Comparison of the effectiveness of different basic functional groups for the reactive compatibilization of polymer blends

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Reactive compatibilization of immiscible polymer blends has been attracting a very considerable research interest in the past few years. While a wide variety of functionalized polymers having acidic groups are commercially available, potentially reactive polymers containing basic functional groups have rarely been developed. In this study, glycidyl methacrylate (GMA), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl methacrylate (HPMA), t-butylaminoethyl methacrylate (TBAEMA), dimethylaminoethyl methacrylate (DMAEMA), and 2-isopropenyl-2-oxazoline (IPO) were melt grafted onto a polypropylene (PP) homopolymer. The effectiveness of these functionalized PPs as compatibilizers for PP/(acrylonitrile-*co*-butadiene-*co*-acrylic acid) rubber (NBR) blends was evaluated in terms of improvement in impact properties and blend morphology. It has been found that IPO and GMA are effective in compatibilizing the PP/NBR blends, with a nine-fold improvement in impact energy over pure PP and an uncompatibilized PP/NBR blend. The other functional groups are much less effective for the blend system where carboxylic acid is the coreactive group.

(Keywords: polymer blends; reactive compatibilization; basic functionalization)

INTRODUCTION

The development of new polymeric engineering materials has been dependent, not only on the synthesis of new polymeric species, but also on the ability to effectively combine different polymers with complimentary properties. As these combinations are virtually always phase separated it is usually necessary to compatibilize them so as to control the morphology of the material in an appropriate manner. Preformed block or graft copolymers are used but not as extensively as their potential utility might suggest, due to the need for particular copolymer designs and the complications involved in synthesizing them.

Another interesting approach is to create these block or graft copolymers *in situ* during the polymer blend preparation through an interfacial chemical reaction between specially selected functional polymers. If two coreactive polymers are incorporated, with one each in the two immiscible phases, they can form the appropriate bridging copolymers at the interface in the blends. If care is exercised in the copolymer selection and the quantities used are minimal they can be miscible in their respective host phase and not change the underlying properties of them. Commercial interest in this technique has grown since the initial introduction of toughened polyamides that were prepared using this principle. Reactive compatibilization has also attracted considerable research interest in the past several years and has been reviewed recently by several authors[1-3].

Condensation polymers normally have potentially reactive groups inherent in the backbone and at the chain ends. For instance, the polyamides referred to above have carboxylic acid and/or amine end groups and amide groups in the backbone. Some addition polymers contain potentially reactive groups in their side chains, e.g. carboxylic acid groups in poly(acrylic acid) and ester groups in polyacrylates. In many other cases, however, the polymers need to be functionalized with suitable reactive groups, either through copolymerization or by chemical modification of preformed polymers. Functionalization by melt grafting is an attractive method for preparing reactive polymers on account of its apparent simplicity and potential cost effectiveness. Although there are a number of commercially available polymers containing acidic reactive groups such as carboxylic acid and maleic anhydride, few commercially available polymers that have been purposely functionalized with basic reactive groups have been reported. This is largely due to the scarcity of suitable basic monomers, when taking into consideration their toxicities, difficulties in preparation and handling, instabilities, and cost effectiveness, etc. However, there have been developmental polymers with basic functionality. A well-known example of these is the reactive polystyrene developed by the Dow Chemical Company[4]. Research efforts have also been made to prepare functionalized polyolefins containing basic reactive groups. Glycidyl methacrylate (GMA) has been grafted on to low-density polyethylene[5] and PP[6]. Dimethylaminoethyl methacrylate (DMAEMA) and t-butylaminoethyl methacrylate (TBAEMA) have been grafted onto linear low-density polyethylenes[7-9], and DMAEMA has also been grafted on to ethylene–propylene

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rubber[10]. Recently, a novel process of making primary amine functionalized polyolefins by copolymerization of masked functional monomers has been patented[11,12].

The overall objectives of this study were to functionalize a PP homopolymer with various basic functional groups via a melt grafting process and to evaluate the effectiveness of each basic functional group in compatibilizing polypropylene/nitrile–butadiene rubber blends. The grafting monomers were selected to represent oxazoline and glycidyl functionalities, secondary and tertiary amines and two different hydroxyl functionalities.

EXPERIMENTAL

Materials

The polypropylene (PP) used in these studies was a nonreactive homopolymer which was obtained from the Shell Company (GE6100). It had a weight-average molecular weight of 650 000, a number-average molecular weight of 45 000, and a melt-flow index of 1.0 dg $\mathrm{min^{-1}}$ (ASTM D1238, 230°C and 2.16 kg). Functionalized PPs were prepared by the melt grafting of 2-isopropenyl-2-oxazoline (IPO), glycidyl methacrylate (GMA), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl methacrylate (HPMA), dimethylaminoethyl methacrylate (DMAEMA), and t-butylaminoethyl methacrylate (TBAEMA), onto the PP homopolymer. The functionalized PPs were purified and blended with the PP homopolymer in the desired proportions so as to control the amount of functional groups in the PP matrix. The molecular weights of the functionalized PPs were significantly lower than the PP homopolymer, as a result of chain scission which occurred during melt grafting, and had melt-flow indices in the range 15–30 dg $\mathrm{min^{-1}}$. However, the reduction in molecular weight did not present a problem because the grafted PP was only used in limited concentrations in the matrix phase, thus having minimal effects on the impact properties. Values of the degree of grafting for the various functionalized PPs are listed in *Table 1*, with the results obtained by using ^{1}H n.m.r. spectroscopy.

All of the monomers, with the exception of IPO, were reagent grade chemicals, which were obtained from the Aldrich Chemicals Company. The IPO was synthesized in our laboratory by the reaction of 2-ethyl-2-oxazoline with formaldehyde, according to the procedure published elsewhere[13].

The rubber used in these studies was Krynac X7.50 (formerly Krynac 221) nitrile rubber, obtained from the Polysar Company, and is a terpolymer of acrylonitrile/butadiene/acrylic acid (27/66/7). The acrylic acid provides the necessary functionality for reactive blending, with the acrylic acid reactive groups present in a large excess when compared to its coreactive group. The weight-average molecular weight of the rubber was 3.1×10^5 g $\mathrm{mol^{-1}}$.

Melt grafting

The melt grafting of the various monomers onto the PP homopolymer was carried out at 180°C on a Haake Rheomix 600 batch mixer equipped with roller blades, operating at 100 rev $\mathrm{min^{-1}}$ A peroxide initiator, Lupersol 101, which consisted of a 90% solution of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane with a half-life of ~0.6 min at 180°C, was used as received from the Lucidol Division, ATOCHEM North America. In a typical grafting process, 0.24 g of the initiator was mixed with 3.0 g of the monomer and the mixture was added to 44 g of solid PP. The wet mixture was then fed into the preheated Haake mixer and allowed to react for 6 min. The reaction product was removed from the mixer and dissolved in refluxing toluene or *o*-dichlorobenzene at a concentration of ~4% (wt/vol). The solution was precipitated into seven volumes of methanol, filtered, washed, and dried under vacuum at 75°C for 48 h. The purified product was characterized using both *FT*i.r. and n.m.r. spectroscopy. Duplication of the dissolving–precipitating procedure was conducted on small portions of the purified grafted polymers. *FT*i.r. and n.m.r. measurements showed that the percentages of grafting for all of the grafted polymers were not altered after the second purification, when compared to those from a single purification. This indicates that a single purification step is sufficient for the removal of any residual monomers and homopolymers.

Table 1 Degrees of grafting of various functionalized polypropylenes

Monomer	GMA	HEMA	HPMA	TBAEMA	DMAEMA	IPO
Degree of grafting (wt%)	0.8	0.4	1.0	1.0	0.3	0.2

FT*i.r. and n.m.r. measurements*

Thin films 0.1–0.2 mm in thickness) of the purified grafted polypropylenes were compression moulded at 210°C under a pressure of 13.8 MPa for 1 min. *FT*i.r. spectra of these thin films were recorded on a Bomem MB-120 *FT*i.r. spectrometer at room temperature using a resolution of 4 $\mathrm{cm^{-1}}$. Solutions suitable for n.m.r. measurements were prepared by dissolving 20–30 mg of the purified grafted polymers in 0.5 ml of either *o*-dichlorobenzene-d_4 or toluene-d_8 with heating. ^{1}H n.m.r. spectra of the purified grafted polymers were recorded on a Bruker n.m.r. spectrometer (400 MHz), which was equipped with a high temperature probe and a heating device.

Preparation of PP/NBR blends

PP/NBR blends were prepared using the same Haake mixer as used for the grafting process. Throughout this work, the same NBR rubber was used, with the rubber phase content kept constant at 20 wt% in all of the blends, and the same processing conditions were used to prepare all of the PP/NBR blends. The PP homopolymer and a desired amount of a functionalized PP were mixed first in the batch mixer for 2 min at 210°C and 100 rev $\mathrm{min^{-1}}$. The rubber was then added to the mixture and the mixing was continued for a further 4 min. The blend materials were then ground into small pellets in preparation for injection moulding.

Blend morphology

The morphological structures of the blends were studied using scanning electron microscopy (SEM). Samples were fractured under liquid nitrogen and etched at 70°C for 10 min in 1 M chromic acid solution to remove the rubber phase. The etched surfaces were then vacuum coated with gold and examined using a JEOL JSM 840 microscope.

Impact testing

Unnotched impact tests were performed on a Rheometrics RDT-5000 instrumented falling weight impact tester. Disc-shaped specimens with a thickness of 3.2 mm and a diameter of 37 mm were injection moulded at 230°C. The impact tests were carried out at 7.6 m s^{-1} at a temperature of 23°C. A minimum of 25 tests were made for each sample and the mean impact energies were reported.

RESULTS AND DISCUSSION

Functionalization of polypropylene

*FT*i.r. spectra obtained for all of the purified grafted PPs, with the exception of IPO grafted material, showed a new peak at ~1730 cm^{-1}, confirming that the grafting process was successful. For the HEMA and HPMA grafted PPs a broad new peak centred at 3420 cm^{-1} was also present, and was identified as being due to the hydroxy groups. *Figure 1* shows examples of the *FT*i.r. spectra of the GMA, TBAEMA, and HEMA grafted PPs. The grafting was also confirmed using ^1H n.m.r. spectroscopy and *Figure 2* shows the spectrum of the GMA grafted PP as a representative example. The degree of grafting was calculated from the ratio of the integral of the peaks located at approximately 4.05 and 4.35 ppm (assigned for the two hydrogen atoms that are adjacent to the ester oxygen atom) to the integral of the peaks that occur between 0.5 and 1.8 ppm (assigned for the six hydrogen atoms of PP). The result obtained was 0.8 wt% grafting, based on the PP mass. The same procedure was used for determining the degree of grafting for the other five grafted PPs, although the chemical shifts for each monomer graft were different. The degree of grafting of each monomer onto PP (in weight percent) is given in *Table 1*.

It has to be mentioned here that trials have been made by Gallucci and Going[5] on the melt grafting of GMA onto PP by using both dicumyl peroxide and benzoyl peroxide as initiators. However, it was claimed by these authors that GMA cannot be grafted onto PP using the melt grafting process. In this present study, the grafting of GMA, as well as the other five monomers, onto PP is clearly demonstrated by the results obtained from *FT*i.r. and ^1H n.m.r. spectroscopy. In addition, the effectiveness of IPO and GMA grafted PPs in PP/NBR reactive compatibilization studies further confirms that grafting has been realized in molten PP (see below). The contradiction between the results obtained in this study and those reported in the literature may be due to the different initiators that were used.

Blend morphology

The effect of the functionalized PPs in compatibilizing PP/NBR blends was first observed in SEM images. *Figure 3* shows the SEM micrographs of PP/NBR blends with 25 wt% of the different functionalized PPs in the matrix phase. Clearly, there were no significant differences in the morphologies of the blends when HEMA, HPMA, TBAEMA, and DMAEMA functionalized PPs were introduced into the matrix phase (see *Figures 3a–d*). The particle sizes and size distributions are similar to those of the PP/NBR blends which contain no functionalized components (see *Figure 4a*). However, the particle size was greatly reduced and the size distribution became more uniform when 25 wt% of GMA functionalized PP (*Figure 3f*) or IPO functionalized PP (*Figure 3e*) was added to the matrix phase. This indicates, indirectly, that chemical reactions have occurred between the glycidyl or oxazoline groups in the PP matrix with the carboxylic acid functionality in the NBR rubber phase during the blending process. These results are consistent with literature reports of chemical reactions between GMA functionalized polyolefins and small molecules containing carboxylic acid groups[5,14] as well as chemical reactions between oxazoline groups on polystyrene backbones with carboxylic acid groups on polyethylene backbones[15–17]. The effect of the concentration of the GMA functionalized PP on the morphology of the PP/NBR blends is shown in *Figure 4*. The rubber particle size decreased with increasing concentration of the GMA functionalized PP in the PP matrix phase.

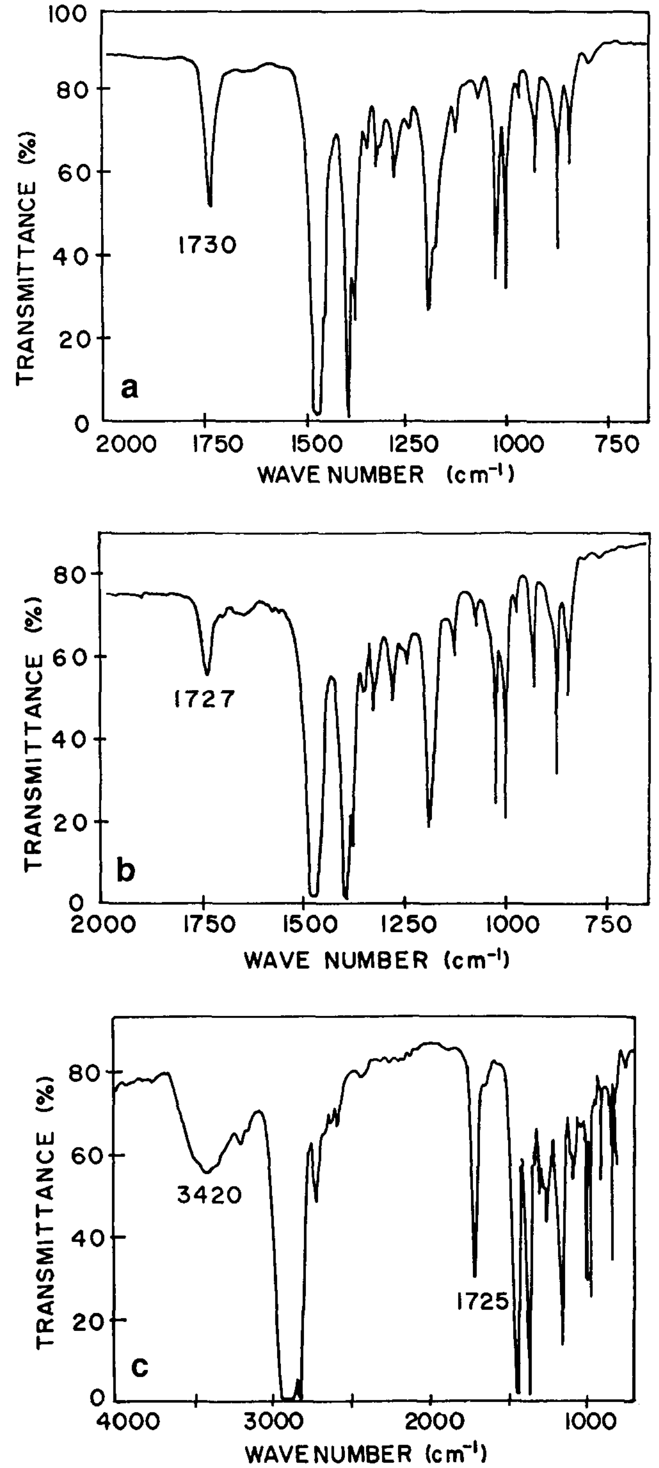

Figure 1 *FT*i.r. spectra of: a, GMA grafted PP; b, TBAEMA grafted PP and; c, HEMA grafted PP

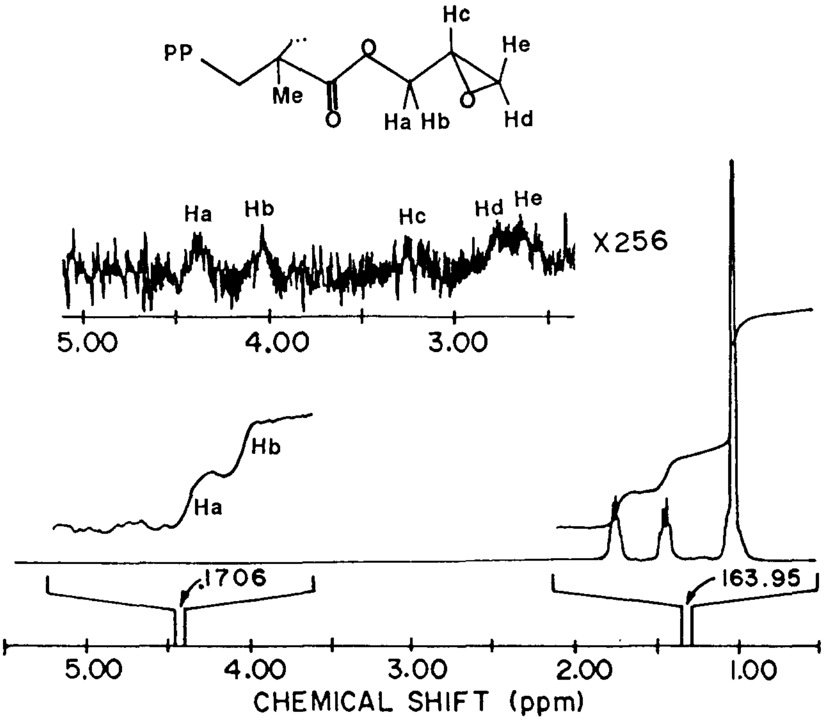

Figure 2 ^{1}H n.m.r. spectrum of GMA grafted PP

Impact properties

Figure 5 shows the effect of the functionalized PPs on the impact energy of the PP/NBR blends. There were minor impact energy improvements in the blends when HEMA and TBAEMA grafted PPs were introduced into the matrix phase. These improvements may be due to possible hydrogen bonding interactions between either the hydroxy group of HEMA or the secondary amine group of TBAEMA with the carboxylic acid group in the NBR rubber phase. The improvements in impact energies decreased slightly with increasing concentration of these functionalized PPs in the PP matrix phase. One likely reason for this is the lower molecular weights of the functionalized PPs. The impact energies of PP/NBR blends having HPMA and DMAEMA grafted PPs in the matrix phase were actually lower than blends without any functionalized component in the matrix phase, indicating that there were no significant interactions between the HPMA or DMAEMA groups with the carboxylic acid groups in the NBR rubber phase. This is due to the fact that the tertiary amine functionality cannot form an amide linkage by reacting with carboxylic acid and the secondary hydroxy group in HPMA is much less active than a primary hydroxy group in esterification reactions. In addition, the hydroxy and amino groups of HPMA and DMAEMA are not strong hydrogen bonding donors or acceptors because of the presence of alkyl substituents. The increase in impact energy observed in the PP/NBR blends containing 25 wt% of DMAEMA functionalized PP in the matrix phase may be a result of potential ionic interactions between the tertiary amino group and the carboxylic acid group at these relatively high concentrations of reactive groups.

The impact energies of PP/NBR blends with GMA or IPO functionalized PPs as compatibilizers were dramatically improved. The PP/NBR blends went through a brittle–ductile transition as the concentration of the functionalized PPs in the matrix phase reached a level of 13 wt% in the case of IPO functionalized PP, and 25 wt% in the case of GMA functionalized PP. Up to a ten-fold improvement in impact energy was observed when the brittle–ductile transition was reached. The transition in the blends containing GMA functionalized PP as compatibilizer did not occur at as low a concentration of compatibilizing copolymer (when compared to the IPO system), and the impact energy showed only a gradual improvement. This may partly be explained by considering the grafting mechanism and the nature of the grafts. Although the degree of grafting of GMA is higher than that of IPO, the number of grafts may not be higher since the length of the grafts could be very different. IPO grafts are believed to be single units because no IPO homopolymer is observed to form during melt grafting[13]. The grafts of GMA could be much longer, however, because this monomer homopolymerizes[5]. Therefore, the number of grafts in GMA grafted PP may actually be lower than in the IPO grafted system. The number of IPO grafts was estimated to be approximately 2.5 per PP chain[18], while the number of GMA grafts per PP chain is likely to be much lower than this. In other words, some PP chains may not have any GMA grafts at all, resulting in a lower efficiency of compatibilization and the more gradual increase in the impact strength towards the brittle–ductile transition point.

The kinetics of these interfacial reactions have not been considered here. All blends were processed only for 4 min and it is possible that some of these functional groups would have led to greater impact improvements if blending were prolonged. In earlier work[15–17], in which poly(styrene-*co*-vinyloxazoline) was blended with poly(ethylene-*co*-acrylic acid), slower reactions were evident than was the case for the IPO in this study. While the systems are different this may indicate the greater reactivity of a grafted pendent functional group, when compared to one that had been copolymerized into the main chain, as has been previously reported by Nagano[19].

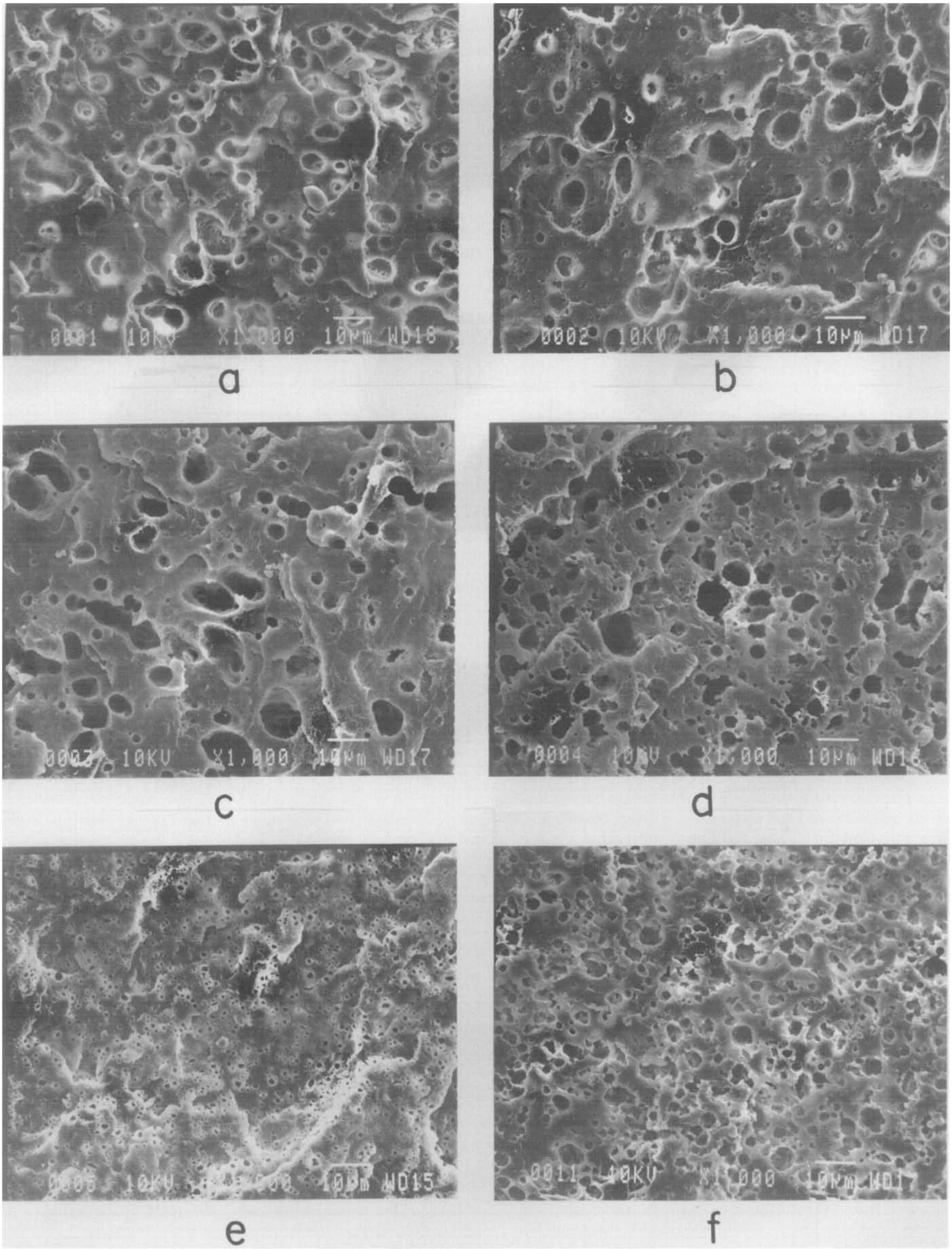

Figure 3 SEM micrographs obtained for PP/NBR blends containing 25 wt% of different functionalized PP in the matrix: a, HPMA; b, HEMA; c, TBAEMA; d, DMAEMA; e, IPO and; f, GMA

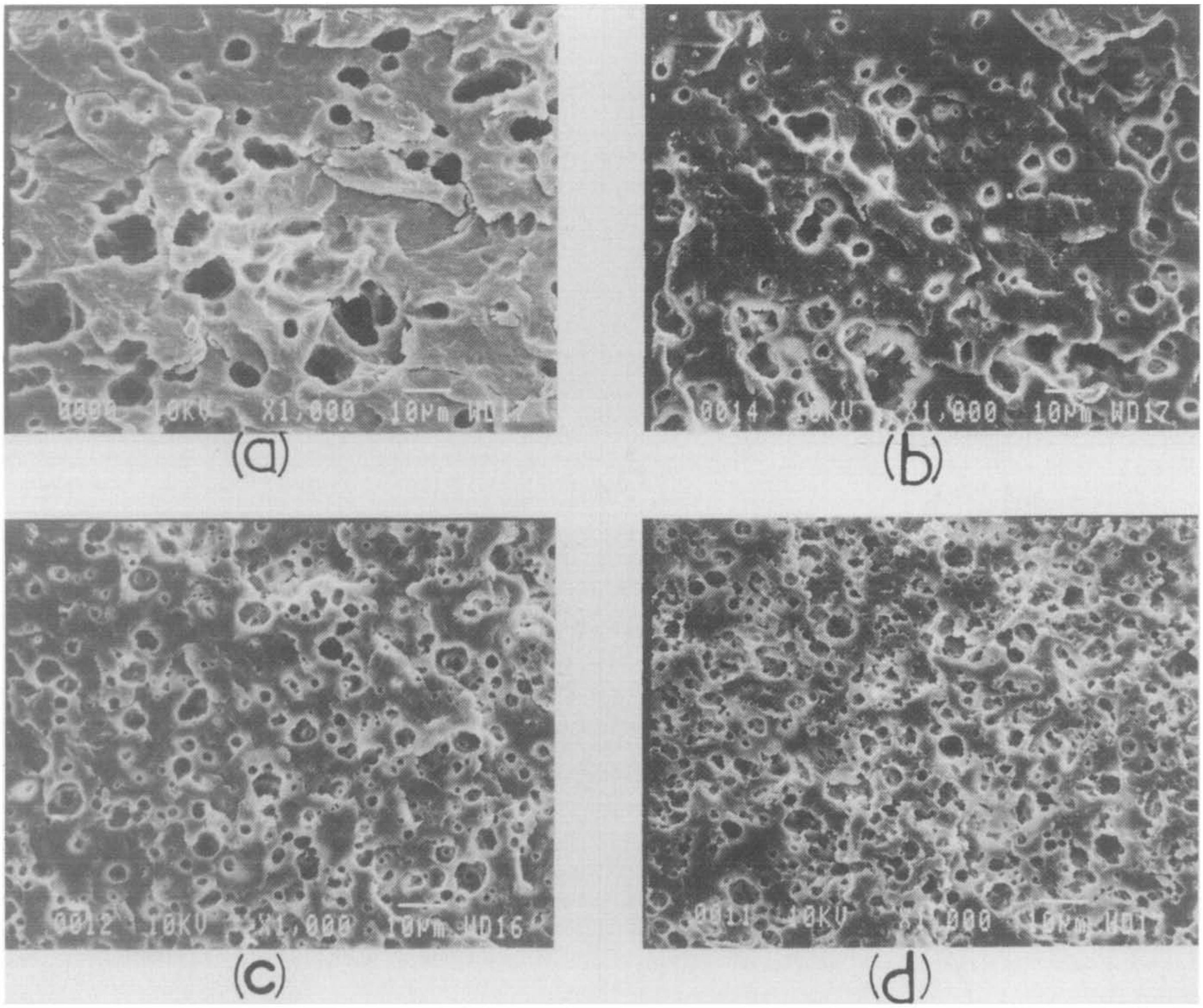

Figure 4 SEM micrographs obtained for PP/NBR blends containing different concentrations of GMA functionalized PP in the matrix: a, 0 wt%; b, 2 wt%; c, 13 wt% and; d, 25 wt%

The effects of the functionalized PPs as compatibilizers on the maximum loads of PP/NBR blends were very similar to those observed for the impact energies. No significant improvements were observed in PP/NBR blends containing HEMA, HPMA, TBAEMA, and DMAEMA functionalized PPs in the PP matrix phase, while the maximum loads borne by the PP/NBR blends increased by up to three-fold when GMA or IPO functionalized PPs were introduced into the PP matrix phase (see *Figure 6*).

Modes of impact failure

Figure 7 shows the typical force–displacement impact curves, obtained using the instrumented impact tester, for PP and PP/NBR blends with various amounts of GMA grafted PP in the PP matrix. The maximum loads for both pure PP and the nonreactive PP/NBR blend and their total displacements were small. The force decreased rapidly after the maximum force was reached, indicating brittle failure. As GMA grafted PP (13 wt%) was introduced into the PP matrix phase the maximum load and total displacement were significantly improved. However, the force dropped quickly to zero after the maximum force was reached, again indicating brittle failure. Only when 25 wt% of GMA grafted PP was added to the PP matrix phase did the blend then become ductile, with the force decreasing slowly in a stable manner after the maximum force was achieved, while at the same time the total displacement increased significantly. It is believed that the progressively higher maximum loads observed with the more effective addition of rubber do not indicate higher true yield strengths, but rather indicate that at the relatively high speed of this impact test the brittle materials shatter before absorbing the full load associated with their true yield strength.

Visual examinations of the impacted samples showed that there was no significant stress-whitening in the nonreactive blends and only a slight stress-whitening in the reactive blends below the brittle–ductile transition. For reactive blends above this transition, stress-whitening of the whole fractured surface was observed. It is believed[20] that in toughened pseudoductile polymers stress-whitening is mainly caused by cavitation of the rubber particles.

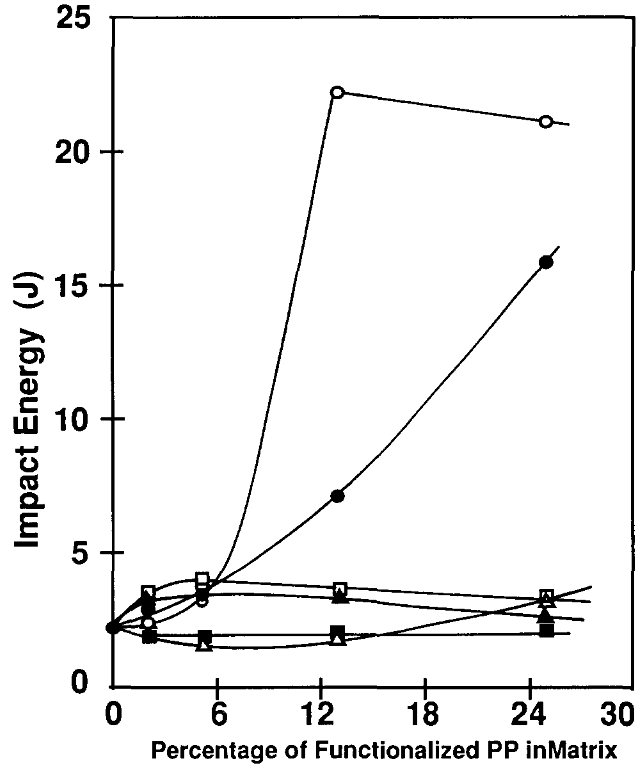

Figure 5 Effects of different functionalized PPs on the impact energy of PP/NBR blends: ■, HPMA; ●, GMA; ▲, TBAEMA; □, HEMA; ○, IPO and; △, DMAEMA

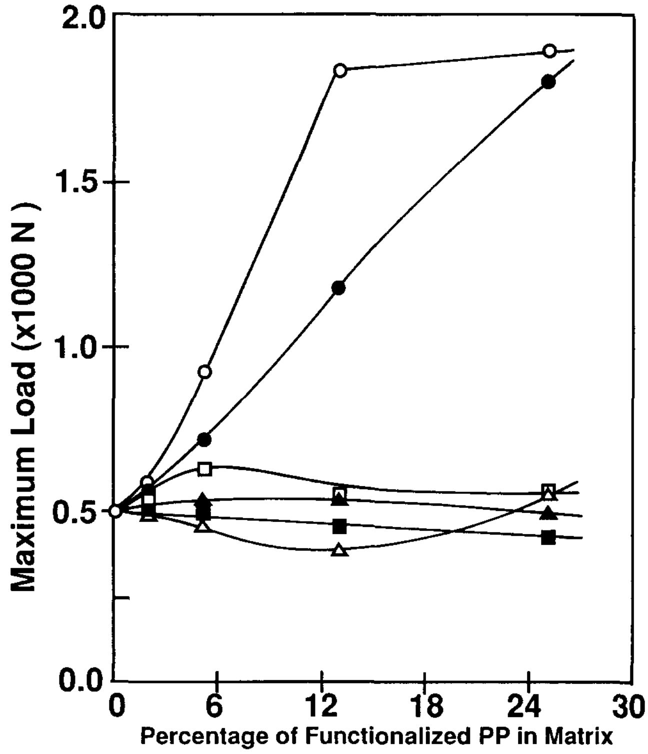

Figure 6 Effects of different functionalized PPs on the maximum load of PP/NBR blends: ■, HPMA; ●, GMA; ▲, TBAEMA; □, HEMA; ○, IPO and; △, DMAEMA

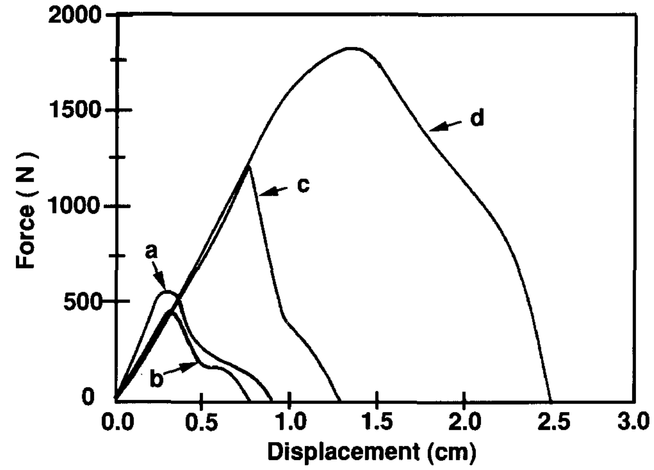

Figure 7 Force–displacement curves of: a, PP; b, nonreactive PP/NBR blend; c, reactive blend containing 13 wt% GMA functionalized PP and; d, reactive blend containing 25 wt% GMA functionalized PP

Comparison with amine functionalized polyethylenes

Due to the low toxicity[21] and potential high reactivity of vinyl monomers containing amine functionalities, the research in this laboratory has been focused for the last five years on the melt grafting of DMAEMA and TBAEMA onto polyethylene and reactive processing studies using such amine functionalized polyolefins[22–25]. The reactive compatibilization of polystyrene having maleic anhydride functionality (PS–MA) and linear low-density polyethylene with melt grafted amino groups (PE–A) has been mostly investigated[22–25]. SEM observations constantly showed significant improvement in the morphology of these reactive blends (PS–MA/PE–A), relative to that of the nonreactive blends. However, the reactive blends only demonstrated a moderate improvement in impact and tensile strengths (up to 50%), when compared to the nonreactive blends. The absence of any major improvement in the mechanical properties of the PS–MA/PE–A reactive blend system may be due to the lack of interlocked phase morphology that is also required, in addition to strong interfacial adhesion, for PS toughening with PE[26].

In a recent study[25] using TBAEMA grafted PE in PMMA/PE reactive compatibilization, the PMMA phase contained 10 wt% emulsion copolymerized methacrylic acid. Up to a six-fold increase in impact strength was observed for the reactive blends, when compared to the nonreactive blends. However, either a high reaction temperature (230°C) or a prolonged processing time (10–30 min) was necessary to achieve any high mechanical-property improvement. Furthermore, the major changes observed in this system were for proportions where the dispersed phase was the brittle PMMA. These observations suggest that the reactions between the carboxylic acid and the secondary amine functionalities are probably very slow. This present work does not show any major improvements in the impact properties of PP/NBR reactive blends when using TBAEMA functionalized PP, which may be due to the low reaction temperature and short processing time that was employed. More extensive investigations are required in order to draw a definitive conclusion on the effectiveness of TBAEMA grafted polymers in reactive compatibilization of polymer blends.

CONCLUSIONS

1. GMA, HEMA, HPMA, DMAEMA, TBAEMA, and IPO have been successfully grafted onto PP in the melt, with the degrees of grafting ranging from 0.2 wt% for IPO to 1.0 wt% for TBAEMA and HPMA.

2. IPO and GMA grafted PPs were effective compatibilizers for PP/NBR blends. Up to a ten-fold increase in impact energy was observed, with the toughened blends going through a brittle–ductile transition at relatively low concentrations of functionalized PPs in the matrix phase.
3. HEMA, HPMA, DMAEMA, and TBAEMA grafted PPs were not effective in compatibilizing PP/NBR blends under the processing conditions employed (210°C) when using carboxylic acid as the complementary reactive group in the rubber phase.

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