

Recycling of polycarbonate by blending with maleic anhydride grafted ABS

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Received 9 January 2004; received in revised form 7 June 2004; accepted 13 July 2004
Available online 30 July 2004

Abstract

Recycling of used polycarbonate (PC) was conducted via melt blending with maleic anhydride grafted ABS (ABS-g-MA) using a twin-screw extruder. The toughness of waste PC was greatly improved through the modification of ABS-g-MA. The toughening mechanism was explored based on the morphology of the blends. The grafting of MA onto ABS was considered a key factor, which resulted in a special morphology of ABS domains dispersed in PC matrix. At a certain PC/ABS-g-MA weight ratio, the ABS domains connected together forming a network and gave rise to a maximum of the notched impact strength.

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Keywords: Recycling; Polycarbonate; Maleic anhydride

1. Introduction

Polycarbonate (PC) is one of the important engineering plastics possessing excellent mechanical performance coupled with high transparency. Recycling of this plastic material after the end of first life cycle is receiving increasingly more attentions [1]. The disadvantages of PC include high melt viscosity and notch sensitivity. Used PC usually suffered from crazing caused by light, radiation and chemicals present in the service environment, which make the problem of notch sensitivity even worse. Approaches were developed to decrease the notch sensitivity and enhance the processability without reducing its superior toughness. Blending PC with other thermoplastics constituted the most popular practices [2,3], of which ABS was frequently selected as a modifier.

While neat ABS usually does not achieve a satisfactory toughening, some core-shell particles were employed as a co-modifier [4]. However, the introducing of external components will result in additional repulsion among the

segments, the mechanical properties may be negatively influenced. Recently, maleic anhydride grafted ABS (ABS-g-MA) was widely employed to modify polymers, such as polyamide [5], polypropylene [6], polyethylene terephthalate [7], as well as PC [8]. It is interesting to note that diverse observations were obtained regarding the role of the MA grafting. Neelakantan [8] found that ABS-g-MA achieved fine and lamella dispersion in PC matrix and resulted in excellent toughening. Tjong [9] reported that maleic anhydride grafted polypropylene may promote the dispersion of ABS in PC matrix. However, Paul [10] suggested that virgin ABS can be well dispersed in PC without the aid of a compatibilizer.

Generally speaking, the purposes of MA grafting is either to achieve a polarity match or to introduce reaction sites. However neither is likely in the case of PC. The segments of ABS are more polar than those of PC, being grafted with MA will increase instead of decrease the polarity difference. Common senses suggested that the OH groups on the ends of PC chains might be linked with the anhydride groups via esterification. However, at the extremely low concentration of terminated OH groups and in the very short time of extrusion, no substantial esterification could be expected and few evidence of esterification was reported in the

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literatures. For this reason, the role of MA-grafting, especially on ABS, remained a problem to be properly clarified.

In this paper, the recycling of used PC was conducted using the conventional modifier ABS-g-MA. Special attentions were paid to the role of MA grafting and the relationship among the grafting, morphology, and the impact strength, which was considered as a measure of toughness.

2. Experimental

2.1. Materials

Waste polycarbonate was received as pellets; the material was used as sun umbrellas for 10 years. Maleic anhydride (MA, AR) and dicumyl peroxide (DCP, AR) were supplied by BEIJING Chemical Reagent Co., China. ABS (Trade no. 301) was purchased from LANZHOU Petrochem. Co., China, whose composition is styrene 58 wt%, butadiene 17 wt%, and acrylonitrile 25%).

2.2. Maleic anhydride grafting

ABS, maleic anhydride (MA) and dicumyl peroxide (DCP) were first mixed in a Brabender mixer (PLV-151, Germany) at 220 °C to carry out the grafting for various length of time. The obtained mixture was fed into a twin-screw extruder (ZSK-25WLE, Germany) at a screw speed of 75 rpm. The temperatures at three zones of the barrel and at the die were 220, 230, 240, and 220 °C, respectively. The strands extruded were quenched into water and cut into small granules by a pelletizer.

2.3. Blends preparation

The waste PC and ABS-g-MA pellets were dried separately at 130 and 110 °C, respectively, in a vacuum oven for 10 h. The mixtures of the pellets of various weight ratios were melt-blended using a twin-screw extruder (ZSK-25WLE, Germany). The screw speed was 100 rpm and the temperatures at three zones of the barrel and at the die were 240, 250, 260, and 250 °C, respectively. The obtained extrudate was pelletized.

2.4. Determination of impact strength

Pellets of the PC/ABS-g-MA blends were vacuum dried at 130 °C for 12 h and the impact bars were injection moulded using an injector (Auckland M20-55, Switzerland). The impact strength test was carried out according to ASTM D256.

2.5. Determination of degree of grafting

The infrared spectra of ABS-g-MA samples were recorded with Shimadzu F-1000 FTIR spectrophotometer. The relative degree of grafting was determined by taking the area ratio of absorbance at 1780 and 2240 cm^{-1} (A_{1780}/A_{2240}).

2.6. Transmission electron microscopy (TEM)

The morphology was examined by TEM. The samples were cryogenically microtomed using a diamond knife. The microchips were stained with ruthenium tetroxide (RuO_4) by soaking them in the vapor of a 2 wt% aqueous solution of RuO_4 for 30 min. A Hitachi H-800 (Japan) transmission electron microscope was used to view the samples.

3. Results and discussion

3.1. The grafting degree

The grafting formulation and the resulted grafting degrees are presented in Table 1. The grafting degree was determined based on the FTIR spectra shown in Fig. 1. The peaks located at 1780 and 2240 cm^{-1} can be assigned to the stretched vibration absorbance of the carbonyl and nitrile groups, respectively. Since the nitrile groups on the ABS were unaffected during the grafting, the ratio of the absorbency at 1780 cm^{-1} over that at 2240 cm^{-1} (A_{1780}/A_{2240}) was taken as a measure of the relative grafting degree. Table 1 shows that the grafting degree was affected by either reaction time or the loading of MA. At a constant loading of MA, the relative grafting degree increased with increasing reaction time. At a constant reaction time, the relative grafting degree increased with increasing loading of MA. Not all the grafted ABS resins in Table 1 were used in this work, only two, No. B₄ and B₅ were employed.

3.2. Morphology

The samples shown in Figs. 2 and 3 were stained with ruthenium tetroxide (RuO_4). Among the various units in ABS and PC, butadiene units are the quickest to be stained, styrene units the second, the others are slow. The ABS used in this paper contains two kinds of segments: copolymers of styrene/butadiene and of styrene/acrylonitrile, which grafted each other. As a result, within a limited staining time, the styrene/butadiene segments appeared black, styrene/acrylonitrile segments gray, and the others white.

Fig. 2 showed the morphologies of the blends of PC and ABS with or without grafting of MA, with ABS constituting the dispersed domains in a sea of PC. The left side presented a higher magnification (100,000 \times) and the right side a lower one (20,000 \times). From the right side one may notice that as the grafting degree of MA increased, the size of the

Table 1
Relative grafting degree of ABS with maleic anhydride

Sample No.	Weight parts			Reaction time in Bra-bender (min)	Degree of grafting
	ABS	MAH	DCP		
A1	100	3.5	0.1	5	1.75
A2	100	3.5	0.1	8	2.13
A3	100	3.5	0.1	10	2.59
A4	100	3.5	0.1	15	2.82
A5	100	3.5	0.1	20	3.11
B1	100	0.5	0.1	5	0.15
B2	100	1.5	0.1	5	0.37
B3	100	2.5	0.1	5	1.46
B4	100	3.5	0.1	5	1.75
B5	100	4.5	0.1	5	2.75
B6	100	5.5	0.1	5	3.15

dispersed domains of ABS seemed not changed or even a little increased. One may concluded that the MA grafting did not result in a better compatibilization between PC and ABS, for if the MA grafting might improve the compatibility between PC and ABS, the size of the dispersed domains would have been decreased with increasing MA grafting. As a result the role of MA grafting should be something else.

The left side of Fig. 2 shows the detailed morphology of the ABS domains. Fig. 2(a) showed that the unmodified ABS islands appeared tightly compacted and the boundary between the islands and the sea was sharp. However, when ABS was grafted, domains were no longer compacted particles, but loose ‘cocoons’ with some gray species inside. The higher the grafting degree, the looser the cocoons. In other words, the MA grafting ‘inflated’ the ABS domains. As mentioned above, the ABS in this work composed of two

kinds of segments, styrene/butadiene and styrene/acrylonitrile ones, with the latter more polar than the former. When unmodified, they excluded each other. What one has seen in the micrographs Fig. 2(a) as islands are solely styrene/butadiene segments not including styrene/acrylonitrile ones. The MA grafting occurred most likely on the former, which became matching in polarity with the latter and as a result, the dispersed domains were seen to be inflated. It is now clear that the role of MA grafting was the compatibilization between two kinds of segments of ABS. More precisely, the grafting of styrene/butadiene segments helped it enwrapped the styrene/acrylonitrile segments and thus moderated the repulsion between those polar segments and the non-polar PC ones.

Fig. 3 shows the morphologies of the blends of various PC/ABS-g-MA weight ratios. When the amount of ABS-g-MA was low (Fig. 3(a), PC/ABS-g-MA = 1/0.25), the

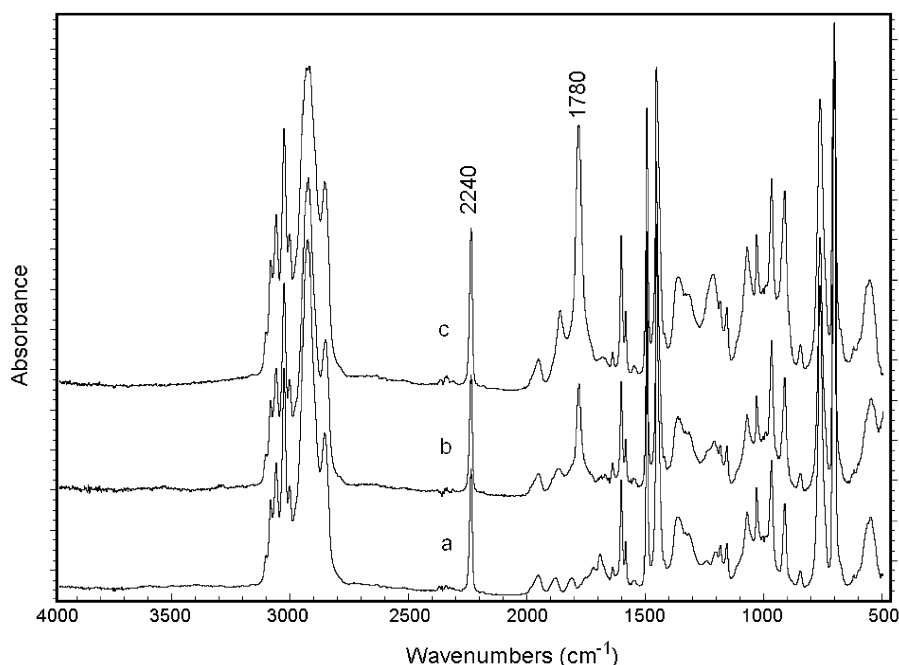


Fig. 1. FTIR spectra of neat and MA grafted ABS (a) neat ABS; (b) and (c) are the samples No. B₄ and B₅ in Table 1, respectively.

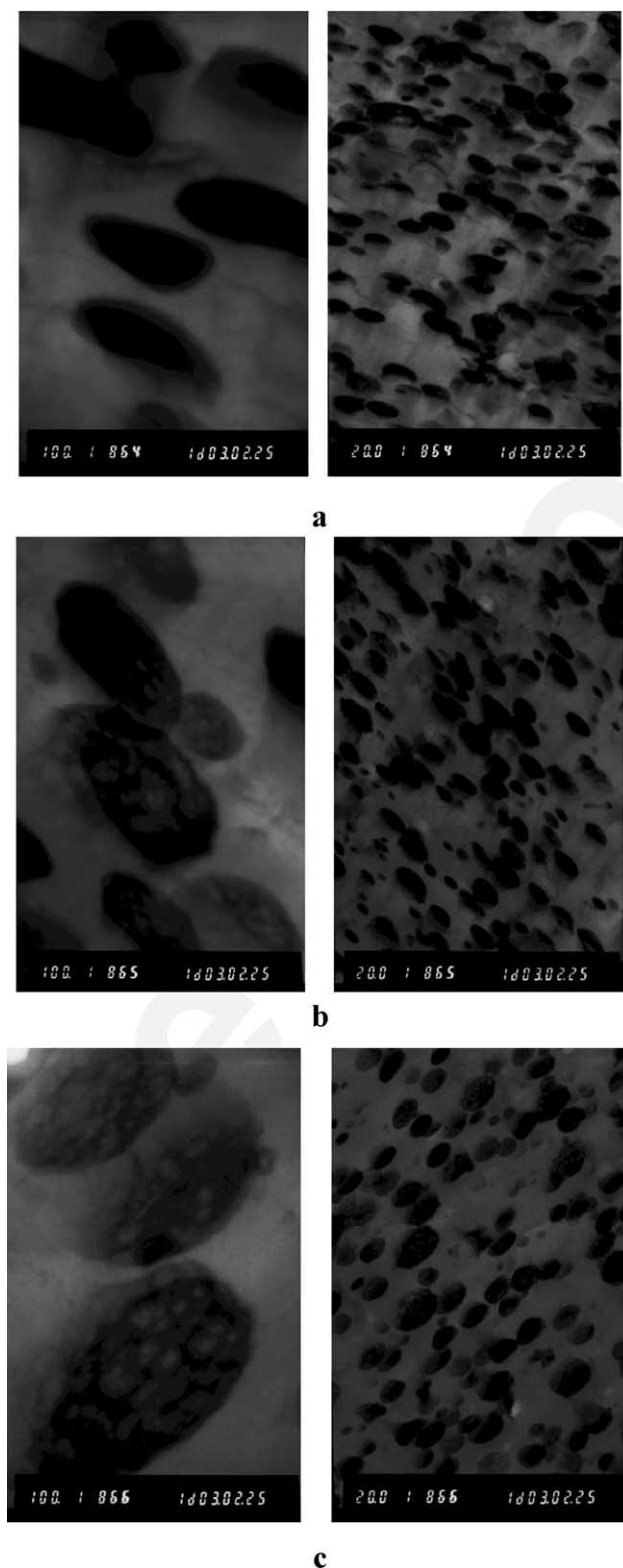


Fig. 2. TEM micrographs of blends of PC and ABS-g-MA of different grafting degrees. Relative degree of grafting: (a) zero, (b) 1.75; (c) 2.75. PC/ABS-g-MA = 1/0.25 w/w.

morphology was a typical sea/island one. As the content of ABS-g-MA increased, the isolated domains tended to coagulate (Fig. 3(b)). When the PC/ABS-g-MA weight ratio was 1/0.75 (Fig. 3(c)), one noticed an interesting transition of the dispersed domains to a network, in which the ABS domains seemed numerous pearls connected together. Such a transition of the dispersed domains to a network was also found in a blend of MA grafted styrene-*b*-ethylene/butylenes-*b*-styrene (SEBS) dispersed in poly(2,6-dimethyl-1,4 phenylene oxide) (PPO) [11]. The formation of network was because the H-bonds introduced by the grafting of MA. In the present case, the generation of the network was probably originated from the same mechanism. This was another role of the MA grafting in addition to the aforementioned enwrapping. However, at higher amount of ABS-g-MA (Fig. 3(d)) the morphology resumed the sea-island structure, this probably because the intra-domain coagulating force became larger than the inter-one.

It should be mentioned that the ABS used in this work possessed a high acrylonitrile content (25 wt%) and a low butadiene content (17 wt%), which may be responsible for the special morphology behaviors.

3.3. Impact strength

The impact strength of the various PC/ABS-g-MA blends was presented in Tables 2 and 3. The impact strength of new PC ranges around 60 kJ/m², but that of the used resins is much lower, only about one fourth of the new one. This is one of the reasons that ABS-g-MA had to be introduced to improve the impact strength. In common senses, the increase in impact strength could be attributed to the rubber components of ABS, i.e. styrene/butadiene segments, which toughened the PC via the well-known mechanisms [12]. However, as discussed in the previous section, ABS domains are themselves a complicated system, the over-simplified explanation was not quite suitable. As shown in Table 2, the impact strength of PC/neat ABS was even much lower than that of waste PC. Before the rubber component can act, first, the repulsion between the polar styrene/acrylonitrile segments and the non-polar PC ones should be moderated and second, the modulus of the domain should be suitably increased in order to match the high value of PC matrix. MA grafting of ABS can well accomplish the two requirements. As seen in the Fig. 2, the styrene/acrylonitrile segments (high polarity) were partially

Table 2

Impact strength of blends of PC and ABS-g-MA of different grafting degrees. Relative degree of grafting: (a) zero, (b) 1.75; (c) 2.75. PC/ABS-g-MA = 1/0.25 w/w

No.	Degree of grafting	Charpy notched impact strength (kJ/m ²)
1	0	5.4
2	1.75	28.6
3	2.75	49.5

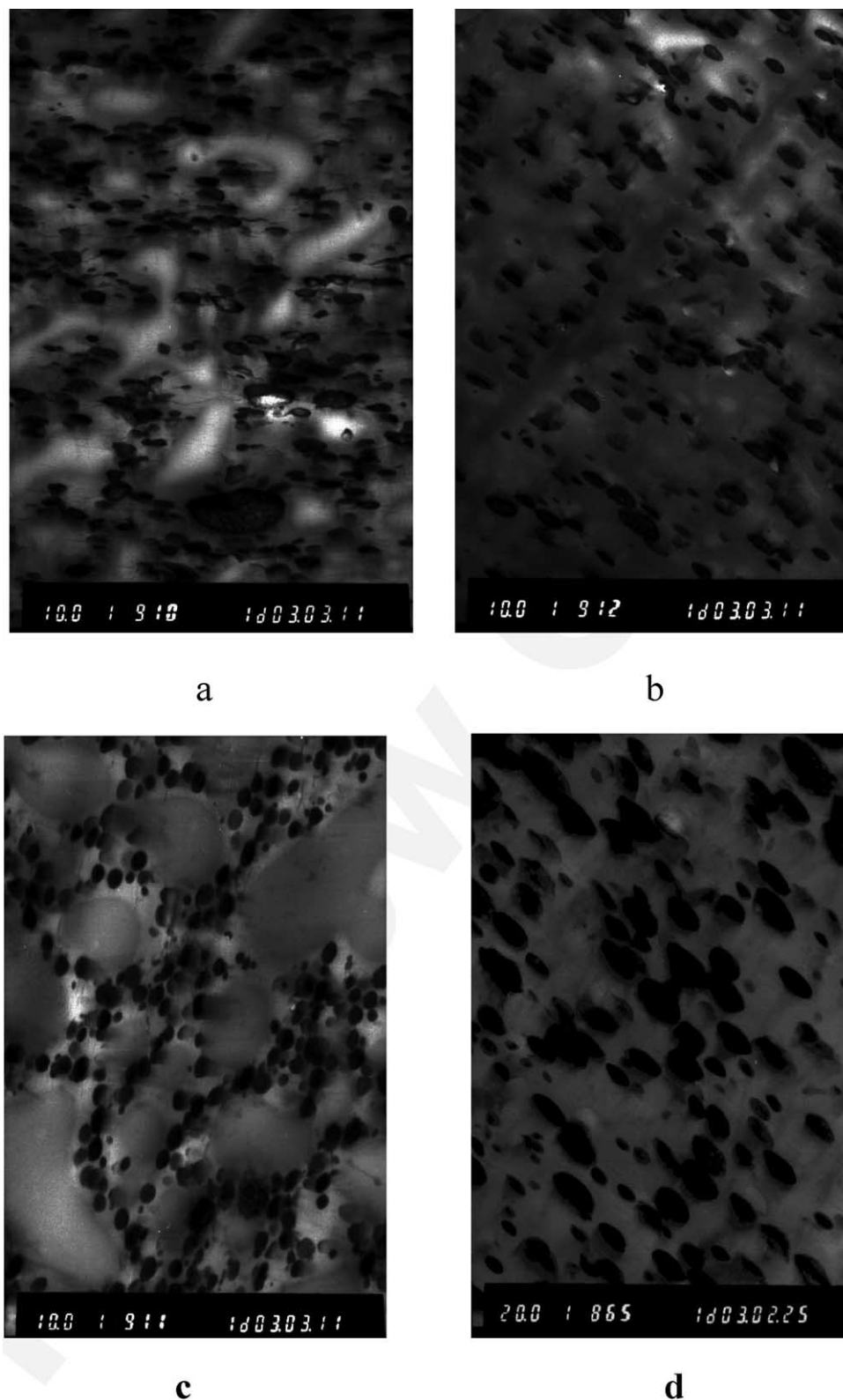


Fig. 3. TEM micrographs of blends of PC/ABS-g-MA. PC/ABS-g-MA (w/w)=(a) 1/0.25; (b) 1/0.50; (c) 1/0.75; (d) 1/1. Relative degree of grafting of ABS: 1.75.

wrapped by styrene/butadiene segments (moderate polarity), and the former may increase the modulus of the domains. With such a microstructure, the toughness of PC can well be increased via mechanisms like microcracking

and crack deflection. Table 2 shows that higher the degree of MA grafted, the higher the impact strength of the blends. In Table 3, one may observe another major role of ABS-g-MA played. The impact strength of the blend was initially

Table 3

Impact strength of the blends of PC/ABS-*g*-MA. PC/ABS-*g*-MA (w/w)= (a) 1/0.25; (b) 1/0.50; (c) 1/0.75; (d) 1/1. Relative degree of grafting of ABS: 1.75

No.	Weight ratio of PC/MA- <i>g</i> -ABS	Charpy notched impact strength (kJ/m ²)
1	100/0	15.8
2	100/25	28.6
3	100/50	43.0
4	100/75	46.3
5	100/100	40.6

increased with increasing amount of ABS-*g*-MA, until a maximum was exhibited at a PC/ABS-*g*-MA weight ratio of 1/0.75. This weight ratio was in coincidence with that for the formation of a network of ABS domains shown in Fig. 3. Such a semi-flexible network may not only prevent the propagation of crack via a ‘pinning’ effect, but also promote the formation of the shear bands. It was therefore concluded that the network of ABS domains contributed the maximum of impact strength. At higher ABS-*g*-MA contents, the blend resumed the island/sea morphology and the impact strength decreased slightly, however, it still remained a high level. One may notice that the maximum value of the impact strength was only three fourth of that of virgin PC, however, for the waste PC had been used for ten years, the recycling was successful.

4. Conclusion

Waste polycarbonate (PC) can be effectively toughened

by maleic anhydride grafted ABS (PC/ABS-*g*-MA). It was found that in this particular system, the effect of maleic anhydride grafting onto ABS was not an improvement of compatibilization but the generation of special morphology of ABS domains. First, different segments of ABS were combined in an enwrapped structure, which partially eliminate the repulsion between the polar segments and the non-polar PC ones; second, at a certain PC/ABS-*g*-MA weight ratio, the dispersed ABS domains connected together forming a network, which gave rise to a maximum of impact strength.

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