Reactive Compatibilization of Blends of PET and PP Modified by GMA Grafting

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Summary: The melt radical grafting of glycidyl methacrylate (GMA) onto isotactic polypropylene (PP) was carried out in Brabender internal mixer and the influence of reaction procedure, radical initiator concentration and addition of co-monomer (styrene) on the grafting efficiency was examined. The viscosity, the thermal behaviour and melt rheology of PP-*g*-GMA samples was then analysed as a function of grafted GMA content. Blends of poly(ethylene terephthalate) (PET) with PP and PP-*g*-GMA (5.2 wt% GMA), prepared in internal mixer, were characterised by SEM, DSC and melt viscosimetry. The morphological analysis of PET/PP-*g*-GMA blends (80/20, 50/50 w/w) pointed out a marked improvement of phase dispersion (with particle size of about 0.6 μm for 80/20 blend) and interfacial adhesion, as compared to non-compatibilized PET/PP blend. The results of mixing torque and thermal analysis supported the occurrence of in-situ compatibilization reaction between epoxy groups of GMA modified PP and carboxyl end-groups of PET in the melt.

Keywords: blends, functionalization, poly(ethylene terephthalate), polypropylene, reactive compatibilization

Introduction

In situ compatibilization of blends of polyolefins with polar polymers, as polyesters and polyamides, can be efficiently performed by suitable modification of polyolefin chains with reactive groups (i.e., carboxyl derivatives, epoxies, etc.) able to give rise, during melt blending, to chemical reactions with the functional groups of the polar component.[1] The formation of a graft copolymer between the polymer components causes a reduction of interfacial tension with an improvement of phase dispersion and promotes adhesion through interpenetration and entanglements at the polymer-polymer interface.

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The free radical grafting of GMA onto polyolefins (PE, PP, EPR, etc) has been investigated by several authors in the recent years,[2-5] however only a few studies dealt with the compatibilization of blends of GMA modified polyolefins with Nylons or polyesters.[6-10] The use of GMA in reactive compatibilization presents several advantages as compared to other reactive monomers (acrylic acid, maleic anhydride, etc.),[10] due to the higher reactivity of epoxy group toward carboxyl, hydroxyl or amino groups, absence of water formation during the reaction and less environmental risk.

The present paper is aimed at examining the melt grafting procedures of GMA onto PP and the compatibilizing efficiency of the grafted polyolefin in blends with PET. The influence of reagents concentration and addition of a co-monomer (styrene) on the grafting degree and the properties of PP-*g*-GMA copolymers has been first analysed. Then, the morphology and the thermal and rheological behaviour of blends PET/PP-*g*-GMA with different composition have been studied and compared with those of unmodified PET/PP blends.

Experimental

Materials

Isotactic PP (Novolen 1100 N, Targor) with MFR =12 g/10 min (230 °C, 2.16 kg) and PET (SINCO Engineering) with I.V.= 0.74 dl/g were used throughout. Before use the materials were carefully dried under vacuum in order to reduce the moisture content: PET samples were heated up to 170 °C for 4 hours, PP was dried at 80°C. Glycidyl methacrylate (GMA, 97% purity) and styrene (STY, 99% purity) were purchased from Aldrich and used as received. Bis[1-(*tert*-butylperoxy)-1-methylethyl] benzene (BTP), dicumyl peroxide (DCP) and benzoyl peroxide (BPO), commercial products from Aldrich, were used as free radical initiators without further purification.

Grafting Procedures

The grafting was carried out at 190 °C in a Brabender Plasticorder internal mixer with sigma rotors rotating at 50 r.p.m., under nitrogen stream. The variation of torque moment during reaction was recorded against the time of mixing. Three different addition procedures were tested for the grafting experiments:[9] *A*) PP (pellets) was first introduced into the mixing chamber for 2 minutes in order to melt, then GMA and the initiator were added and the mixing continued for additional 5 minutes; *B*) PP (pellets), GMA and the initiator were pre-mixed at

room temperature, then fed into the mixer at 190°C and mixed for 5 minutes; *C*) similar to the previous one, but using a limited amount of PP (10% of the total amount) ground into powder. To enhance the grafting efficiency of GMA, styrene was also used as a co-monomer, in molar ratios from 0.5 to 1.5 with respect to GMA.[3, 4]

The reaction products were purified by dissolution in refluxing xylene and precipitation into acetone at room temperature, under continuous stirring, in order to remove the unreacted monomers (GMA, STY), the homopolymerized GMA and GMA-STY copolymer (soluble in acetone). The precipitate, PP-*g*-GMA, was filtered, washed again with acetone and dried under a vacuum at 80°C overnight. The purified samples were then compression moulded into thin films and analysed by FTIR in order to determine the amount (in wt%) of GMA grafted onto PP. The solution viscosities of PP and grafted copolymers were measured at 135 ± 0.1 °C with an Ubbelhode viscosimeter in tetrahydronaphtalene. The molecular weight of the samples was calculated from intrinsic viscosity values using the relation reported by Danusso *et al.* for isotactic polypropylene.[11] The grafting conditions, the reagents concentration and the GMA content of PP-*g*-GMA copolymers examined are listed in Table 1.

Table 1. Grafting conditions, GMA content and molecular weight of PP-*g*-GMA copolymers.

Sample code	$[GMA]_g$ (wt%)	Grafting Procedure	BTP (wt%)	$[GMA]_i$ (wt%)	$[STY]_i/[GMA]_i$ (mol/mol)	M_v
PP	-	-	-	-	-	92000
PP-*g*-GMA1	0.4	B	0.2	5.7	-	41000
PP-*g*-GMA2	1.0	C	0.4	5.7	-	43000
PP-*g*-GMA3	2.7	B	0.4	5.7	1/1	32000
PP-*g*-GMA4	4.7	C	0.2	7.4	1/1	n.d.
PP-*g*-GMA5	5.2	C	0.4	7.4	1/1	25000

Blending and Characterization

Binary blends PET/PP and PET/PP-*g*-GMA5 with composition 80/20 and 50/50 w/w were prepared in the Brabender mixer (260 °C, 50 rpm, 7 min) under nitrogen flux, recording the torque moment until reaching of stationary conditions. Plain PET and PP were also processed in the mixer at 260 °C and 190 °C (50 rpm, 7 min.) respectively.

The morphology of the blends was examined by a Jeol T300 scanning electron microscope (SEM) on samples fractured in liquid N_2 and sputter-coated with Au. The size distribution of the dispersed phase in the blends was then analysed by measuring a consistent number of

particles (200-300) for each sample by an image analysis programme (Scion Image). A polarizing optical microscope (Leitz Ortholux) equipped with hot stage was employed for analysing the phase structure in the blends. Thermal properties of the modified polyolefins and blends were examined with a Perkin Elmer DSC-II differential scanning calorimeter using a standard heating/cooling rate of 10 °C/min. Temperatures and heats of phase transitions were determined respectively from the maxima and areas of the crystallization and melting peaks. The degree of crystallinity was calculated from the values of melting enthalpy. Melt viscosities were measured at 180 °C by a CEAST capillary rheometer (L/D = 40) in the shear rate range 10^1–10^3 s^{-1}.

Results

GMA Grafting onto PP

The amount of grafted GMA in PP-*g*-GMA samples was determined from area ratio of FT-IR peaks at 1730 cm^{-1} (stretching of the carbonyl group of GMA) and at 2722 cm^{-1} (combination band), typical of the PP skeleton.[12] The latter peak was chosen as an internal reference. Quantitative measurements of grafted GMA were performed by using a calibration plot, as shown in Figure 1, obtained by the 1730/2722 peak ratios of PP-*g*-GMA samples with known GMA content, independently determined by a titration procedure in xylene solution.[13]

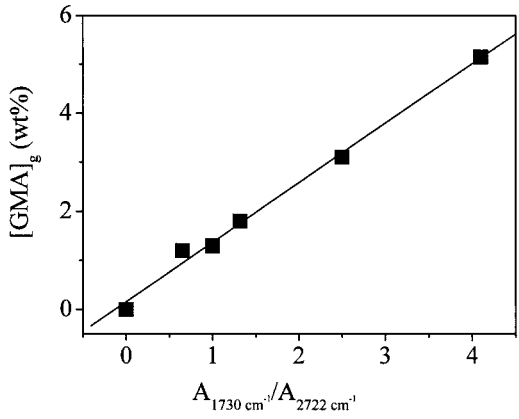

Fig. 1. Amount of grafted GMA vs. the ratio of FT-IR peak areas at 1730 and 2722 cm^{-1}.

The grafting degree of PP-*g*-GMA copolymers obtained by the various procedures *A*, *B* and *C*, with the same initial amount of GMA monomer ($[GMA]_i$= 5.7 wt%) and different content of peroxide (BTP), is reported in Table 2. In all cases the highest grafting degree was obtained by applying the procedure *C*. This can be ascribed to a better absorbency of monomer and initiator onto PP powder, giving rise to a more fast and complete reaction of polymer radicals with GMA. Among the three tested peroxides, BTP showed the highest grafting efficiency ($[GMA]_g$= 3.6 wt%) as compared to DCP ($[GMA]_g$= 2.4 wt%) and BPO ($[GMA]_g$= 1.0 wt%) in the same reaction conditions. The lower efficiency of BPO is likely due to its shorter half-lifetime.

Table 2. Amount of GMA grafted onto PP for different grafting procedures ($[GMA]_i$ = 5.7 wt%).

BTP content	Grafting Degree (wt%)		
(wt%)	A	B	C
0.2	0.1	0.4	0.6
0.4	0.3	1.5	2.3

The effect of amount of BTP on the grafting degree of copolymers is shown in Figure 2. The amount of grafted GMA increases with the peroxide concentration up to reach a maximum, corresponding to $[GMA]_g$= 4 wt%. For BTP contents > 0.5 wt%, degradation of PP and homopolymerisation reaction of GMA became prevailing, as indicated by the rapid decrease of torque, and thus of melt viscosity, following the grafting reaction. The grafting yield also increases with increasing the initial concentration of GMA and then level off at a value ($[GMA]_g$= 3-5 wt%) which depends on the amount of peroxide. Similar results have been reported for GMA melt grafted polypropylenes by using different radical initiators.[3,4]

According to literature reports [3-5], the addition of STY as co-monomer significantly promotes GMA grafting, owing to the higher reactivity of STY toward PP forming styryl-macroradicals, which in turn can easily react with GMA. As shown in Figure 3 for the grafting reaction in the presence of STY, with increasing the ratio STY/GMA (mol/mol) the grafting yield of GMA increases up to three-times as compared to the reaction without co-monomer. When the monomers ratio is higher than 0.5, the amount of the polymerised GMA exceeds that of grafted GMA. On the other hand, the addition of STY reduces the degradation of PP chains as evidenced (Figure 3) by the increase of mixing torque recorded at the end of the grafting process.[14] These samples were completely soluble in hot xylene indicating that no cross-linking

takes place during the grafting reaction, owing to possible combination of PP-styryl macroradicals, as suggested by Wong and Baker.[12]

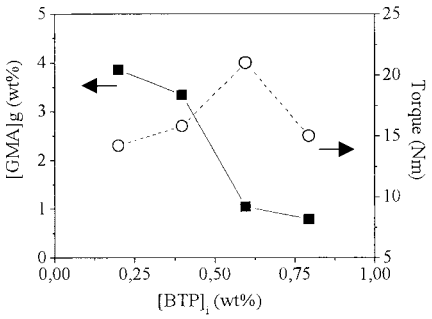

Fig. 2. Amount of grafted GMA and torque variation as a function of peroxide concentration [BTP] ([GMA]$_i$ = 5.7 wt%, procedure *B*).

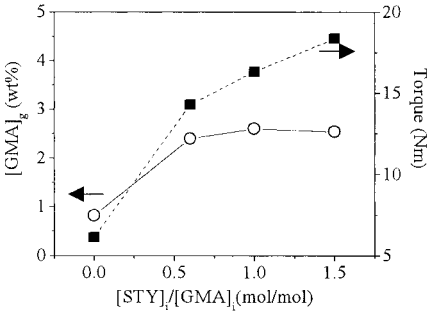

Fig. 3. Amount of grafted GMA and final mixing torque as a function of molar ratio [STY]/[GMA] ([GMA]$_i$ = 5.7 wt%, [BTP] = 0.2 wt%, procedure *B*).

Characterization of PP-g-GMA Copolymers

PP-*g*-GMA copolymers with different GMA content were analysed by viscosimetry, DSC and melt rheometry. Viscosity measurements of polymer solutions in tetrahydronaphtalene pointed out that the average molecular weight (M*v*) decreases with increasing the grafting degree from ca. $9.2*10^4$ for PP to $2.5*10^4$ for PP-*g*-GMA5 (Table 1). Samples with smaller GMA content (0.4-1.0 wt%) display a variation of M*v* comparable with that of samples with higher grafting degree, indicating that the decrease of molecular weight is mainly due to the presence of initiator at the reaction temperature, which induces large chain scission effects.[6]

Table 3. DSC data for PP-*g*-GMA samples on cooling and 2nd heating run (10°C/min).

Sample	T_c (°C)	ΔH_c [a] (J/g)	T_m (°C)	ΔH_m [a] (J/g)	X_{cr} [b] (%)
PP	111.6	99.5	158.6, 165.5	104.5	57.5
PP-*g*-GMA1	112.1	99.5	160.0, 165.2	100.3	53.1
PP-*g*-GMA2	111.8	100.3	158.0, 165.1	105.3	55.8
PP-*g*-GMA3	119.5	102.4	160.6	108.7	57.5
PP-*g*-GMA4	120.1	95.3	162.8	102.8	54.5
PP-*g*-GMA5	119.1	87.4	160.6	86.9	46.0

[a] Per gram of polymer component
[b] $X_{cr} = \Delta H_m / \Delta H_m^{\circ}$ with ΔH_m° = 188.9 J/g for PP

Crystallization temperatures (T_c), melting temperatures (T_m) and relevant heats of transition (ΔH_c , ΔH_m) of PP homopolymer and PP-*g*-GMA samples are summarized in Table 3.

Compared with pure PP, the crystallisation and melting behaviour of PP-*g*-GMA is markedly affected by the content of grafted GMA; in particular, with increasing the amount of grafted GMA T_c is shifted to higher temperature (from about 112 °C to 120 °C). These findings suggest that the nucleation process of PP crystals is enhanced in the GMA grafted polymers. Similar effects have also been observed for ethylene-propylene copolymers and PP modified with GMA[15,16] and they were ascribed to the nucleating capability of grafted groups. However, it must be taken into account that other factors such as the presence of reaction impurities, molecular chain fractionation, etc., could significantly affect the crystallization of these copolymers.

A decrease of the overall crystallization (and melting) enthalpy is observed mainly for the sample with higher grafting degree (PP-*g*-GMA5), which implies a lower crystallinity degree due to the presence of GMA groups. The melting and reorganization phenomena of crystals are also influenced by the grafting degree: PP homopolymer and copolymers with lower GMA content display characteristic double melting peak (ca. 158-165 °C), whereas a single melting peak is observed for copolymers with GMA content > 1 wt%. For these latters an additional endothermal peak appears at lower temperature (ca. 147 °C), whose intensity increases with the amount of grafted GMA. Most likely, this peak could be ascribed to the presence of less perfect crystals of low molecular weight and/or GMA richest polypropylene chains.

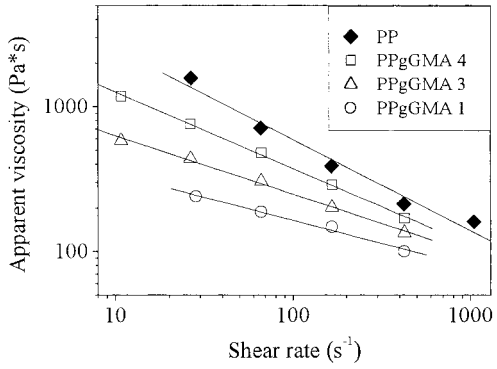

Fig. 4. Apparent melt viscosity of PP and GMA grafted PP samples vs. shear rate.

The rheological data, reported in Figure 4, show that the melt viscosity of the modified polylpropylenes is lower than that of homopolymer, as a consequence of chain scission phenomena during the grafting process.[8] However, the melt viscosity of PP-*g*-GMA samples increases with increasing the GMA grafted content and this could be ascribed to the effect of polar interactions between GMA groups in the copolymer chains, even if the occurrence of cross-linking between grafted chains can not be excluded at higher GMA contents.[12]

Blends of PET with PP and PP-g-GMA

SEM micrographs of PET/PP and PET/PP-*g*-GMA5 blends (80/20 and 50/50 w/w) are shown in Figure 5. Blends of PET and PP (Figures 5a-b) show the typical morphology of incompatible systems with a rough dispersion of the components and no adhesion between matrix (PET) and dispersed phase (PP). Otherwise, blends of PET and GMA modified PP (5,2 wt% GMA) show a more homogeneous morphology with finer dispersion of polyolefin phase and strong interfacial adhesion (Figures 5c-d).

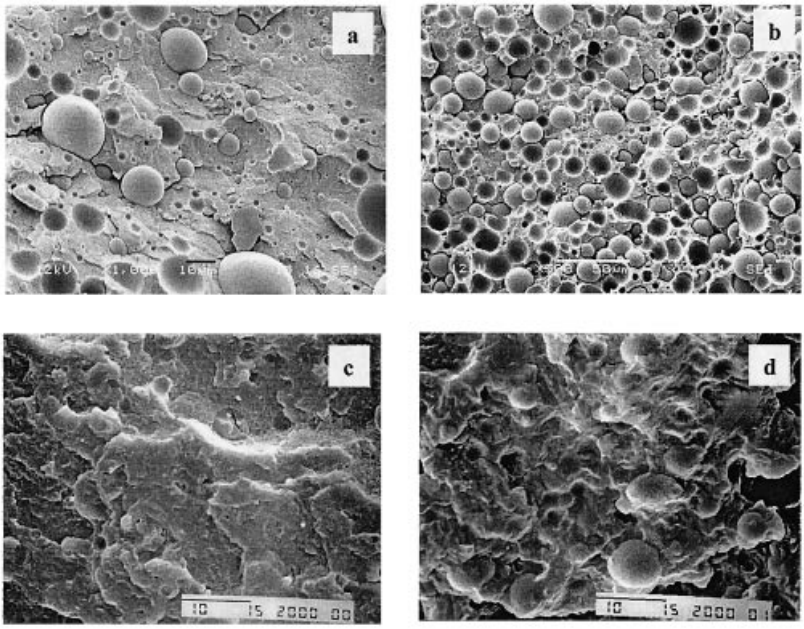

Fig. 5. SEM micrographs of fracture surfaces of blends PET/PP 80/20 (a) and 50/50 (b); PET/PP-*g*-GMA5 80/20 (c) and 50/50 (d) (bar length in figs. a, c, d: 10 μm; fig. d: 50 μm).

A wide particle size distribution is generally observed for the non-compatibilized blends, characterized by extended coalescence phenomena of dispersed phase due to the higher melt viscosity of PP as compared to PET. The number-average diameter, d_n, of dispersed particles is reported for all examined blends in the chart-bar of Figure 6. For blends with higher PET content (80/20) the average size of polyolefin particles decreases from about 2.6 μm for the non compatibilized blend to about 0.6 μm for that with PP-*g*-GMA5, while in the blends with composition 50/50, where PET is the continuous phase, the average size of PP dispersed phase changes from about 8 μm for PET/PP to 2.4 μm for PET/PP-*g*-GMA5. The compatibilizing effect resulting for the blends with modified PP is to be related with the interactions occurring at interface between epoxy groups of GMA and carboxyl end-groups of PET, leading to a drastic decrease of interfacial tension and suppression of coalescence.[17]

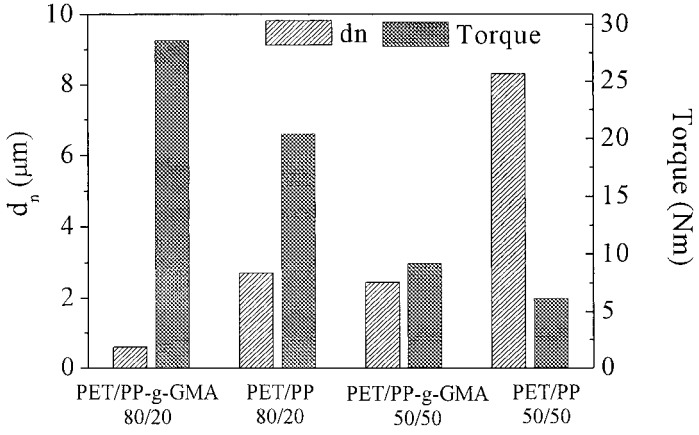

Fig. 6. Average diameter (d_n) of dispersed phase and final mixing torque for PET/PP and PET/PP-*g*-GMA5 blends.

The presence of intermolecular interactions in the modified blends is supported by the variation of mixing torque, as a consequence of changes of melt viscosity due to copolymerization reactions between the polymer components.[18, 19] As shown in Figure 6, a significant increase of torque has been found for PET/PP-*g*-GMA5 blends with respect to PET/PP blends at same composition. The higher torque value of the blend PET/PP-*g*-GMA5 80/20 can be related with the molar ratio between the reactive groups (mol COOH/mol GMA= 0.27) which is greater than that of PET/PP-*g*-GMA5 50/50 blend (mol COOH/mol GMA= 0.07). Further, it must be

noticed that, due to the bifunctionality of PET chain, additional reaction of hydroxyl end-groups of polyester with PP-g-GMA may occur giving rise to crosslinking phenomena.[10, 19]

The DSC analysis of the various blends showed a marked influence of the composition and GMA content on the crystallization behaviour of both polymer phases (Table 4). For PET/PP blends a shift of T_c of PP to higher temperature than that of pure PP (111.6 °C) was observed, indicating a nucleating effect of PET matrix (or likely its impurities) on the dispersed polyolefin. For PET/PP-*g*-GMA5 blends, a more pronounced increase of T_c of PP phase up to 122 °C was found, similar to that previously described for plain PP-*g*-GMA copolymers (see Table 3). Moreover, the melting parameters (T_m, ΔH_m) and the crystallinity of polymers in the blends with PP-*g*-GMA5 are generally lower than that of PET/PP blends (and pure components), in agreement with the enhanced phase dispersion of the formers. In particular, the lowest crystallinity value of PP (26.5%) is observed for PET/PP-*g*-GMA5 80/20 blend, which displays the lowest dispersed particle size.

Table 4. DSC data for PET/PP blends on cooling and 2nd heating run (10°C/min).

Sample	PET				PP			
	T_c (°C)	ΔH_c [a] (J/g)	T_m (°C)	ΔH_m [a] (J/g)	T_c (°C)	ΔH_c [a] (J/g)	T_m (°C)	ΔH_m [a] (J/g)
PET	182.0	-39.3	247.8	35.1				
PP					111.6	-100.0	165.5	104.5
PET/PP 80/20	185.9	-39.3	248.3	34.7	116.5	-96.1	162.5	92.8
PET/PP 50/50	179.7	-34.7	247.1	33.0	115.0	-100.3	163.5	101.1
PET/PP*g*GMA 80/20	189.8	-38.5	247.5	29.7	122.0	(-	160.5	(50.1)
PET/PP*g*GMA 50/50	181.2	(-13.4)	243.5	28.4	120.4	-96.1	163.7	77.7

[a] Per gram of polymer component

Conclusions

The study of radical grafting of GMA onto PP in the melt showed that the grafting degree of the polyolefin can be enhanced by a suitable control of reactions parameters and procedures (monomer concentration, type and content of radical initiator, addition of co-monomer) which affect the grafting mechanism, as well as the chain degradation of PP and secondary reactions (GMA hopolymerization, crosslinking). The addition of styrene as co-monomer significantly improves the GMA grafting.

The molecular weight, the melt viscosity and phase behaviour of examined PP-*g*-GMA copolymers are strictly depending on the content of grafted GMA. With increasing the GMA

content, a large change of crystallization and melting temperatures was found, as compared to PP homopolymer, suggesting the presence of PP crystals with different perfection and chain structure.

Blends of PET with PP-*g*-GMA5 displayed a neat improvement of phase dispersion and adhesion with respect to PET/PP blends. Mixing torque and DSC data supported the occurrence of reactions between GMA modified PP and PET in the melt, likely leading to the formation of a graft copolymer, acting as compatibilizer. The compatibilizing effect of GMA grafted PP in the examined blends (80/20 and 50/50) can be interpreted by taking into account the molar ratio between the epoxy groups and the functional end-groups of PET chains.

The improvement of phase morphology and physical-mechanical properties observed for PET/PP blends compatibilized with PP-*g*-GMA, as compared to those compatibilized with maleic anhydride grafted PP,[20] support the higher efficiency of GMA grafted polyolefin.

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