Comparison of Carboxylated and Maleated Polypropylene as Reactive Compatibilizers in Polypropylene/Polyamide-6,6 Blends

CLAYTON C. BOHN, JR., STEVEN C. MANNING, ROBERT B. MOORE

Department of Polymer Science, University of Southern Mississippi,
P.O. Box 10076, Hattiesburg, Mississippi 39406-0076

ABSTRACT: Using reactive extrusion, polypropylene is functionalized with maleic anhydride and compared on an equimolar basis to polypropylene that is functionalized with an asymmetric, carboxylic acid containing peroxide. The grafting efficiency for the asymmetric peroxide is double that obtained for the maleic anhydride system. Moreover, the asymmetric peroxide yields a functionalized material with minimal molecular weight degradation and desirable mechanical properties, relative to maleic anhydride-grafted polypropylene. In compatibilized blends of polypropylene and nylon 6,6, the polypropylene that was functionalized with the asymmetric peroxide is found to be an improved compatibilizer compared to that of maleic anhydride-grafted polypropylene. The differences in mechanical properties of the two different functionalized polypropylene materials and their respective blends are rationalized on the basis of the grafting efficiency, molecular weight degradation during reactive extrusion, and effect of free functional species on the ability to form graft copolymers in compatibilized blends. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2398–2407, 2001

Key words: functionalized polypropylene; MAH-grafted polypropylene; reactive extrusion; polypropylene /polyamide blends; blend compatibilization

INTRODUCTION

Functionalization of polyolefins is commonly achieved by grafting a polar monomer such as maleic anhydride (MAH) onto the polymer backbone using reactive peroxides.[1–12] This reaction can be performed in solution[1] or in the melt[11,12] and may be an economic way to make these inherently nonpolar polymers more compatible with a variety of other polar polymers. For example, enhanced minor-phase dispersion and interfacial

adhesion has been observed with blends of MAH-functionalized polypropylene (MAH–PP) with nylon 6 (ref. 13) and when MAH–PP was used as a compatibilizing agent in blends of PP with nylon 6,6.[12,14,15]

During a typical melt graft reaction of MAH onto PP, the reactive radicals (i.e., the decomposition products from the peroxide initiators) abstract hydrogens from the PP backbone to form tertiary radicals along the chains. These polymeric radicals then add to the reactive double bond of MAH to form randomly distributed grafts.[1,8] While the initial product of this free-radical addition reaction is another radical, recent ^{13}C-NMR studies of MAH-grafted PP showed that the graft sites of the final product contain predominately single succinic anhydride rings.[2,8]

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The possibility for continued MAH homopolymerization into block side chains has been suggested to be unlikely based on frequent intramolecular chain-transfer reactions[8] (i.e., the grafted succinic anhydride radical is capable of abstracting a hydrogen from a neighboring propylene unit) and ceiling temperature considerations[2,16] [i.e., poly-(succinic anhydride) is relatively unstable[17] at typical melt temperatures of ca. 180°C]. Furthermore, only a minimal fraction of the grafted MAH groups is likely form crosslinks between PP chains.[8,18]

In addition to the desirable grafting reactions, PP has also been shown to degrade during peroxide-initiated functionalization by a tertiary radical β-scission (i.e., chain scission at the site of the polymeric radicals).[4,8,19,20] If the peroxide-initiated polymeric radical does not encounter a graftable molecule (e.g., MAH) within a relatively short period of time, the polymeric radical will rearrange and cleave the PP chain. This β-scission process results in a lowering of the average molecular weight of the PP and yields short PP chains with radical and olefinic end groups.[1,7,21] At low MAH concentrations, the secondary anhydride radicals often contribute to the formation of tertiary polymeric radicals via intramolecular chain transfer, and this rearrangement has, consequently, been found to promote PP degradation.[8]

Elf Atochem N.A. developed a series of asymmetric, functional peroxides (peroxyesters) bearing carboxylic groups that may be used to graft acidic functionality *directly* onto polyolefin chains.[22] While this new functionalization procedure is similar to the more conventional MAH grafting procedure, functionalization with asymmetric functional peroxides differs in that the initiating component and the polar grafting moiety are both contained on the same peroxide molecule. The original hypothesis in the use of these new peroxides in reactive processing was that highly reactive alkyl radicals from the thermal decomposition of the asymmetric peroxides abstract hydrogens from PP. Subsequently, the less reactive radicals (containing the acid functionality) couple with the polymeric radicals to form the grafts. Since these grafts are created during a radical termination step rather than in a chain mechanism, undesirable β-scission may be minimized.[22] Moreover, in contrast to the MAH grafting procedure, which relies on the diffusion of MAH to the polymeric radical, the abstraction and grafting processes with the asymmetric peroxides are likely to occur within the same "melt cage."[12] This favorable

proximity of the initiating and grafting species has been suggested to lead to an enhanced grafting efficiency with a somewhat diminished molecular weight reduction (i.e., the grafting reaction can occur before β-scission).[22]

In our previous studies,[12,22,23] the grafting efficiency of asymmetric functional peroxides was optimized by slight variations in their chemical structures. The highest grafting efficiency was obtained with Luperox PMA®, which contains a *t*-butyl initiating component and a reactive double bond in the grafting moiety. It is also important to note that these reactive double bonds on the grafted units have been shown to offer a probable crosslinking mechanism that partially offsets the undesirable molecular weight reduction typically observed with the free-radical-induced MAH grafting processes. Moreover, the alkenyl radical (containing the acid functionality) produced from the thermal decomposition of Luperox PMA® is highly reactive and capable of an additional mechanism involving, first, H-abstraction followed by addition to the polymeric radical.[22] This new abstraction–coupling mechanism further enhances the grafting efficiency with Luperox PMA®.

In this study, we compared the grafting efficiency of a carboxylic acid containing peroxide to that of the conventional MAH/peroxide system in a reactive extrusion process with PP. In addition, the compatibilizing efficiency of this carboxylated PP (f-PP) is compared to that of MAH–PP in blends of PP with nylon 6,6 (PA-6,6). To properly compare the compatibilizing efficiency of the two functionalized materials, f-PP and MAH–PP must be generated in the presence of *equimolar* amounts of initiating and grafting components. Our recent study suggested that f-PP is a slightly better compatibilizer than is MAH–PP;[12] however, the two functionalized materials were prepared using significantly different feed concentrations of the reactive components. Therefore, to directly evaluate the consequence of different grafting efficiencies and concentration of free, ungrafted species in the functionalized PP, this study investigated the compatibilizing efficiencies of f-PP and MAH–PP materials that have been generated on an equimolar basis. The compatibilizing efficiencies of the functional materials were evaluated based on the observed physical properties of the PP/PA-6,6 blends.

EXPERIMENTAL

Materials

PP with an M_n of 44,400 g/mol was obtained from Montell USA, Inc. (Wilmington, DE). Polyamide 6,6 (Vydine 21) with an M_n of 18,000 g/mol and an amine end-group concentration of 45 μeq/g was obtained from Solutia, Inc. (Pensacola, FL). The peroxide initiators, Lupersol 101® and Luperox PMA® (i.e., the asymmetric, functional peroxide) were supplied by Elf Atochem, N.A. (King of Prussia, PA). MAH was obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Preparation of Functionalized PP by Reactive Extrusion

Carboxylic acid-grafted PP (f-PP) was prepared by reactive extrusion using an asymmetric, functional peroxide, shown in Scheme 1. The f-PP was processed by premixing 0.5 wt % Luperox PMA® with PP; this feed composition yields a total of 26.6 μeq/g of the carboxylic acid functionality that is available for grafting. This mixture was extruded in a Haake Rheocord 90 counterrotating twin-screw extruder with three mixing zones and a rheological slit die. The resonance time in the extruder was about 7 min at a screw speed of 15 rpm. The temperature for each zone was set at T_1 = 150°C, $T_2 = T_3$ = 180°C, and T_4 (die) = 170°C, and the extrusion was conducted under a N_2 atmosphere.

MAH–PP was prepared by premixing 0.26 wt % MAH, 0.39 wt % Lupersol 101®, and PP. The compositions of MAH and Lupersol 101® were chosen to yield the same feed concentrations of grafting and initiating species as in the carboxylic acid grafting procedure (i.e., 26.6 μeq/g), described above. Lupersol 101 P20® was used during this experiment, which consists of 20% Lupersol 101® on a PP carrier. The mixture was then extruded in the twin-screw extruder at a screw speed of 15 rpm. Due to the higher thermal stability of Lupersol 101®, relative to that of Luperox PMA®, the temperatures in each zone was main-

tained at $T_1 = T_2 = T_3 = T_4$ = 200°C to ensure a comparable decomposition half-time of the peroxide. This extrusion was also conducted under a N_2 atmosphere.

A nonaqueous, titrimetric procedure described in our previous study[22] was used to determine the grafting efficiency for each functionalization procedure. To eliminate the potential contribution of unreacted functional groups (i.e., free carboxylic acid groups or anhydride species), the "as-extruded" functionalized PP was first purified by precipitation, using the following procedure: The extrudate was first dissolved in xylene at 130°C to a concentration of 5% (w/v) and then precipitated into methanol. After filtration, the precipitate was washed with pure methanol and dried at 60°C *in vacuo*. Note that this sample purification procedure was only employed for this titrimetric procedure, and the purified material was *not* used in the subsequent blend formulations.

Using the above purification procedure, small quantities of highly functionalized, low molecular weight PP have been found to remain in solution during the precipitation step. This material was reclaimed from the xylene/methanol filtrate by evaporating off the solvent. The recovered low molecular weight functionalized PP was then washed in deionized water to remove any ungrafted functional groups and dried *in vacuo* at 60°C. Prior to titration, the MAH–PP was heated under a vacuum for 96 h at 115°C to convert all of the grafted species to the anhydride form. The titrimetric assays for the purified functionalized PP and the recovered low molecular weight functionalized PP were combined to give an overall grafting efficiency for each functionalization procedure.

The molecular weights of the PP samples were measured with high-temperature size-exclusion chromatography (SEC) using a differential refractive index detector. The samples were dissolved in filtered 1,2,4-trichlorobenzene (TCB) at 145°C. A 0.1 wt % antioxidant (butylate hydroxytoluene) was used to stabilize the samples. The SEC column set was heated to 145°C and calibrated using 25 polystyrene standard samples with molecular weights ranging from 950 to 15×10^6 g/mol. The polystyrene calibration curve was converted to one for PP using Mark–Houwink coefficients for polystyrene and PP in TCB.

Reactive Compatibilization of PP/PA-6,6 Blends

Blends of pure PP, the functionalized PP, and nylon 6,6 were premixed to obtain an overall com-

Scheme 1 Luperox PMA®.

position of 80/20 (PP/functionalized PP)/PA-6,6. The functionalized PP (i.e., MAH–PP and f-PP) was used without purification (i.e., the raw functionalized PP was used as extruded and thus contained both grafted and free, ungrafted species) and added to the blends to yield overall compositions of the functionalized PP ranging from 5 to 60 wt %; the balance of the final 80 wt % PP component was pure PP. The blends were then extruded under a N_2 atmosphere at 15 rpm, with a temperature profile of $T_1 = 200°C$, $T_2 = T_3 = T_4 = 270°C$. Samples for physical testing (i.e., notched Izod bars and tensile specimens) were then prepared by injection molding the blend regrinds under a N_2 atmosphere on a Boy 15S injection molder.

Notched Izod impact tests were performed with a Custom Scientific Instrument CSI 137-053, as per ASTM D-256. Impact strengths were taken as an average of about 15 samples; the average experimental error was about ±10% for these measurements. Tensile tests were performed on molded dog-bone samples with a Material Test System MTS 810 coupled with a microconsole MTS 458-20. All tensile properties were taken as an average of about 15 dog-bone specimens. Representative stress–strain plots were chosen from the average tensile properties (i.e., elongation to break, modulus, yield stress, etc.) and reported to reflect the average properties of the respective samples.

RESULTS AND DISCUSSION

The titrimetric analyses of the purified, functionalized PP samples yielded grafted functional group concentrations of about 11 and 4.5 μeq/g, for the f-PP and MAH–PP samples, respectively. Based on the total feed concentration of 26.6 μeq/g of graftable functionality, these titration results indicate overall grafting efficiencies of about 40% for the f-PP system and 17% for the MAH–PP system. As suggested in our previous studies,[12,22] the enhanced grafting efficiency observed when using Luperox PMA® may be attributed to the advantage of having both the initiating and grafting species on the same molecule. During the melt phase, the functionalization procedure, the formation of a polymeric radical followed by the grafting of the carboxylate functionality is likely to occur within a single "melt cage." Furthermore, the thermal decomposition of the asymmetric, functional peroxide yields a grafting

Figure 1 Relative concentrations of (solid symbols) free and (open symbols) grafted functional groups with respect to the composition of functionalized PP in a blend system: (▼) MAH–PP; (●) f-PP.

radical that bears an active double bond and is capable of reacting with the polymeric radical by either a coupling or addition mechanism. In contrast, the MAH species must diffuse through the viscous melt to find the polymeric radicals before grafting can occur.

Since functionalized PP is typically applied as a reactive component in polymer blends,[3,12–15,23–25] it is important to recognize the consequence of simply altering the grafting efficiency from 17 to 40%. Based on the titration results, Figure 1 is used as a guide to demonstrate graphically the calculated influence of these distinctly different grafting efficiencies on the relative concentrations of free and grafted functional groups with respect to blend composition. When the functionalized PP is merely diluted by a second component (i.e., pure PP), it is obvious that the concentration of free MAH species in the blend dominates the concentration of the grafted species. It is important to note here that this high concentration of free MAH in typical MAH–PP products[7] has raised serious concerns with respect to potential environmental hazards of free MAH in the commercial applications of MAH–PP. With the f-PP system, however, the levels of the free species are appreciably lower than are those observed with MAH–PP, and the concentrations of grafted species are significantly enhanced. When simply considering the statistical probability of a reaction with a grafted functional group (e.g., in a reactive compatibilization scheme), it is apparent that the f-PP system would be more likely to yield a desired product. This aspect will be explored in specific detail (see below) for compatibilized blends of PP and PA-6,6.

Table I Molecular Weights of PP Extruded in the Presence of Luperox PMA® and Lupersol 101®

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)
Pure PP	44,400	257,500	686,000
PP + 0.5 wt % Luperox PMA®	40,900	196,000	470,000
Pure PP	38,157	167,417	414,797
PP + 0.5 wt % Lupersol 101®	23,516	55,898	95,083

Mechanical Properties of Functionalized PP/PP Blends

In typical reactive compatibilization schemes using functionalized PP, the PP component of the blend contains a mixture of the reactive compatibilizer and pure PP. If the product of the peroxide-initiated, reactive extrusion procedure (i.e., the reactive compatibilizer) suffers from significant molecular weight degradation through β-scission, then the overall mechanical integrity of the PP component in the blend may be compromised. This undesirable consequence of reactive extrusion is often observed with MAH-grafted PP and may severely limit the range of useful compatibilizer concentrations in blend formulations. For example, the data in Table I compares the molecular weights of the pure PP samples to those of the polymer extruded in the presence of 0.5 wt % of Luperox PMA® and Lupersol 101. Clearly, a much greater reduction in molecular weight is observed for the sample reacted with Lupersol 101, relative to the sample reacted with Luperox PMA®.

Figures 2 and 3 show a comparison of the mechanical properties of f-PP and MAH–PP in blends with pure PP. For strains up to 25% (Fig. 2), the f-PP samples at 80 and 100% compositions show tensile properties that are quite similar to that of the pure PP sample. In contrast, the 80 and 100% MAH–PP samples show brittle failure at less than 5% strain. This behavior may be attributed to significant differences in the relative molecular weights of the functionalized PP with respect to the pure PP sample. We previously suggested that the double bond on the grafting portion of Luperox PMA® is capable of forming crosslinks,[22] which act to counter the undesirable molecular weight reduction (through β-scission) during reactive extrusion. As the molecular

Figure 2 Representative stress–strain plots for blends of functionalized PP with pure PP: (· · · · ·) pure PP; (- - - -) 100 wt % f-PP; (—) 80 wt % f-PP; (— · · —) 100 wt % MAH–PP; (- · · · · -) 80 wt % MAH–PP.

weight of the f-PP is maintained, the toughness of the sample is enhanced. Furthermore, the observed increase in yield stress for the f-PP samples may also be attributed to the presence of crosslinks. Without this potential for forming a significant quantity of crosslinks, reactive functionalization with MAH yields a low molecular weight product with poor tensile properties.

The impact data for the f-PP and MAH–PP blends with PP (shown in Fig. 3) further demonstrate the effect of the different grafting/crosslinking mechanisms on the mechanical properties of the two functionalized PP systems. Over the entire composition range, the impact

Figure 3 Effect of functionailized PP composition on the impact properties of blends containing (○) f-PP and (●) MAH–PP with pure PP.

Table II   Tensile Data for the 80:20 Blends of PP and PA-6,6 Containing Variable Quantities of Functionalized PP

Tensile Data	Wt % Functionalized PP in the Blend[a]							
	0	5	10	20	30	40	50	60
f-PP								
Modulus (MPa)	1090	1162	1087	1135	1126	1107	1118	1170
Tensile strength (MPa)	25	26	27	27	25	24	23	22
% Elongation at break	12.1	11.8	11.9	15.0	>25	4.0	5.6	4.6
MAH-PP								
Modulus (MPa)	1090	993	963	1018	1084	1074	1065	1173
Tensile strength (MPa)[b]	25	28	28	28	27	27	24	24
% Elongation at break	12.1	13.2	13.3	8.4	5.5	5.8	4.4	3.6

[a] Total blend composition of 80:20 (PP + functionalized PP)/PA-6,6.
[b] Maximum stress at yield.

properties of the f-PP system remain relatively constant with only a minimal depression in impact strength, relative to the pure PP sample. On the other hand, the consequential deterioration in molecular weight for the MAH–PP sample yields much lower impact strengths, which tend to decrease with increase in the composition of MAH–PP. In blends with other polymers (e.g., compatibilized PP/PA blends), these poor mechanical properties of the PP phase are likely to adversely affect the overall mechanical properties of the compatibilized blend (particularly for blends in which the MAH–PP/PP component constitutes the major phase[15]).

Compatibilization of PP/PA-6,6 Blends with Functionalized PP

The tensile data for 80:20 blends of PP with PA-6,6 containing variable quantities of functionalized PP are shown in Table II. The moduli and tensile strengths for all of the blends containing functionalized PP are comparable to those observed for the base blend (i.e., without functionalized PP). In addition, for the blends containing up to 10 wt % functionalized PP, the elongations at break are quite similar to that of the base blend. For higher compositions of functionalized PP, however, there are significant differences in the elongation behavior between the samples containing f-PP and MAH–PP. With f-PP, the elongation at break increases significantly (above that of the base blend) at a composition of 30 wt % f-PP, followed by a distinct change to brittle failure for compositions greater than 40 wt % f-PP. In contrast, the blends containing MAH–PP never

show an enhanced elongation above that of the base blend. Instead, the blends containing greater than 10 wt % MAH–PP fail at elongations well below that of the base blend and show a continued decrease in elongation with increasing MAH–PP contents.

The contrasting behavior in tensile properties for the two compatibilizers is further illustrated in the representative stress–strain plots of Figure 4. With 30 wt % f-PP, the tensile specimens extend to 25% elongation without failure. However, the blend containing 30 wt % MAH–PP fails at only about 5% elongation, well below that of the base blend. Furthermore, as evidence of a synergistic enhancement in properties, the f-PP compatibilized blend pro-

Figure 4   Representative stress–strain plots for PP/PA-6,6 blends containing (— ·· —) 30 wt % of f-PP and (- - -) MAH–PP. Stress–strain plots of the pure PP, pure PA-6,6, and the base blend (·····) without a compatibilizer are shown for comparison.

duces a stress–strain profile that is intermediate to those of the pure PP and PA-6,6 samples, and unlike the pure materials, the compatibilized system resists necking up to 25% elongation.

The notable differences in tensile behavior of these blends may be explained by considering the effects of free (ungrafted) functional species on the desired formation of *in situ* block copolymers between the functionalized PP and PA-6,6. For each of the 80:20 PP/PA-6,6 blends studied here, the amine end-group concentration in the blend is constant at about 9 μeq/g. As shown in Figure 1 (at 30 wt % functionalized PP), the blend containing MAH–PP contains very few grafted MAH units relative to the concentration of free species. In comparison, the blend containing f-PP has over twice the number of grafted species and a lower number of free species, relative to the MAH–PP system. During the reactive compatibilization process, the reaction of the free species with the amine end groups is expected to create "end caps" and, consequently, yield a decrease in the concentration of amine end groups available for reaction with the grafted species in the desired formation of graft copolymers.[7] Since enhanced tensile properties of these compatibilized blends are attributed to the presence of *in situ* formed copolymers,[12,13,15] the improved grafting efficiency of the f-PP system (relative to that of the MAH–PP system) allows for the creation of a greater concentration of interfacially active graft copolymers. For the MAH–PP system, the high concentration of free MAH effectively limits the formation of the graft copolymer[7] and thus yields incompatible blends with poor mechanical properties.

While the f-PP system demonstrates superior compatibilization behavior at compositions up to 30 wt %, it is important to note that the tensile properties for *both* the f-PP and MAH–PP systems are poor at compositions greater than 30 wt %. This observation suggests that once the 1:1 stoichiometry of functional species to amine end groups is exceeded, the excess free functional species in both systems begin to compete predominantly for the available PA end groups;[12] this competing reaction limits the relative concentration of graft copolymers at the interface and consequently decreases the interfacial adhesion.[15,26,27] Furthermore, while the data in Figure 2 indicate that the f-PP material is tougher than both the pure PP and the MAH–PP, it is surprising that all the blends containing greater than 30 wt % compatibilizer (either f-PP or MAH–PP) display tensile properties far worse than those of the

Figure 5 Effect of the total concentration of functional species on the impact properties of 80:20 PP/PA-6,6 blends containing variable compositions of (●) f-PP and (◆) MAH–PP. The dashed vertical line represents the constant amine end-group concentration in the blends, and the impact strengths of (■) pure PA-6,6 and (▼) pure PP are shown for comparison.

base blend. This behavior may be attributed to the presence of low molecular weight functionalized PP (i.e., as a result of free radical initiated β-scission during the initial functionalization process) that tends to build up at the interface. Note that the potential crosslinking reaction proposed to occur during the formation of f-PP is *not* expected to completely eliminate the formation of low molecular weight polymer.[22] Since these relatively short chains of functionalized PP are very mobile (i.e., rapid diffusion in the melt) and the reactive chain ends are expected to partition to the interface,[28] it is likely that the areal density of PP-*g*-PA copolymers bearing low molecular weight PP blocks (at the PP/PA-6,6 interface) will increase with the weight fraction of functionalized PP in the blend.[26] With a high interfacial concentration of low molecular weight grafted PP brushes extending into the PP phase, the areal density of chain entanglements across the interphase will be low, resulting in poor interfacial adhesion.[29] Consequently, in the heterogeneous blend systems containing high compositions of the compatibilizer, the diminished concentration of the graft copolymer and the presence of low molecular weight species at the interface cause the blends to fail at low elongations, regardless of the compatibilizer type.

In agreement with the data in Table II and Figure 3, the impact properties of the PP/PA-6,6

blends (Fig. 5) show profound differences between the f-PP and MAH–PP compatibilized systems. The impact strength data in Figure 5 are plotted with respect to the total microequivalents of functional species in the blends and correspond to f-PP and MAH–PP compositions ranging from 0 to 60 wt % (at increments of 10 wt % in the blends). For the f-PP compatibilized system, the impact strengths of the blends increase up to a value near that of pure PA-6,6 at a functional group concentration of about 8 μeq/g (i.e., corresponding to a f-PP composition of 30 wt %). At higher f-PP compositions, the functional group concentration exceeds that of the amine end-group concentration, and the impact strengths subsequently decrease to a value near that of the base blend at about 16 μeq/g (i.e., at a functionalized PP composition of 60 wt %). In contrast, the impact properties of the MAH–PP compatibilized blends show a steady decrease (below that of the base blends) over all MAH–PP compositions. From our previous studies,[12] the enhanced impact properties of these blends were found to correlate with a significant reduction in the dimensions of the minor phase (i.e., PA-6,6) and attributed to the interfacial activity of the *in situ* formed graft copolymers.

For these compatibilized blends, the highest impact strength should be obtained with a functional group concentration that produces a near 1:1 stoichiometry between the total functional group concentration (grafted and ungrafted) and the amine end groups.[12,13] At higher compatibilizer contents, a stoichiometric imbalance exists with an excess of free functional species. Under this situation, the grafted functional groups must compete with the relatively mobile free species for reaction with the amine end groups. As the quantity of free functional species is increased, the number of amine end groups available for graft copolymer formation is reduced (i.e., by end-capping reactions), rendering fewer copolymers at the interphase. With a low concentration of graft copolymers, the PP/PA-6,6 interface is destabilized with poor interfacial adhesion, and thus the blend develops undesirable mechanical properties.

For the MAH–PP compatibilized system, it is interesting to note that the impact properties of the blends in Figure 5 never exceed that of the base blend. This behavior suggests, in agreement with the data in Figure 3, that the mechanical properties of the continuous PP phase dominate the properties of the PP/PA-6,6 blends. With an increasing composition of MAH–PP in the blends, the inherent molecular weight degradation (by β-scission) compromises the mechanical integrity of the major phase. Consequently, the poor impact properties for the MAH–PP system observed in Figure 3 are reflected in the mechanical properties of the PP/PA-6,6 blends shown in Figure 5. While it is still likely that graft copolymers between MAH–PP and PA-6,6 are being formed, the drop in impact strength below that of the base blend suggests that the low molecular weight of the MAH–PP segments yields graft copolymers that are incapable of promoting strong interfacial adhesion through the required chain entanglements with the PP phase.[29] In contrast, the f-PP system has been shown (Table I) to maintain a relatively high molecular weight[22] and thus yields blends that demonstrate impact properties that are principally dependent on the stoichiometry of reactive functionalities.

CONCLUSIONS

PP has been functionalized, via reactive extrusion, with MAH and with an asymmetric functional peroxide. For a direct comparison of the grafting efficiencies resulting from the two different functionalization procedures, the reactive components were processed on an equivalent basis by the use of equimolar amounts of initiating and grafting species. Based on a total feed concentration of 26.6 μeq/g of graftable functionality, titration results indicated overall grafting efficiencies of about 40% for the f-PP system and 17% for the MAH–PP system.

In comparison to the MAH–PP system, the enhanced grafting efficiency for the f-PP system was attributed to the advantage of having both the initiating and grafting species on the same molecule and to the presence of a reactive double bond on the grafting radical formed by the thermal decomposition of Luperox PMA®. With respect to the low grafting efficiency of the MAH–PP system, the undesirable effects of molecular weight degradation by β-scission was found to dominate the mechanical properties of MAH–PP/PP blends. For increasing compositions of MAH–PP, the tensile and impact properties were severely compromised. In contrast, blends of f-PP with PP showed relatively stable tensile and impact properties over all blend compositions. This behavior was attributed to the ability of the reactive double bond on the grafting portion of Luperox PMA® to

form crosslinks, which counteract the undesirable molecular weight degradation of f-PP by β-scission during reactive extrusion.

MAH–PP and f-PP were also compared as reactive compatibilizers for blends of PP and nylon 6,6. For the MAH–PP system, the consequences of molecular weight degradation and a low grafting efficiency were found to adversely affect the resulting mechanical properties of the PP/PA-6,6 blends. At low MAH–PP compositions, little enhancement in tensile properties was observed. For MAH–PP compositions of 20 wt % and greater, tensile data for the blend samples showed brittle failure at elongations well below that of the uncompatibilized blends. In contrast, blends compatibilized with f-PP showed a remarkable enhancement in toughness at a composition of 30 wt %. This observation was attributed to the relatively high grafting efficiency for the f-PP system, which allowed for the creation of a greater concentration of interfacially active graft copolymers. For higher compositions of f-PP, however, the tensile behavior shifted to brittle failure similar to that observed with the MAH–PP system. The drop in tensile properties for both compatibilized blend systems at compositions above 30 wt % was attributed to (1) the presence of excess free functional species that are capable of forming end caps on the PA-6,6 chains and thus inhibiting the desired formation of graft copolymers and (2) to a buildup of low molecular weight functionalized PP at the interface. These changes in the chemical composition of the interphase combine to yield poor interfacial adhesion.

For the f-PP compatibilized samples, the impact properties of blends containing only 20 wt % PA-6,6 were found to increase to near that of pure PA-6,6 at a compatibilizer composition of 30 wt %. For higher compositions of f-PP, however, a decrease in impact properties (to values near those of the base blend) was observed. This behavior was attributed to a stoichiometric imbalance between the total functional group concentration and the amine end groups. In contrast to the behavior of the f-PP compatibilized systems, blends containing MAH–PP were found to yield impact properties that decreased (below that of the base blend) over all MAH–PP compositions. This behavior was attributed to a low concentration of graft copolymers (i.e., due to the low grafting efficiency and high free MAH concentrations) and to a low interfacial adhesion resulting from the relatively low molecular weight of the MAH–PP (i.e., poor chain entanglement at the interface).

Therefore, the overall results of this comparative study indicate that reactive extrusion with Luperox PMA® yields a functionalized PP with an enhanced grafting efficiency that may be used as a highly effective reactive compatibilizer in PP/PA-6,6 blends. Moreover, in comparison to the use of MAH–PP, the production of f-PP yields a functional material that does not suffer from significant molecular weight degradation and offers an alternative that may minimize the potential environmental hazards often encountered in systems containing high concentrations of free MAH. While this study suggests that, on an equivalent basis, f-PP is a somewhat better compatibilizer, it is recognized that MAH–PP can be prepared using higher feed concentrations and optimized extrusion parameters to produce a compatibilizer that is as effective as is the f-PP system. Under these conditions, however, it is important to develop processes that can improve grafting efficiency (above the typical 20%) and minimize the polymer degradation. We are currently investigating the application of reactive additives and delayed initiation toward achieving an improved process for the preparation of MAH–PP.

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