Compatibilisation of polypropylene and poly(butylene terephthalate) blends by reactive extrusion: effects of the molecular structure of a reactive compatibiliser

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This paper reports on the relative role of the functional group content and the molecular weight of a glycidyl methacrylate (GMA) functionalised PP (PP-g-GMA) as reactive compatibiliser in the compatibilisation of polypropylene (PP) and poly(butylene terephthalate) (PBT) immiscible blends in a co-rotating twin screw extruder. Two series of PP-g-GMA were compared in terms of their compatibilising effects on the morphology and mechanical properties (elongation at break and impact strength) of the blend. The first series of PP-g-GMA had the same molecular weight but different GMA contents while the second series of PP-g-GMA had the same GMA content but different molecular weights. The compatibilising effects of the first series of PP-g-GMA were dictated primarily by the amount of GMA in the blend, i.e., two PP-g-GMA having different GMA contents had the same compatibilising efficiency when the amount of GMA in the blend was the same. For the second series of PP-g-GMA, the higher the molecular weight, the higher the compatibilising efficiency. © *2000 Kluwer Academic Publishers*

1. Introduction

Blending existing polymers has become an important route to obtaining new materials. However, for thermodynamic reasons most polymer pairs are immiscible and their blends are phase separated. They often need to be compatibilised in order to have potentially useful properties. Traditionally, compatibilisation consists of adding a block or a graft copolymer with blocks or grafts identical to or miscible with the base polymers of the blend. Such a copolymer, called a compatibiliser, is preferably located at the interfaces, allowing to reduce the interfacial tension, help the dispersion of the minor phase in the matrix, enhance the interfacial adhesion and stabilise the morphology. A major drawback of this *ex-situ* compatibilisation method is that each polymer blend requires a specific copolymer, whose preparation is often tedious and costly. Also, for dynamic and thermodynamic reasons, there are always some copolymer chains which can not get to the interfaces where they are most needed. Dispersion of the copolymer in a polymer matrix is not always easy and its diffusion to the interfaces is often slow. The copolymer may also form micelles useless for compatibilisation.

Another compatibilisation method is to produce desired copolymers through interfacial reactions between reactive polymers directly during blending. This in-situ or reactive compatibilisation method is more attractive and cost-effective because it allows to produce compatibilisers in-situ at the interfaces without separate preparation step. When two polymers are to be compatibilised and only one contains functional groups and the other one is chemically inert with respect to it, the latter will have to be functionalised. A typical example is the reactive compatibilisation of polypropylene and poly(butylene terephthalate) (PP/PBT) blends [1–4]. PBT usually contains two types of terminal functional groups: carboxylic and hydroxyl. Compatibilisation can be achieved by functionalising the PP with glycidyl methacrylate (GMA), PP-g-GMA, or with an oxazoline, PP-g-OXA. The epoxy or oxazoline groups attached onto the PP backbone can then readily react with the terminal carboxyl group of the PBT leading to a graft copolymer. PP-g-GMA and PP-g-OXA can be prepared by free radically grafting GMA and an oxazoline bearing vinyl monomer onto PP in a screw extruder [4–8]. This approach has also gained a great success for the in situ compatibilisation of polypropylene and polyamide (PP/PA-6) blends. In this case, a maleic anhydride (MA) modified PP is often used as a reactive compatibiliser and is prepared by free radical grafting of MA onto PP [9–11].

Although reactive compatibilisation has found widespread use, few studies are concerned with the relative role of the functional monomer content and the molecular weight of reactive compatibilisers. In the literature [12–15], when a functionalised PP was used as a reactive compatibiliser, variation in functional monomer content was always accompanied by a change in molecular weight. In some cases, variation in functional monomer content was achieved by diluting a highly functionalised PP with an inert PP. This is because controlling both the molecular weight and the functional monomer content of the reactive PP is difficult in a classical free radical grafting process. An increase in functional monomer content is often concomitant with a decrease in molecular weight; conversely, an increase in molecular weight is often accompanied by a decrease in functional monomer content. Another difficulty with functionalised polyolefins is that their molecular weights have to be measured with high temperature size exclusion chromatography, to which few university laboratories have access.

Recently, considerable progresses have been made in the free radical grafting of vinyl monomers onto PP. A so-called co-monomer concept [5, 6, 8, 16, 17] has shown to allow to control both the molecular weight and functional monomer content in an independent manner. Basically, this concept is to add a second monomer (or co-monomer) to promote the free radical grafting of the grafting monomer. Styrene has been found to be most effective.

The aim of this work was to investigate the separate effects of the GMA content and the molecular weight of PP-g-GMA on the compatibilisation of PP/PBT blends. For that purpose, two series of PP-g-GMA were prepared. The first series of PP-g-GMA had the same molecular weight but different GMA contents. The GMA content was expressed as the amount of grafted GMA per 100 grams PP resin (phr). The second series of PP-g-GMA had the same GMA content but different molecular weights. Their compatibilisation efficiency was evaluated in terms of morphology and mechanical properties.

2. Experimental
2.1. Materials
The polypropylene (PP) used in this study was a commercial grade of Montell (Valtec CL101D). It was in the form of porous pellets capable of absorbing large amounts of liquid reagents. Its melting point and melt flow index were 165°C and 0.3 g/10 min (ASTM 1238L 230°C and 2.16 kg), respectively. Its number and weight average molecular weights were 141 and 654 kg/mole, respectively. The poly(butylene terephthalate) (PBT) used was a commercial grade of DSM (Arnite T08200) having a melting point of 223°C. Its number and weight average molecular weights were 28 and 65 kg/mole, respectively. The concentrations of the terminal hydroxyl and carboxyl groups were 0.032 and 0.040 eq/kg, respectively. The viscosity of the PP and PBT as a function of shear rate at 240°C is shown in Fig. 1. The viscosity ratio between the PP and PBT was close to unity at a shear rate of 100 to 200 s^{-1} typical
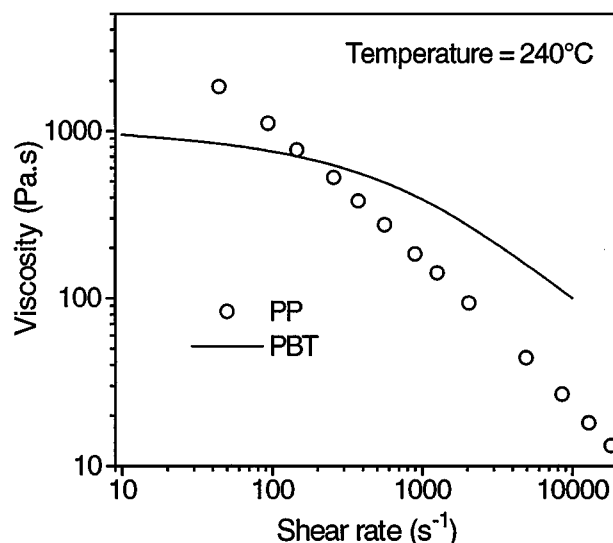

Figure 1 Viscosity as a function of shear rate for the PP and PBT at 240°C.

of a reactive extrusion process. Glycidyl methacrylate (GMA) and styrene (St) necessary for the functionalisation of the PP were purchased from Aldrich and used without further purification. 2,5-Dimethyl-2,5-di(tert-butylperoxy)-hexane (DHBP) was used as free radical initiator. According to the supplier (Akzo France), its half lifetime was about 6 seconds at 200°C.

2.2. Synthesis of PP-g-GMA
Various PP-g-GMA were synthesised in a Werner Pfleiderer ZSK-30 co-rotating self-wiping twin screw extruder. The extruder had a screw diameter of 30.7 mm with an axial distance of 26.2 mm. The screw length-to-diameter ratio (L/D) was 42. Fig. 2 shows the screw profile and set barrel temperature used.

Two series of PP-g-GMA were prepared: the first series had the same molecular weight but different GMA contents, i.e., different numbers of GMA moieties per PP chain and the second series had the same grafted GMA content but different molecular weights. The grafting experiments were done under nitrogen. The barrel temperature was set at 200°C over the entire screw length. The screw speed and the total feed rate of the polymers were always 150 turns per minutes (rpm) and 5 kg/h, respectively. Non-reacted GMA and other volatile products were removed through a venting port using a vacuum pump. Removal of the residual GMA was very important because its presence could affect adversely the compatibilising efficiency of the PP-g-GMA [1]. The grafted GMA content and molecular weight of the PP-g-GMA were determined by Fourier transform infrared spectroscopy and high temperature size exclusion chromatography, respectively. Details about the synthesis and characterisation of the PP-g-GMA can be found elsewhere [5, 7, 8, 16]. Table I shows the recipes employed for the preparation of those two series of PP-g-GMA and some of their characteristics. As can be seen, the control over both the GMA content and the molecular weight of PP-g-GMA was very satisfactory. This is also confirmed by the viscosity

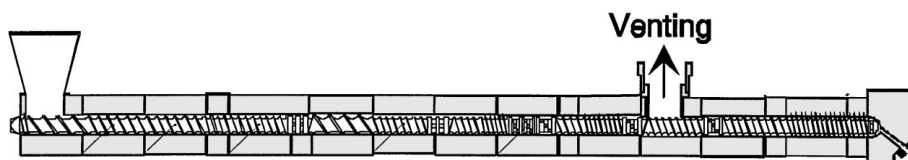|	Code	[GMA]$_i$/[St]$_i$/[DHBP]$_i$ (phr)	[GMA]$_g$ (phr)	$\bar{M}_n$, $\bar{M}_w$ (kg/mole)	n
	PP	0/0/0	0	141, 654	0
1° series	CPP1	5.0/1.0/0.1	1.20 ± 0.15	101 ± 5, 370 ± 10	8
	CPP2	3.0/1.0/0.3	0.60 ± 0.05	103 ± 5, 408 ± 10	4.2
	CPP3	1.0/1.0/0.2	0.20 ± 0.02	105 ± 5, 380 ± 10	1.5
2° series	MPP1	5.0/1.0/0.1	0.60 ± 0.05	130 ± 5, 570 ± 10	5.5
	MPP2	3.0/1.0/0.3	0.60 ± 0.04	108 ± 5, 408 ± 10	4.5
	MPP3	1.5/1.0/0.7	0.60 ± 0.05	70 ± 3, 198 ± 5	3.0

Figure 2 A schematic representation of the co-rotating twin screw extruder (Werner Pfleiderer ZSK 30) used for the synthesis of PP-g-GMA by free radical grafting. Details of the screw profile: 14/14(1)+42/42(2)+28/28(6)+20/20(6)+KB90/5/28(1)+L20/10(1)+42/42(2)+ 20/20(4)+KB90/5/28(1)+L20/10(1)+20/20(2)+14/14(3)+KB45/5/20(2)+KB45/5/28(1)+20/20(2)+14/14(1)+KB45/5/28(1)+L20/10(1)+ 42/42(1)+20/20(2)+KB45/5/28(1)+20/20(4)+14/14(9). The numbers in the parentheses are the numbers of the same type of screw element. X/Y: right handed conveying elements of Y mm long with a screw lead of X mm; KB$X/Y/Z$: kneading blocks; each is Z mm long and contains Y discs which are assembled together X degrees one with respect to the other. This type of screw element is good at mixing. LX/Y: a left-handed screw element which is Y mm long having a screw lead of X mm. This type of screw element generates a negative pressure and often follows up a KB as melt seal.
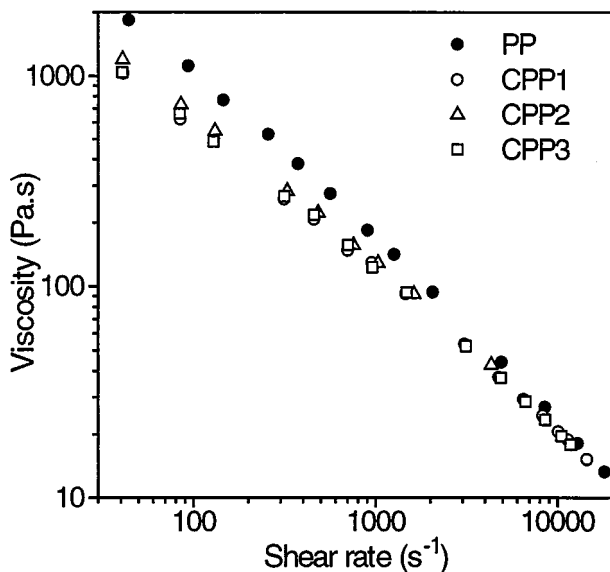

Figure 3 Viscosity as a function of shear rate for the first series of PP-g-GMA whose GMA contents are different but whose number and weight average molecular weight are very close (around 103 000 and 390 000 g/mole, respectively; see Table I). (●) PP, (○) CPP1, (△) CPP2, (□) CPP3. As expected, the three PP-g-GMA have similar viscosities.
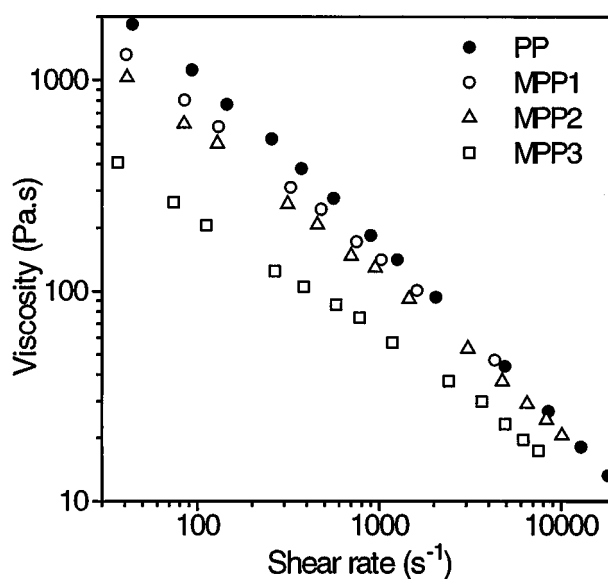

Figure 4 Viscosity as a function of shear rate for the second series of PP-g-GMA whose molecular weights are different but whose GMA contents are almost the same (0.6 phr; see Table I). (●) PP, (○) MPP1, (△) MPP2, (□) MPP3. As expected, the three PP-g-GMA have different viscosities.

data (see Figs 3 and 4). As expected, the viscosity of the first series (CPP1, CPP2 and CPP3) was almost the same while that of the second series followed the order: MPP1 > MPP2 > MPP3.

2.3. Preparation of PP/PBT blends

In this work, the composition of the PP/PBT blends was always 80/20 by weight, unless specified otherwise. The extruder and screw profile used for making the blends were the same as those for the free radical grafting of GMA onto the PP. Unless stated otherwise,

the feed rate and screw rotation speed were 5 kg/h and 150 rpm, respectively. The set barrel temperature was 240°C (see Fig. 2). Prior to blending, the PP and PP-g-GMA pellets were dried at 80°C under a hot air circulation overnight in order to remove the moisture and residual GMA in the PP-g-GMA. The PBT was subjected to similar treatment at 105°C.

2.4. Mechanical characterisation
Tensile and impact tests were carried out on the PP/PBT blends to evaluate the compatibilisation performance of the PP-g-GMA. The tensile test (ASTM 638-71A) allowed to measure the Young's modulus (E), yield strength (σ_y), strength at break (σ_b) and elongation at break (ε_b) of the blends while the impact test (ISO 6603/2) gave their impact strength. The specimens for both tests were obtained with an injection-moulding machine of type Billon 50. All zones of the injector were at 240°C and the mould was at 60°C. Prior to injection-moulding, the pellets of the blends were dried at 105°C under a hot air circulation overnight. Before tensile and impact testing, the specimens were stored at room temperature for at least three days.

The tensile test was carried out with a hydraulic testing machine of type Instron 8031 at room temperature. The tensile rate was 50 mm/min, unless specified otherwise. Five specimens were tested for each blend and their values were number-averaged to represent the blend without any data elimination. In cases where some of the five specimens did not break within the span of the machine (260%), additional specimens were tested till the number of broken specimens was five. The impact test was done at 23, 0 and −20°C, respectively, with a Rosand falling weight impact tester (IFWI-5). The inner diameter of the support was 40 mm, that of the hemispherical striker 10 mm. The striker weighed 25 kg. The diameter and thickness of the specimens were 50 and 3 mm, respectively. At least five specimens were used for impact test. Some mechanical properties of the two series of PP-g-GMA are shown in Table II. All PP-g-GMA had similar mechanical properties, except for MPP1 whose mechanical properties were better than those of the other PP-g-GMA and were close to those of the initial PP. This is because the molecular weights of all PP-g-GMA were smaller than that of the PP except for MPP1 whose molecular weight was close to that of the PP (see Table I).

2.5. Morphology characterisation
Morphology of some specimens used for the tensile testing was visualised with a scanning electron microscope (SEM) of type Cambridge Stereoscan 120. Because the PBT particles in most compatibilised blends were about 1 μm, the surfaces of cryofractured specimens was subjected to dichloroacetic acid treatment at room temperature overnight under mild stirring to remove the PBT phase. The solvent etching allowed to have good visualisation. A semi-automatic digital image analysis technique was used for determining the dispersed phase domain size from SEM photographs using NIH Image software. The particle size was characterised by two quantities: number and weight average particle diameters, d_n and d_w, which are defined below:

$$d_n = \frac{\sum n_i d_i}{\sum n_i}$$

$$d_w = \frac{\sum n_i d_i^2}{\sum n_i d_i}$$

At least 200 particles were counted in order that the values of d_n and d_w were statistically meaningful.

3. Results
3.1. Influence of the GMA content in PP-g-GMA
In order to examine the compatibilising performance of different PP-g-GMA having the same molecular weight but different grafted GMA contents for the PP+PP-g-GMA/PBT (80/20) blend, various blends were made using CPP1, CPP2 or CPP3 as reactive compatibiliser. The amount of the PP-g-GMA varied between 0 and 60 wt.% with respect to the total blend (PP+PP-g-GMA+PBT). Keep in mind that in a compatibilised PP/PBT blend, the PP phase was actually made of the PP and PP-g-GMA, the sum of the two being always 80 wt.% of the total blend.

Fig. 5 shows the compatibilising performance of the above three PP-g-GMA in terms of elongation at break at two tensile testing speeds: 50 (Fig. 5a) and 150 mm/min (Fig. 5b). For all three PP-g-GMA, the elongation at break of the PP/PBT blend increased with increasing amount of PP-g-GMA. Moreover, the higher the GMA content in the PP-g-GMA, the steeper the slope of increase. For example, when 30 wt.% PP-g-GMA was present in the blend, the elongation

TABLE II Selected mechanical properties of the two series of PP-g-GMA used in this study (CPP1, CPP2, CPP3; MPP1, MPP2 and MPP3). E: Young's modulus, σ_y: yield stress, σ_b: stress at break, e_b: elongation at break. "NB" stands for "not broken" within the span of the machine (260%)

Material	E (MPa)	σ_y (MPa)	σ_b (MPa)	e_b (%)	Impact (J) at 0°C
PP	1190 ± 10	27.2 ± 0.7	24.2 ± 0.1	NB	24 ± 1.7
CPP1	980 ± 11	21.7 ± 0.2	18.8 ± 0.1	NB	23 ± 2.1
CPP2	1002 ± 10	20.8 ± 0.3	17.6 ± 0.1	NB	25 ± 3.4
CPP3	1010 ± 12	20.9 ± 0.4	17.4 ± 0.1	NB	25 ± 1.8
MPP1	1180 ± 16	27.0 ± 0.3	24.2 ± 0.1	NB	21 ± 3.2
MPP2	1002 ± 16	20.8 ± 0.1	17.6 ± 0.1	NB	23 ± 1.4
MPP3	1072 ± 5	23.2 ± 0.2	15.7 ± 0.1	NB	19 ± 3.2
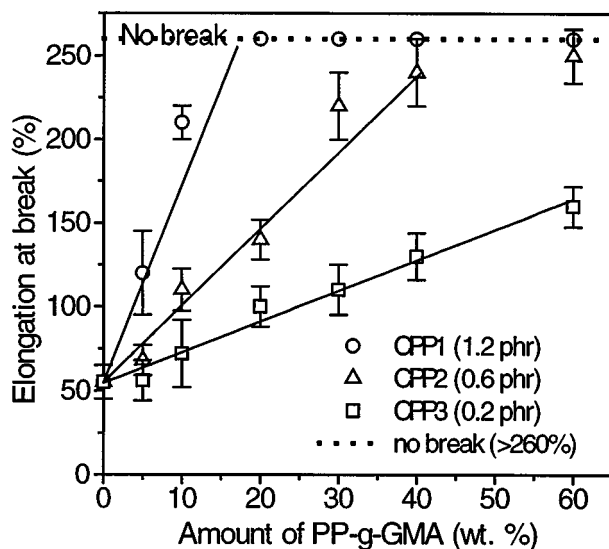
(a)
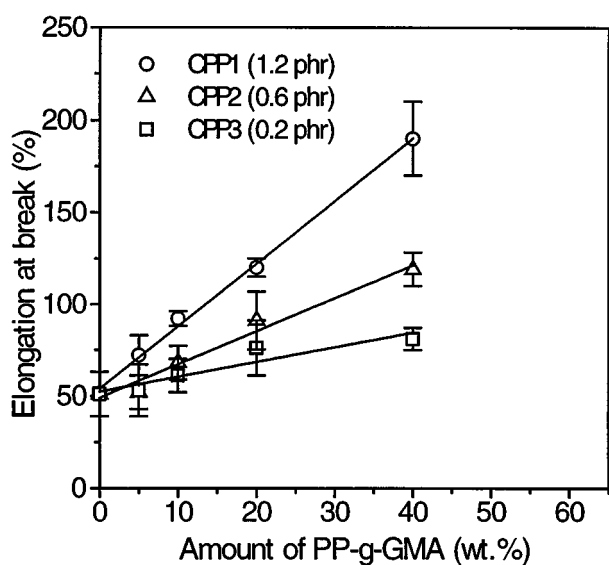
(b)

Figure 5 Elongation at break of the PP+PP-g-GMA/PBT (80/20) blend as a function of the amount of PP-g-GMA. (a) tensile testing speed = 50 mm/min, (b) tensile testing speed = 150 mm/min. (○) CPP1 (1.2 phr), (△) CPP2 (0.6 phr), (□) CPP3 (0.2 phr). Solid lines: linear relationship between the elongation at break and the amount of PP-g-GMA.
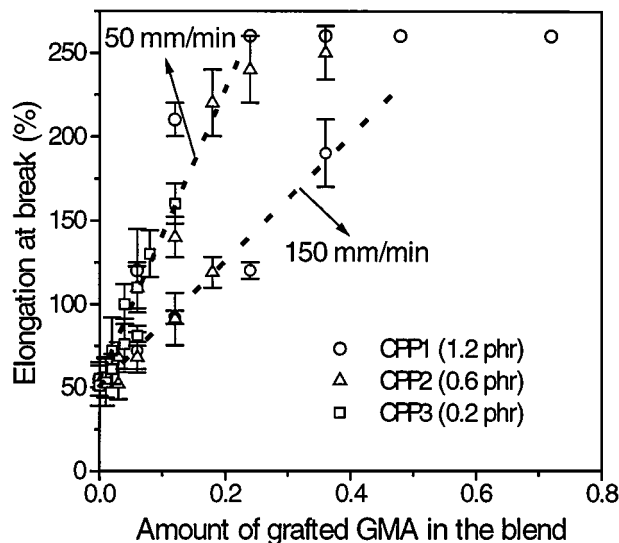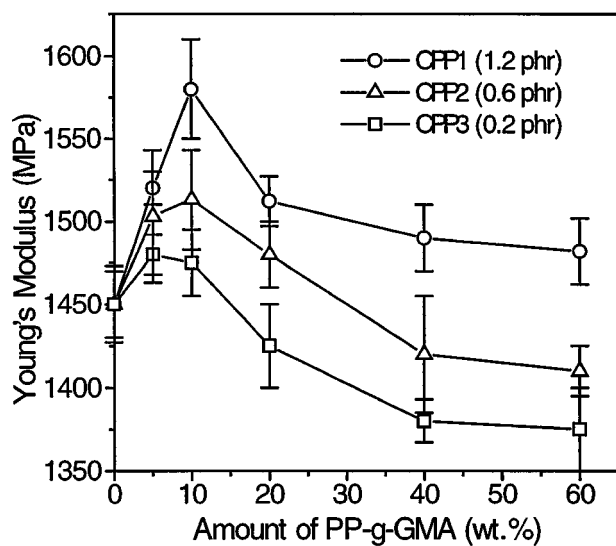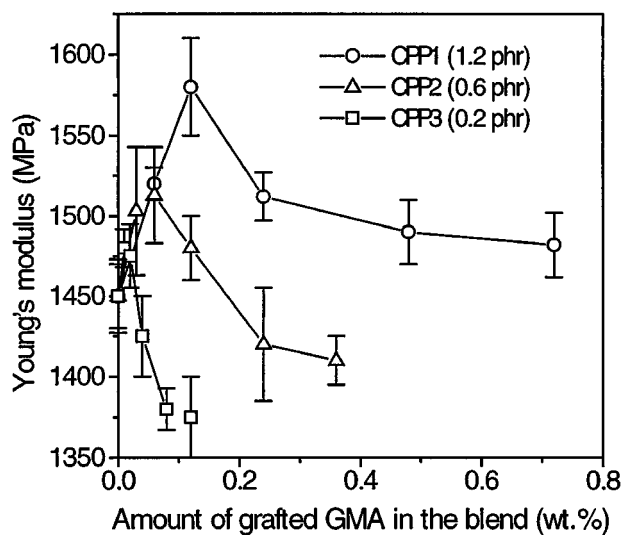

Figure 6 Elongation at break of the PP+PP-g-GMA/PBT (80/20) blend as a function of the amount of GMA in the blend. (a) tensile testing speed = 50 mm/min, (b) tensile testing speed = 150 mm/min. (○) CPP1 (1.2 phr), (△) CPP2 (0.6 phr), (□) CPP3 (0.2 phr). Dashed lines: linear relationship between the elongation at break and the amount of GMA in the blend.

at break of the blend at 50 mm/min was about 100% for CPP3, 200% for CPP2 and more than 260% for CPP1. In the latter case, the specimens did not break within the span of the tensile machine (260%). It is also interesting to note that whatever the tensile testing speed (50 or 150 mm/min), there seemed to be a linear relationship between the elongation at break and the amount of PP-g-GMA in the blend for the three PP-g-GMA, provided that the elongation at break was below 260%. These results show that when the molecular weight of PP-g-GMA is fixed, the elongation at break of the PP/PBT (80/20) blend was determined by the GMA content in the PP-g-GMA. In fact, it is the amount of GMA in the blend that dictated the elongation at break of the blend. This is illustrated in Fig. 6 in which the data of the elongation at break of the PP/PBT blend in Fig. 5 are plotted against the amount of GMA in the blend. All data points in Fig. 5a and b fall on

two single lines, corresponding to two different tensile speeds (50 and 150 mm/min), respectively. Similar results were obtained for compatibilised PP/PBT (70/30) blends.

Fig. 7a shows the effect of adding a PP-g-GMA on the Young's modulus of the PP/PBT (80/20) blend. Over the entire concentration range in PP-g-GMA from 0 to 60 wt.%, the smaller the GMA content in the PP-g-GMA, the lower Young's modulus of the PP/PBT blend. The latter followed the order: CPP1 (1.2 phr) > CPP2 (0.6 phr) > CPP3 (0.2 phr). This can be explained by the fact that on the basis of an equal amount of GMA in the blend, the higher the GMA content in the PP-g-GMA, the higher the amount of copolymer between the PP-g-GMA and the PBT was expected to be. The contribution of the interphase between the PP and PBT to the overall Young's modulus would become non-negligible. For all three PP-g-GMA, the Young's modulus of the compatibilised PP/PBT blend first increased with increasing amount of PP-g-GMA and then decreased slightly. The increase in Young's modulus was likely related to the molecular weight build-up in the interphase between the PP and PBT. The subsequent decrease in Young's modulus was probably due to the fact that the values of Young's modulus of the PP-g-GMA were smaller than that of the inert PP (see Table II). When the amount of PP-g-GMA reached a certain threshold with respect to that of the inert PP, the magnitude of decrease in the Young's modulus of the PP phase caused by an increase in the amount of PP-g-GMA would no longer be compensated for by the gain resuting from the copolymer formation in the interphase between the PP and PBT. This is better illustrated in Fig. 7b, in which Young's modulus is plotted against the amount of GMA in the blend. On the basis of an equal amount of GMA in the blend, the values of Young's modulus differed greatly between CPP1, CPP2 and CPP3. This is because in order for two PP-g-GMA to furnish the same amount of
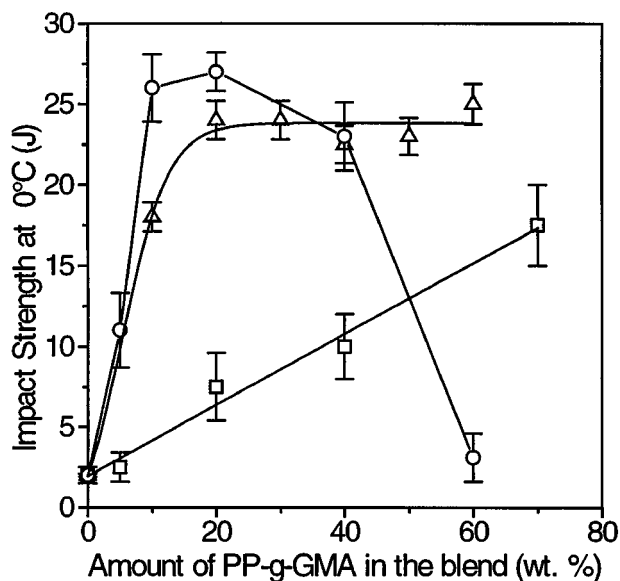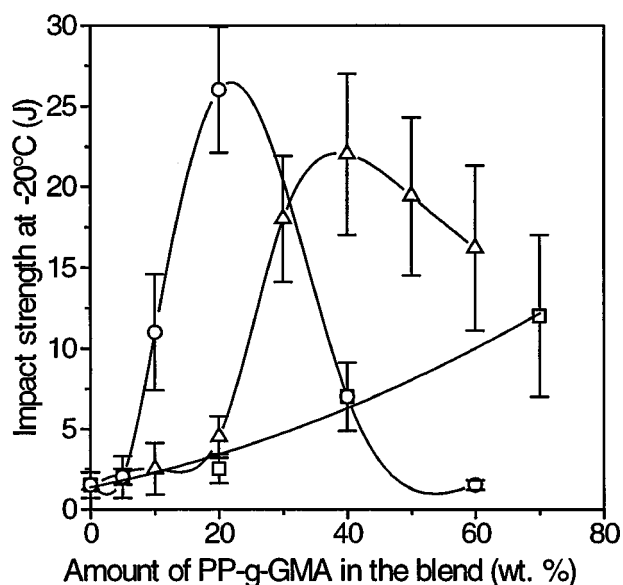
Figure 7 Young's modulus of the PP+PP-g-GMA/PBT (80/20) blend as a function of the amount of PP-g-GMA (a) and that of GMA in the blend (b). Tensile testing speed = 50 mm/min. (○) CPP1 (1.2 phr), (△) CPP2 (0.6 phr), (□) CPP3 (0.2 phr).

Figure 8 Impact strength of the PP+PP-g-GMA/PBT (80/20) blend as a function of the amount of PP-g-GMA in the blend. (a) testing temperature = 0°C; (b) testing temperature = −20°C. (○) CPP1 (1.2 phr), (△) CPP2 (0.6 phr), (□) CPP3 (0.2 phr).

GMA to the blend, the one having a GMA content twice as high as the second one needs only half the amount of the second one. Modulus of semi-crystalline polymers like PP and PBT is very sensitive to changes in crystallinity. In this study, attempts were made to correlate the trend of the Young's modulus with the crystallinity data of the PP or PBT in the PP/PBT blend and failed.

Fig. 8a shows the impact strength of the PP+PP-g-GMA/PBT (80/20) blend at 0°C as a function of the amount of PP-g-GMA for CPP1, CPP2 and CPP3. The results at −20°C are shown in Fig. 8b. For CPP3 whose GMA content was the lowest (0.2 phr), the impact strength of the blend at 0°C increased with increasing amount of PP-g-GMA from 0 to 60 wt.%. In the case of CPP2 (0.6 phr), the impact strength of the blend first increased with increasing amount of CPP2 and then levelled off at a value of about 25 J. As for CPP1 whose GMA content was the highest (1.2 phr), the impact strength of the PP/PBT blend first increased sharply with increasing amount of CPP1, reaching a

maximum of about 27 J, and then decreased with a further increase in the amount of CPP1. Similar results were obtained for the tests done at −20°C, except that the data were more scattered. For both test temperatures, the higher the GMA content in the PP-g-GMA, the faster the increase in the impact strength of the PP+PP-g-GMA/PBT blend. In other words, for the PP+PP-g-GMA/PBT blend to have the same impact strength, smaller amounts were needed for a PP-g-GMA with a higher GMA content. However, when both the GMA content and the amount of PP-g-GMA were high, the PP/PBT blend became brittle. The reason for this has not been fully identified at this point. One possible explanation would be that the higher the GMA content in the PP-g-GMA, the higher the number of the epoxy functionality per PP-g-GMA chain, and the greater the number of the PBT grafts per PP chain in the

graft copolymer. When the amount of the graft copolymer and the number of the PBT grafts per PP chain exceeded certain critical values, the graft copolymer might have formed micelles near the interfaces which could have weaken the interfaces. A more likely explanation is that crosslinking might have taken place between the PP-g- GMA and the PBT under those conditions. Some of the PBT chains inherently contain two carboxylic groups at their chain ends, especially for the PBT used in this study whose carboxylic concentration (0.040 eq./kg) was higher than its hydroxyl concentration (0.032 eq./kg). Both carboxylic and hydroxyl groups could have reacted with an epoxy group, the former being more reactive (ten to twenty times). Crosslinking would occur when both terminal groups of the PBT chains reacted with the GMA grafted PP chains. The degree of crosslinking was expected to increase with increasing number of grafted GMA moieties per PP-g-GMA chain. This is in line with previous studies [2].

The above results indicate that the amount of PP-g-GMA had a marked effect on the impact strength of the PP+PP-g-GMA/PBT blends. This is further confirmed by Fig. 9a and b in which the data in Fig. 8a and b are now plotted as a function of the amount of GMA in the blend. All data points obtained at 0 and −20°C fall on two single bell-shaped curves. The impact strength first increased rapidly with increasing amount of GMA in the blend, reached a maximum of about 25 J corresponding to some 0.2 to 0.3 wt.% GMA, and then decreased more or less rapidly depending on temperature. The breadth of the bell-shaped curve at 0°C was much wider than that at −20°C. This implies that a material which has good properties at moderate temperatures may display poor properties at low temperatures. Also the processing window for obtaining a good material narrows as the temperature under which the material is used is lowered down.

Fig. 10 shows the temperature dependency of the impact strength of the PP/PBT (80/20) blend compatibilised with either 20 wt.% CPP1, CPP2 or CPP3. The choice of 20 wt.% was based on the fact that above this value, the PP/PBT blend system might have become crosslinked. This was particularly so for CPP1 whose GMA content was the highest (1.2 phr). The temperature dependency of the impact strength of the pure PP, the pure PBT and the non-compatibilised PP/PBT blend is also shown for comparison. First of all, the temperature dependency of the impact strength of the pure PP was small between −20 and 23°C. On the other hand, the impact strength of the PBT increased significantly with increasing temperature. Moreover, there seemed to be a brittle—ductile transition between −20 and −10°C. In the case of the non-compatibilised PP/PBT blend, the impact strength was too low to appreciate its temperature dependency. As for the PP/PBT blend compatibilised with 20 wt.% CPP1, CPP2 or CPP3, the higher the GMA content in the PP-g-GMA, the higher the impact strength of the corresponding blend. Moreover, it became less temperature sensitive. For example, the impact strength of the PP/PBT blend compatibilised with CPP3 (0.2 phr) depended very much on temper-
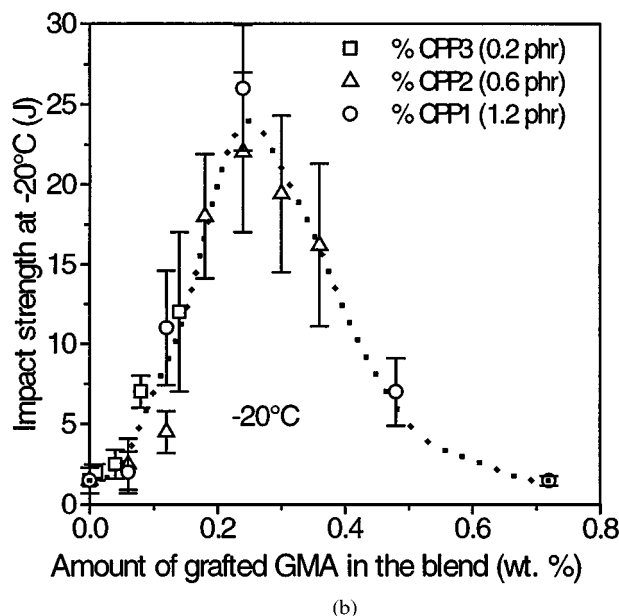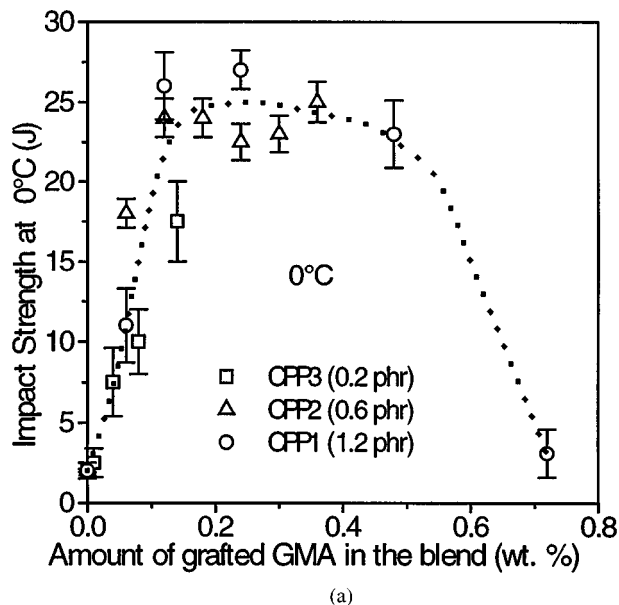

(a)

(b)

Figure 9 Impact strength of the PP+PP-g-GMA/PBT blend as a function of the amount of GMA in the blend. (a) testing temperature = 0°C; (b) testing temperature = −20°C. (○) CPP1 (1.2 phr), (△) CPP2 (0.6 phr), (□) CPP3 (0.2 phr).

ature, whereas that with CPP1 (1.2 phr) was almost temperature insensitive. As for CPP2, the corresponding PP/PBT blend had an intermediate behaviour and displayed a brittle—ductile transition between −20 and −10°C.

Fig. 11 shows the effect of varying the amount of PP-g-GMA on the temperature dependency of the impact strength of the PP+PP-g-GMA/PBT (80/20) blend. While the values of the impact strength of the PP/PBT blends compatibilised with 10, 20 and 40 wt.% CPP2 (0.6 phr) were similar at the room temperature, they were very different at lower temperatures. This implies that in practice, the degree of compatibilisation required for a blend should be optimised with respect to the projected application. It is not good to "under-compatibilise" or "over-compatibilise" a blend.
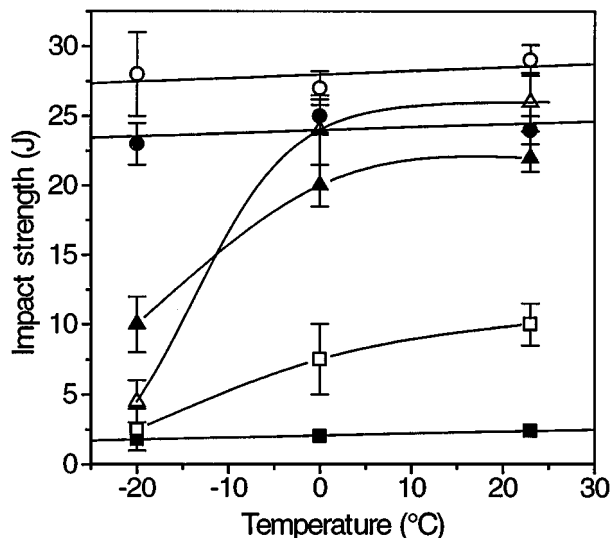
Figure 10 Temperature dependency of the impact strength of the pure PP, the pure PBT, and the non-compatibilised and compatibilised PP/PBT (80/20) blends. (●) PP, (▲) PBT, (■) non-compatibilised PP/PBT (80/20) blend, and (○), (△) and (□) correspond to the compatibilised PP/PBT blends with 20 wt.% CPP1 (1.2 phr), CPP2 (0.6 phr) and CPP3 (0.2 phr), respectively.
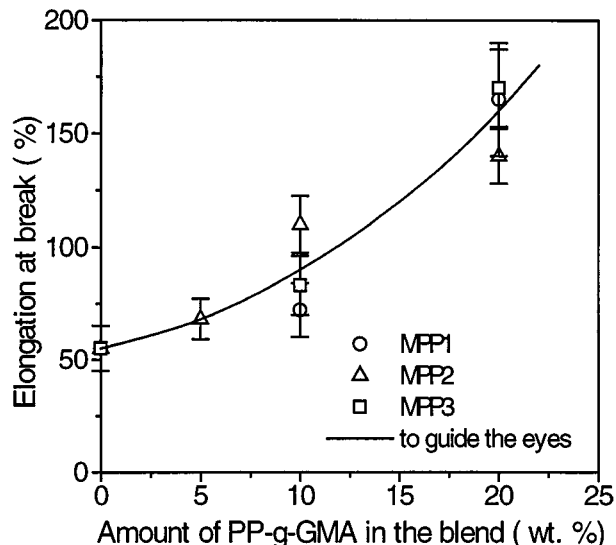

Figure 12 Elongation at break as a function of the amount of PP-g-GMA in the PP+PP-g-GMA/PBT (80/20) blend for three reactive compatibilisers whose GMA contents are the same but whose molecular weights are different. Testing speed = 50 mm/min. (○) MPP1, (△) MPP2, (□) MPP3.
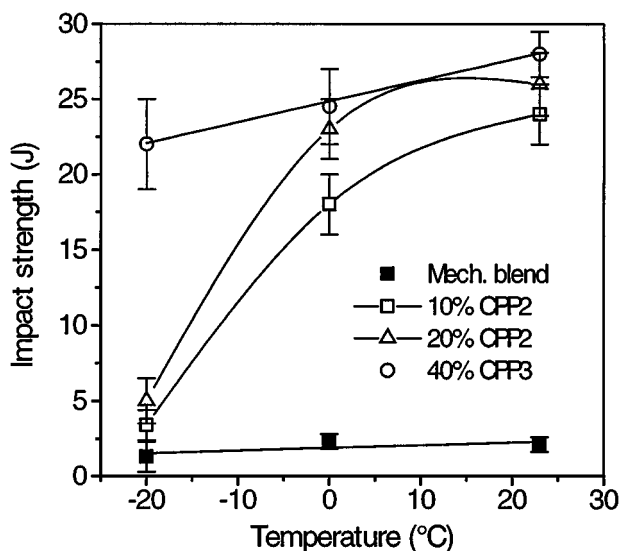

Figure 11 Temperature dependency of the impact strength of the PP/PBT (80/20) blends in the presence of varying amount of CPP2 (0.6 phr) as reactive compatibiliser. (■) 0 (non-compatibilised blend), (○) 10 wt.%, (△) 20 wt.% and (□) 40 wt.%.

Figure 13 Influence of PP-g-GMA's molecular weight on the temperature dependence of the impact strength of the compatibilised PP+PP-g-GMA/PBT (80/20) blend. (△) 20 wt.% MPP2, (□) 20 wt.% MPP3.

3.2. Influence of PP-g-GMA's molecular weight

In order to examine the effect of PP-g-GMA's molecular weight on its compatibilising performance, various PP+PP-g-GMA/PBT (80/20) blends were produced in the presence of MPP1, MPP2 and MPP3 as reactive compatibiliser. They had the same GMA content (0.6 phr) and different molecular weights (see Table I). The amounts of the compatibilisers in the blends were chosen not to exceed 20 wt.% in order to minimise changes in the viscosity ratio between the PBT and PP phases. Fig. 12 compares the value of the elongation at break of the PP+PP-g-GMA/PBT (80/20) blend as a function of the amount of PP-g-GMA in the blend for the above three reactive compatibilisers. Their com-
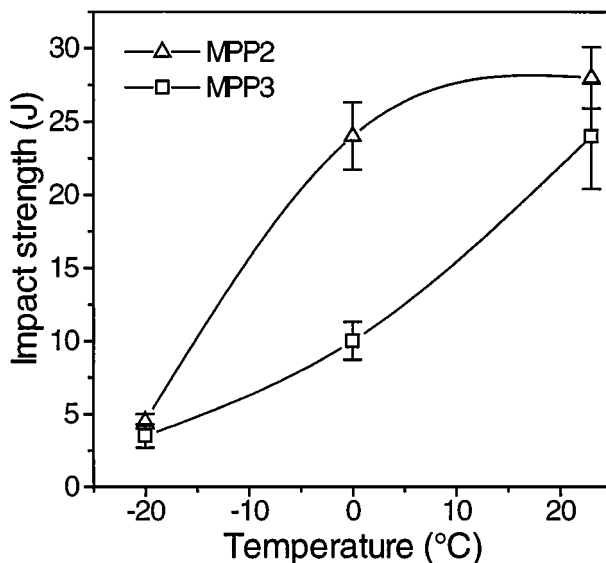
patibilising efficiency was very similar in terms of the elongation at break of the blend. The latter increased with increasing amount of PP-g-GMA. Fig. 13 compares the values of the impact strength of the PP/PBT blends compatibilised with 20 wt.% MPP2 and MPP3, respectively. The PP/PBT blends compatibilised with the two compatibilisers exhibited similar properties at −20 and 23°C, respectively. They were brittle at −20°C and ductile at 23°C. However, the impact strength of the PP/PBT compatibilised with MPP2 at 0°C was significantly higher than that with MPP3. This suggests that two PP-g-GMA having the same GMA content but different molecular weights modified the impact behaviour of the PP/PBT blend in a different manner. The one having a higher molecular weight had a greater capability of improving the impact strength of the PP/PBT at moderate temperatures.
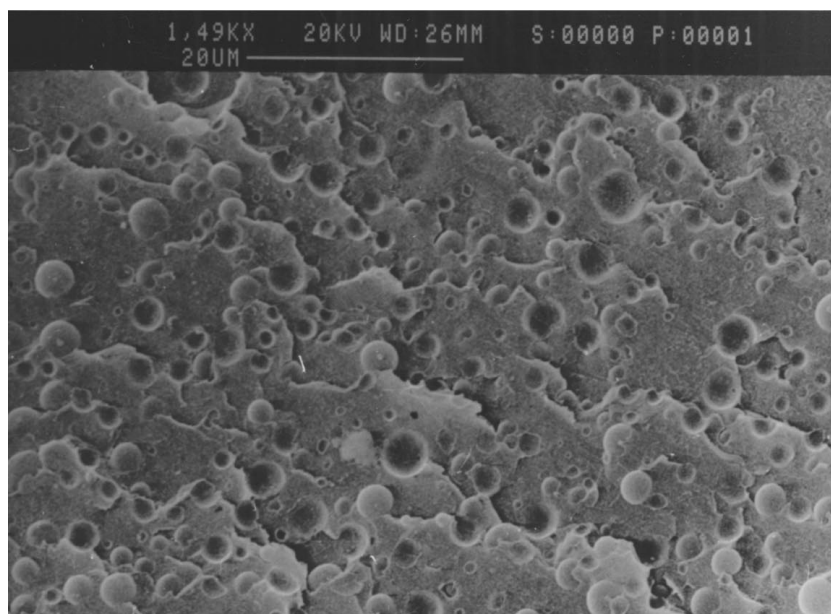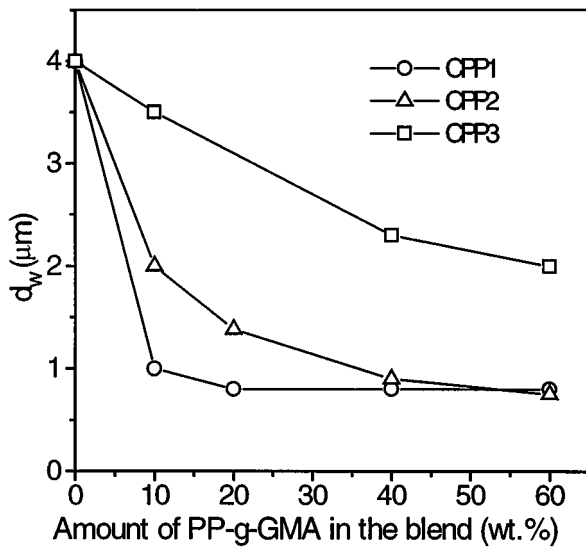
(a)
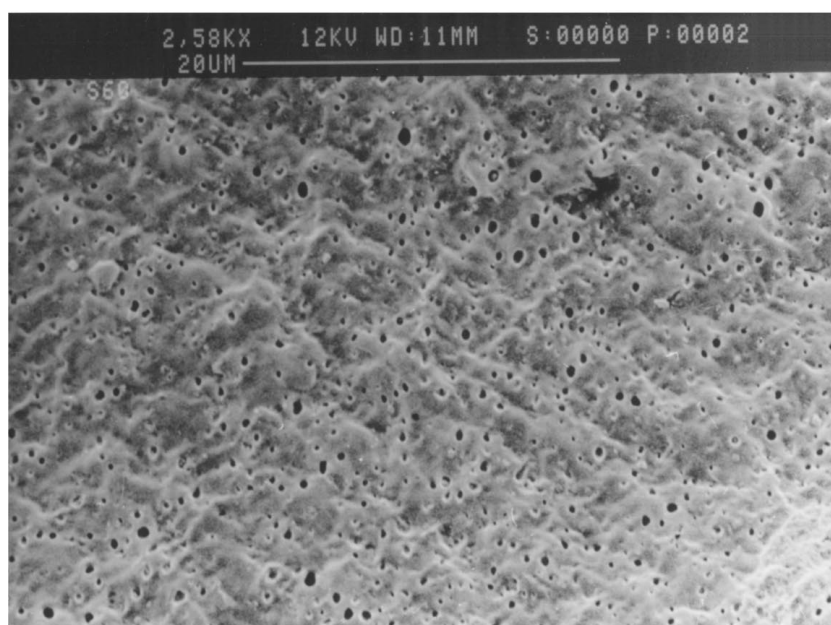
(b)

Figure 14 SEM micrographs of the PP/PBT (80/20) blend with and without PP-g-GMA. (a) Non-compatibilised blend without PP-g-GMA, (b) compatibilised blend with 10 wt.% CPP1.

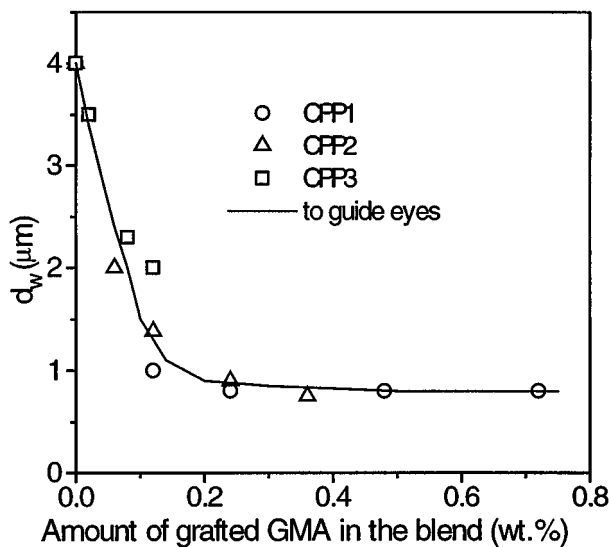## 3.3. Morphology of PP-g-GMA compatibilised PP/PBT blends

Fig. 14 shows the compatibilising efficiency of PP-g-GMA for the PP+PP-g-GMA/PBT (80/20) blend in terms of morphology characterised by SEM. Without PP-g-GMA, the particles of the dispersed phase (PBT) were clearly identifiable with an average size of about 4 μm. When 10 wt.% PP-g-GMA (CPP1) was present, the particle size of the PBT phase became much smaller (~1 μm). In the latter case, the PBT particles were extracted from the PP matrix with a selective solvent (dichloroacetic acid) before SEM analysis in order to improve visualisation. Fig. 15 compares the degree of reduction in the PBT particle size between the first series of PP-g-GMA (CPP1, CPP2 and CPP3). For the three reactive compatibilisers, the particle size of the

PBT phase decreased in an exponential manner with increasing amount of PP-g-GMA, as expected. Also the higher the GMA content in the PP-g-GMA, the faster the particle size reduction. When the particle diameter is plotted against the amount of GMA instead of the amount of PP-g-GMA in the blend, all data points in Fig. 15a fall on a single curve (see Fig. 15b). This shows that for PP-g-GMA possessing the same molecular weight but different GMA contents, it is the amount of GMA rather than that of PP-g-GMA in the blend that controls the morphology of the PP/PBT blend.

Fig. 16 compares the efficiency of MPP2 and MPP3 at reducing the PBT particle size. Since they had the same GMA content (0.6 phr) but different molecular weights (see Table I), the amount of GMA in the PP/PBT blend was directly proportional to that of the

(a)

(b)

Figure 15 Weight average diameter of the PBT particles as a function of the amount of PP-g-GMA (a) or that of GMA (b) in the PP/PBT (80/20) blend for three PP-g-GMA having the same molecular weight but different GMA contents. (○) CPP1 (1.2 phr), (△) CPP2 (0.6 phr), (□) CPP3 (0.2 phr).

Figure 16 Weight average diameter of the PBT particles in the PP+PP-g-GMA/PBT (80/20) blend as a function of the amount of PP-g-GMA for two PP-g-GMA having the same GMA content (0.6 phr) but different molecular weights. (△) MPP2 ($\bar{M}_n = 108$ kg/mole, $\bar{M}_w = 408$ kg/mole), (□) MPP3 ($\bar{M}_n = 70$ kg/mole, $\bar{M}_w = 198$ kg/mole).

which was expected to increase with increasing amount of PP-g-GMA. Since MPP2 and MPP3 had the same GMA content, their compatibilising efficiency was the same. As the amount of PP-g-GMA increased further, changes in the viscosity ratio between the PP and PBT phases would become more and more important and especially for MPP3 whose molecular weight was smaller than that of MPP2, the latter being smaller than that of the virgin PP. Under the reactive extrusion conditions employed in this study, if the characteristic shear rate and temperature were estimated to be 200 s^{-1} and 240°C, respectively, the viscosity ratio between the dispersed phase (PBT) and the matrix (PP+PP-g-GMA) would be about 1.2 and 3.5 in the presence of 20 and 60 wt.% MPP3, respectively. In the latter case, the rheological effects of the compatibiliser might have become important with respect to its chemical effects.

3.4. Influence of processing parameters

Unlike a standard single screw extruder in which throughput is screw speed dependent, a twin screw extruder like the one used in this study is often starve-fed. This means that feed rate or throughput (Q) is smaller than the maximum pumping capacity of the extruder itself so that it is independent of screw speed (N). The effects of these two operating parameters on the mechanical properties of compatibilised PP/PBT blends were examined using a PP/PBT (75/25) blend containing 30 wt.% CPP2 as an example. This system was extruded under the following conditions: either the feed rate was fixed at 5 kg/h and the screw speed was varied from 90 to 240 rpm or the screw speed was fixed at 150 rpm and the feed rate varied from 3 to 10.5 kg/h. The blends obtained under those conditions had almost the same values of the elongation at break and impact strength (see Fig. 17 for the elongation at break of the blend). In other words, these two operating parameters

PP-g-GMA. Both reactive compatibilisers did not always have the same compatibilising efficiency in the concentration range of 0 to 60 wt.%. Below 20 wt.%, both MPP2 and MPP3 displayed a similar compatibilising efficiency. This agrees with the work reported in the literature that the compatibilising efficiency of a compatibiliser depended only slightly on its molecular weight [19, 20]. Above 20 wt.%, however, the compatibilising efficiency of MPP3 was lower than that of MPP2. This difference became more pronounced at higher amounts of PP-g-GMA. More interestingly, in the case of MPP3, the particle size of the PBT phase first decreased with its amount and then increased. This suggests that there were two opposing phenomena that controlled the morphology of the compatibilised PP/PBT (80/20) blend. When the amount of PP-g-GMA was below a certain threshold, say, 20 wt.%, the morphology was dictated by the amount of the copolymer formed,
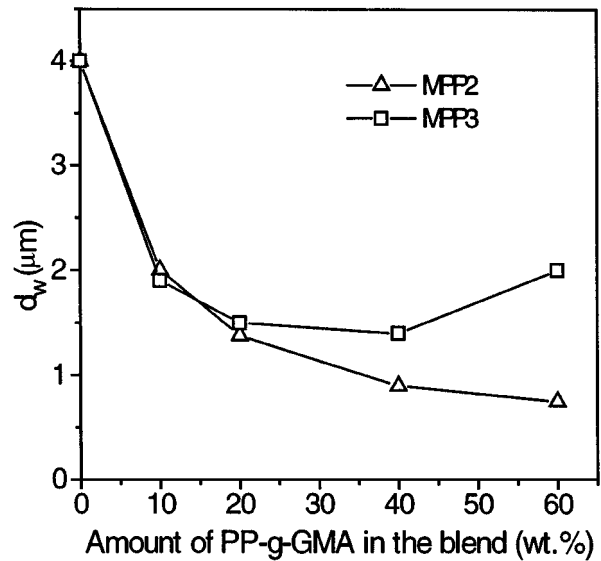
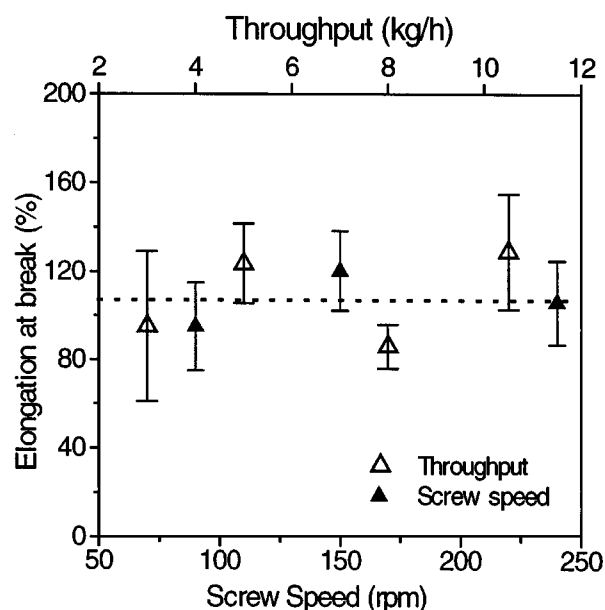*Figure 17* Effects of throughput (△) and screw speed (▲) on the elongation at break of the PP+CPP2/PBT (45+30/25) blend. Tensile speed = 65 mm/min.

had little effect on the mechanical performance of the reactively compatibilised PP/PBT blend. In fact, the morphology of those blends was also very similar. This is in agreement with an earlier study concerning reactively compatibilised PP/PA-6 blend with a maleic anhydride functionalised PP [11].

4. Discussion

It has been shown that for the first series of PP-g-GMA which have the same molecular weight but different GMA contents, their compatibilising efficiency as characterised by the size reduction of the dispersed phase (PBT) is dictated primarily by the amount of GMA rather than by that of PP-g-GMA in the blend. Two PP-g-GMA will lead to the same size reduction in the PBT phase if the amount of GMA in the blend are the same. For example, a PP-g-GMA having a GMA content twice as high as another PP-g-GMA will require only half the amount of the second PP-g-GMA to achieve the same morphology. This finding is very interesting because it implies that under these conditions, both PP-g-GMA would likely have produced the same amount of copolymer. This in turn suggests that the probability for the GMA moieties to react with the carboxylic group of the PBT would be the same for both PP-g-GMA, which is not impossible.

As for the second series of PP-g-GMA which have the same GMA content but different molecular weights, their compatibilising efficiency is similar at low concentrations and different at high concentrations. The compatibilising efficiency of a PP-g-GMA depends primarily on its GMA content and viscosity, the latter being related to its molecular weight. Two PP-g-GMA of the same GMA content but different molecular weights may have the same chemical ability to react with the PBT. However, their efficiency at reducing the size of

the PBT phase may not be the same because of different rheological effects. The conclusion is that the overall compatibilising efficiency of a reactive compatibiliser encompasses two intrinsic properties: its ability to react with its partner (*reactivity*) and its viscosity (*rheology*). Thus, it is important to control both the functional group content and the molecular weight of the reactive compatibiliser to optimise its compatibilising efficiency.

Properties such as elongation at break and impact strength of multiphasic blends are dictated not only by the morphology but also by the interfacial adhesion between the phases. Fig. 15 shows that when the first series of the PP-g-GMA are used as reactive compatibilisers, the size of the PBT phase first decreases with increasing amount of GMA in the blend and then levels off when it is more than about 0.2 to 0.3 wt.%. On the other hand, the elongation at break always increases with increasing amount of GMA (see Fig. 7). This means that when the amount of GMA exceeds a critical threshold, a further increase in the amount of GMA will not bring about changes in the morphology of the blend but will modify the interfacial adhesion between the PP and PBT phases. Elongation at break is a good indication of the interfacial adhesion. An increased elongation at break with increasing amount of GMA likely results in an improved interfacial adhesion [13]. As for the impact strength, its behaviour is more complicated with respect to the amount of GMA (see Fig. 9) and morphology. Nevertheless, inspection of Figs 9 and 15 shows that morphology plays an important role in impact strength because a reduction in the size of the PBT phase is accompanied by an increase in impact strength. However, while a further increase in the amount of GMA does not change the size of the PBT phase, the impact strength of the blend tends to decrease. This is in contrast to the elongation at break. The reason for this is unclear. A possible explanation would be that an increase in the amount of GMA would increase the probability of crosslinking, which would reduce the mobility of the copolymer chains making the interphase brittle. Because the rate of deformation for measuring the elongation at break is much smaller than that for measuring the impact strength, the interphases between the PP and PBT may be ductile enough in tensile test but brittle in impact test.

The importance of PP-g-GMA's molecular weight for the impact strength of the compatibilised PP/PBT blend has been clearly shown in Figs 13 and 16, which compare the compatibilising efficiency of two PP-g-GMA (MPP2 and MPP3) having the same GMA content but different molecular weights. According to Fig. 16, the morphology of the PP/PBT (80/20) blend compatibilised with 20 wt.% MPP2 is almost the same as that with 20 wt.% MPP3. However, these two materials do not have exactly the same impact behaviour. The value of the impact strength at 0°C of the blend compatibilised with MPP2 whose weight average molecular weight 408 kg/mole is significantly higher than that with MPP3 whose weight average molecular weight is much smaller (198 kg/mole). This is an indication of a stronger interfacial adhesion of the blend compatibilised with MPP2.

5. Concluding remarks

This study has addressed the effects of the functional group content and molecular weight of a glycidyl methacrylate functionalised polypropylene (PP-g-GMA) as a reactive compatibiliser on the compatibilisation of polypropylene (PP) and poly (butylene terephthalate) (PBT) immiscible blends in a co-rotating twin screw extruder. The compatibilising efficiency of two series of PP-g-GMA has been examined in terms of morphology and mechanical properties (elongation at break and impact strength) of the blend. The first series of PP-g-GMA have the same molecular weight but different GMA contents. The second series of PP-g-GMA have the same GMA content but different molecular weights.

The compatibilising efficiency of PP-g-GMA is dictated by the GMA content and molecular weight. For the first series of PP-g-GMA, on the same amount of PP-g-GMA basis, the higher the GMA content in the PP-g-GMA, the smaller the PBT particle size and the higher elongation at break and impact strength. However, on the same amount of GMA basis, all PP-g-GMA have the same compatibilising efficiency. In other words, two PP-g-GMA will have the same compatibilising efficiency when the amount of GMA in the PP/PBT blend are the same. A PP-g-GMA having a GMA content twice as high as another PP-g-GMA will need only half the amount of the second PP-g-GMA to reach the same compatibilising efficiency.

Results obtained with the second series of PP-g-GMA show that two PP-g-GMA having the same GMA content but different molecular weights may have the same capability of reacting with the PBT but their efficiency at reducing the size of the dispersed phase (PBT) may be different because of different rheological effects. In other words, the compatibilising efficiency of a reactive compatibiliser is dictated by two parameters: reactivity and viscosity.

The correlation between the mechanical properties of an in situ compatibilised PP/PBT blend and its morphology and the interfacial adhesion is not always obvious. Nevertheless, a reduction in the particle size of the PBT phase is always accompanied by an increase in elongation at break and impact strength. The interfacial adhesion is also an important parameter that controls these properties. Two PP-g-GMA having the same GMA content and different molecular weights may lead to two PP/PBT blends having the same chemical composition and morphology but different properties because of differences in the interfacial adhesion. A PP-g-GMA having a higher molecular weight may yield stronger interfacial adhesion thus better properties. This suggests that the functional group content and molecular weight are two parameters to consider in controlling the compatibilising efficiency of a reactive compatibiliser.

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