatibilizing agent can be synthesized separately and then added to a polymer blend or it can be created by reactive blending, where it is synthesized in situ during the blending process.[6–9] The conventional reactive blending process is called two-step reactive blending. Recent years have seen increasing efforts towards one-step reactive blending[9,10] in which both the functionalization and the reactive blending steps are executed in the same extrusion process. The aim of the present work was to study parameters affecting

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one-step reactive blending of the PP and PA6 in a co-rotating twin screw extruder and comparing the results with those obtained from two-step method.

Experimental Part

Material

The polypropylene (PP) used in this study was a commercial grade (HP 500H) in powder form supplied by Arak Petrochemical Company. Polyamide 6 (PA6) was a commercial product of Poly One (Bergamid, B700-20). Maleic anhydride was obtained from Merck. The free radical melt grafting of MA onto PP was initiated by dicumyl peroxide (DCP) of AKZONOBEL with half life about 15 sec at 200 °C. The polypropylene grafted MA (PP-g-MAH) manufactured by Dupont (fusabond 511D) was also used in two-step compatibilization method.

Characterization

The morphological studies were performed on the cryogenically fractured surface of the samples. In order to achieve a good contrast for quantitative measurements of the dispersed particles size, the dispersed PA6 phase was etched by submerging the samples in 98% formic acid for four hours. The etched samples were then sputter coated with gold and examined by scanning electron microscopy (SEM). The particle size distribution was determined on the bases of at least 400 PA6 particles using image analysis performed on SEM micrographs.

The melt linear viscoelastic properties of the blend components and the blend samples were measured with a Rheometric Mechanical Spectrometer (RMS) (Paar Physica USD200) equipped with parallel plate geometry with diameter of 25 mm at strain of 1% and temperature of 240 °C. The melt linear viscoelastic measurements were performed on the samples in the frequency range of 0.01–1000 rad/s. The relaxation time spectra were calculated by using a non-linear regression regularization method (NLREG) developed by Honerkamp and Weese.[11]

Reactive Blending

PP/PA blend samples with the same composition (80/20) were prepared using two different in-situ compatibilizing processes: one-step and two-step. The reactive blending process was carried out in a modular intermeshing twin screw extruder (Brabender DSE 25) with L/D of 30. The Screw configuration is schematically shown in Figure 1.

In this process, the premixed PP, peroxide and MA were fed through the first feeder of extruder. Polyamide was added to the molten mixture through the second feeder which was positioned at some beyond the first kneading blocks of the twin screw extruder. This allowed the PA6 to be well mixed with PP-gr-MA melt in second kneader blocks where the blending and compatibilization process begin and proceed in the latter zones of the twin screw extruder.

Results and Discussion

As shown in Figure 2 particle size diameter decreases with initial peroxide concentration. The higher the peroxide concentration the larger the quantity of primary radicals

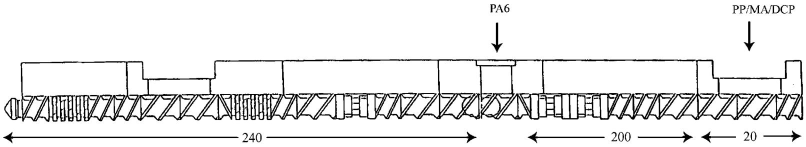

Figure 1.
Screw configuration.

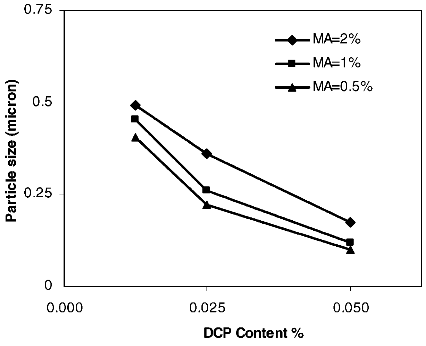

Figure 2.
Variation of particle size with initial DCP content.

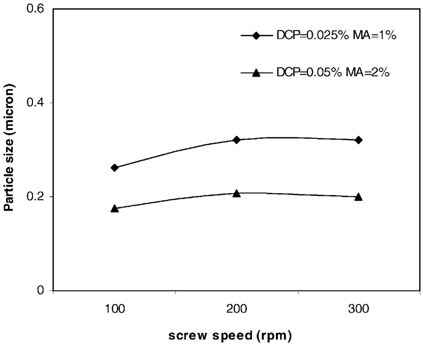

Figure 4.
Effect of particle size versus screw speed.

formed and, consequently, the higher concentration of macroradicals available for the reaction with the maleic anhydride. Thus, as a result there will be a higher level of grafting. Therefore the higher amount of PP-gr-PA graft copolymer will form and dispersed particle size will be reduced by increasing of interfacial interaction.

Figure 3 shows the effect of initial maleic anhydride concentration on PA particle size. It can be seen that the PA particle size increases with increasing MA content. In the MA grafting process there is always unreacted MA monomers. The excess MA can react with PA with higher rate than PP-gr-MA due to its much greater mobility. This reaction will reduce the formation of the PP-gr-PA copolymer.

Figure 4 presents variation of dispersed particle size against screw speed. It could be seen that particle size increases as screw speed increases. The increase in screw speed improves mixing which increases not only the amount of MA grafted on polypropylene but also that of the mixing of the residual MA with PA. The residual MA monomers react with the PA at a higher rate than MA grafted PP resulting in lower formation of the PP-gr-PA copolymer. This decreases the interfacial tension and therefore increases the dispersed particle size. In our previous work,[3] we showed that the storage modulus ratio of the components, G'_d/G'_m (where G'_d and G'_m are the storage modulus of the dispersed phase and matrix, respectively) and its variations by shear rate affects on the particle size. Figure 5 shows the storage modulus ratio of the components of the blend. It can be seen that the elasticity ratio of the blend increases by angular frequency. Thus, the enlargement of the particle size with screw speed can be the result of an increase of the elasticity ratio.

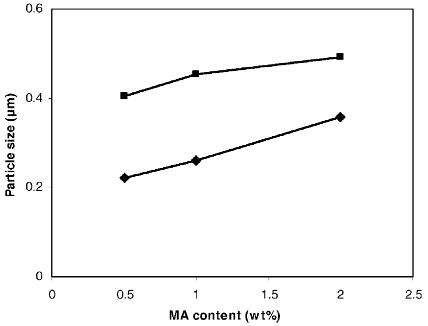

Figure 3.
Variation of particle size with initial MA content.

Figure 6 shows SEM micrographs of two blend samples prepared using two different feeding orders. By comparing this results one may notice that PA particle size in sample prepared via simultaneous feeding is greater than that in samples prepared by separate addition of the PP/MA/DCP mixture and PA through two feeders. This could be attributed to greater affinity of MA with PA compared to that with PP. The feeding rate and screw speed were kept the same for both feeding orders and the experimentally determined mean residence

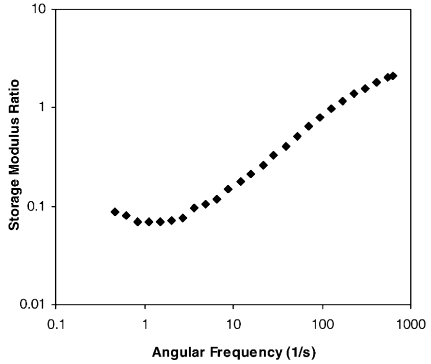

Figure 5.
Storage modulus ratio of the PP/PA blend as a function of frequency, [DCP] = 0.025% [MA] = 1%.

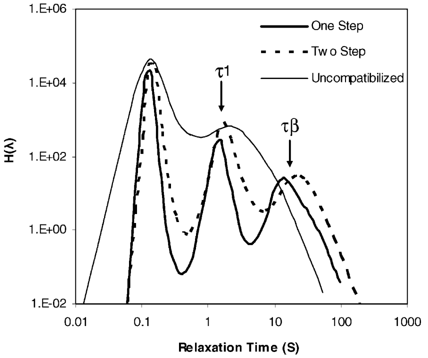

Figure 7.
Relaxation time spectra of the uncompatibilized blend and blends prepared by two different compatibilization methods at a similar grafting level.

time was found to be about 7 minutes for two methods of feeding.

Figure 7 shows the relaxation time spectra of blends prepared by one step method with that produced using two-step method calculated from the dynamic moduli obtained by the oscillation tests with employing the non-linear regression regularization method (NLREG). The peak at shorter time is related to the matrix relaxation. The second peak appears in both uncompatibilized and compatibilized blends can be attributed to the form relaxation time of the droplets (τ_1).

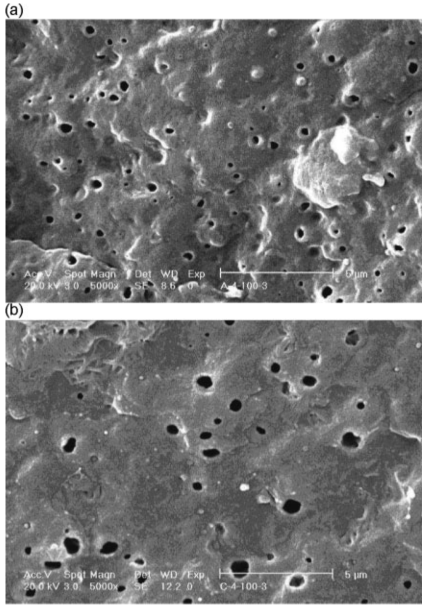

Figure 6.
SEM micrographs of etched samples, a: Separate feeding, b: simultaneous feeding, [DCP] = 0.025% [MA] = 1%.

The Palierne model gives an analytical expression for form relaxation time, τ_1, which expressed as follow[12]:

$$\tau_1 = \frac{R_V \eta_m}{4\alpha} \frac{(19P+16)(2P+3-2\phi_i(P-1))}{10(P+1)-2\phi_i(5P+2)} \tag{1}$$

where R_v, is the average volume weighted radius of the inclusion, η_m and η_d are the Newtonian viscosity of the matrix and the dispersed, respectively, P, α and ϕ_i are the viscosity ratio (η_d/η_m), the interfacial tension and the volume fraction of the dispersed phase, respectively. The form relaxation time of the uncompatibilized blend predicted from Palierne model was found to be 2.16 s which is in excellent agreement with experimental value obtained from the relaxation time spectrum. The shorter form relaxation time of compatibilized blends can be attributed to smaller droplet size compared to that of the uncompatibilized blend.[13,14] Accordingly, the shorter form relaxation time for blend prepared by one-step method can be considered as an indication of smaller droplet size for this blend compared to that of the two-step prepared blend. This is

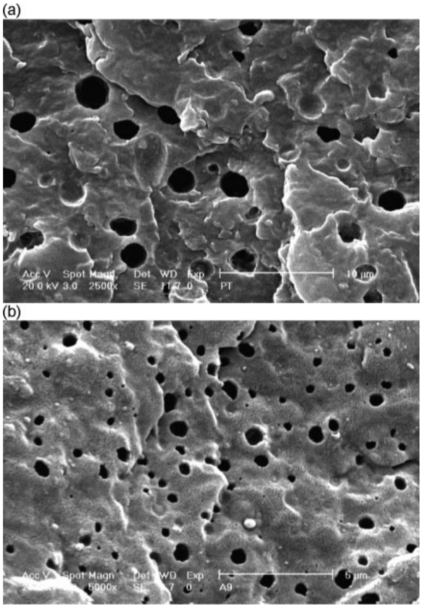

Figure 8.
SEM micrographs of compatibilized blends at a similar grafting level, A: Two-step method (2500×), B: One-step method (5000×).

evidenced by SEM micrographs shown in Figure 8.The longest relaxation time can be related to the interfacial relaxation time (τ_β).[13,15] It can be seen that the interfacial relaxation time of the blend prepared by one-step method is lower than that produced using two-step method. This can be attributed to higher extent of interfacial interaction developed by one-step in-situ compatibilization.

Conclusion

It was shown that the investigated one-step compatibilization method using higher peroxide concentration improves the compatibility of PP and PA by increasing the degree of grafting and copolymer formation. On the other hand a higher MA content increases the amount of excess MA, and the later reacts with PA at a higher rate than with PP-gr-MA. Therefore this process translates to a lower formation of compatibilizing copolymer and thus produces PA with larger particle size.

From the results of SEM micrographs in conjunction with melt viscoelastic measurements it was demonstrated that the efficiency of compatibilization achieved by the one-step method is greater than the one obtained by a two-step method at a similar grafting level. This could be explained in terms of the molecular structure of the compatibilizing copolymer produced in this method.

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