Modification of Recycled Polycarbonate with Core-Shell Structured Latexes for Enhancement of Impact Resistance and Flame Retardancy

Shuangyue Sun, Yadong He, Xiaodong Wang, Dezhen Wu

Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ABSTRACT: Two types of core-shell structured latexes, poly(methyl methacrylate-*co*-butadiene-*co*-styrene) (MBS) and poly(methyl methacrylate-*co*-methylphenyl siloxane-*co*-styrene) (MSiS) were used to modify recycled polycarbonate (PC) for the enhancement of toughness and flame retardancy. The impact strength of the modified PC blends was not improved after melt-blending recycled PC with these two kinds of latexes, probably because the latex particles were not evenly dispersed in the PC matrix because of the incompatibility between PC and PMMA shell of the latexes. Addition of a compatibilizer, e.g. diglycidyl ether of bisphenol-A or poly(styrene-*co*-maleic anhydride), can effectively enhance the toughening effect of recycled PC with core-shell structured modifiers. The presence of compatibilizer in the blends reduces the interfacial tension and introduces a steric hindrance to coalescence, and thus enhances the interfacial adhesion between PC domain and PMMA shell, and improves the dispersion of core-shell structured particles in the PC matrix. The ternary blends achieve a high impact resistance by cavitation of the particles, which relieves the triaxial stress and promotes massive shear yielding of the matrix, and then enables the matrix to fracture by the plane stress ductile tearing mode. Additionally, MSiS has a silicone-based core and can effectively retard the combustion of recycled PC. The blends containing 7 wt % MSiS and 3 wt % compatibilizer can achieve a UL94 V-0 rating in vertical burning test. We proposed that, during combustion, a fine dispersion of MSiS particles in the PC matrix facilitates the rapid migration of MSiS and formation of a uniform and highly flame resistant char barrier on the surface of the modified PC. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2451–2464, 2010

Key words: recycled polycarbonate; core-shell structured latexes; blends; toughening; flame retardancy

INTRODUCTION

Polycarbonate (PC) is one of the most important engineering thermoplastics used in a wide variety of applications because of its desirable properties including optical clarity, high heat deformation temperature, toughness, electrical insulation, and weathering resistance. As PC possesses a high heat distortion temperature (132–138°C), this makes it particularly useful for structural elements operating at the elevated temperatures. Another advantage of PC relates to its transparency and exceptional clarity, which has lead to applications in safety glazing, roofing panels, light covers, automotive headlamp lenses, greenhouse double glazing, water bottles, compact disks, and ophthalmic applications. In addition, PC can also be widely used in housings (e.g. telecommunications, office appliances, and home entertainment), switch boxes, control parts (e.g. push buttons and dials), light sockets, and electronic connectors and covers.[1,2] The annually consumed amount of this polymer exceeds several million metric tons. In recent years, the interest in recycling of PC has expanded dramatically and this is a trend that will undoubtedly continue into the future,[3] which may be explained by (i) limited natural resources, (ii) rising waste-handling costs, and (iii) environmental regulations related to land-filling and incineration of plastics. However, post-consumer PC usually underwent a series of degradation problems caused by light, radiation, and chemicals present in the service environment. This leads to a reduction in molecular weight and intrinsic viscosity, which in turn decreases the mechanical properties and especially the impact strength of recycled PC.[4–7]

One natural approach to enhance the toughness of recycled PC is to blend it with some rubbery impact modifiers. In addition, some of the applications for recycled PC require a good nonflammable property. Therefore, the enhancement of flame retardancy is

also desirable for demanding these applications of the post-consumer PC when performing the modification for improving impact resistance. The rubber-toughened virgin PC has received considerable attention for many years. The impact toughness of virgin PC could be improved effectively by blending with various rubbers like polyolefins,[8–11] core-shell structured latex particles like poly(methyl methacrylate-co-butadiene-co-styrene) (MBS),[12–19] styrenic copolymers such as poly(styrene-co-maleic anhydride), and poly(styrene-co-butadiene),[20–22] thermoplastic polyurethane and copolyether ester elastomer.[23–25] However, one particularly attractive method is the use of emulsion-made core-shell structured latex particles as impact modifier as they offer particles of a predetermined size, in contrast to the rubber in other forms, where the size of the particles formed may depend on the details of mixing process as well as the interfacial adhesion between two polymers.[26] This, of course, assumes that it is possible to mix the fixed particles into matrix in such a way that all agglomerates of these particles are broken up and that the particles are individually dispersed in the matrix. The big advantage of using core-shell structured particles is to ensure the desired particle shape and their uniform dispersion in the matrix phase, while the introduction of core-shell structured latex particles not only can provide effective toughening but can also retain other desirable mechanical properties of the matrix. Cheng et al.[18] studied the effect of three different butadiene-based impact modifiers on the toughness of PC and found that maximum toughness was obtained by using these core-shell structured impact modifiers. In accordance with the report by Tanrattanakul et al.,[27] owing to a good compatibility between the PMMA shell and PC, MBS particles were uniformly dispersed in the blend, which in turn gave rise to the best low temperature toughness. Parker et al.[28] conducted an investigation of toughening mechanisms in core-shell rubber modified PC and concluded that cavitation of rubber particles occurs first, followed by massive shear yielding of the matrix. El-Aasser et al.[29] have explained the effect of shell thickness and shell polymer molecular weight on the impact properties of modified PC on the basis of interactions at the matrix modifier interface. Nevertheless, there are hardly reports that MBS is used as an impact modifier to improve the impact properties of post-consumer PC.

Presently, flame-retardant technologies of PC have been developed extensively.[30] However, PC has usually been imparted with flame retardancy by incorporation of a flame retardant. The most prevailing flame retardants used for PC are halogenated organic compounds[31] and organophosphates.[30] The flame-resistant efficiency of halogen-containing flame retardants is high in most cases. Nevertheless,

because of environmental pollution problems, many studies have been diverted to the flame-retardants free of bromine and chlorine. As for phosphorus-containing flame retardants, to obtain any noticeable improvement in combustion resistance, the flame retardant content typically varies from 5 up to 30% by weight percentage, and thus, they often adversely affect many of the desirable physical and mechanical properties of PC. Various silicone polymers as flame retardants have been tried to use for polymers in recent years. Silicone possesses a characteristic of high heat resistance, nontoxicity and no generation of toxic gasses during combustion. Moreover, the addition of relatively small amount of silicone to polymeric materials can significantly improve their flame retardancy. Zhou et al.[32] investigated poly(methylphenyl siloxane) (PMPS) as flame retardant for PC. The results indicated that the limited oxygen index of the PC containing 5 wt % of PMPS was 34% and the addition of PMPS enhanced the thermal stability of PC and promoted the formation of char. Iji et al.[33] used several types of silicone copolymers as flame retardant in PC. Branched silicone copolymers containing a mixture of methyl and phenyl groups along the chain and end-capped by methyl groups proved the most effective in enhancing the flame retardancy of PC. According to these researchers, the superior flame retardant effect of the branched silicones was because of their excellent dispersion in PC and their quick migration from the inside of the PC to the surface during combustion, where they formed a uniform and highly flame resistant char barrier.

In this work, there are two aspects of investigations on the toughening and imparting the flame retardancy for recycled PC. On one hand, we employed a kind of core-shell latexes with a rubbery polybutadiene (PB) core and a plastic poly (methyl methacrylate) (PMMA) shell as an impact modifier to toughen recycled PC. On the other hand, in consideration of the poor miscibility between silicone derivatives and PC, a core-shell structured flame retardant, which has a poly(dimethyl siloxane) (PDMS) core and a PMMA shell, was incorporated into recycled PC. The blends containing the core-shell structured flame retardant were expected to further enhance not only the flame retardancy but also the impact properties. The degree to which core-shell particles can be dispersed individually in a polymer matrix depends on certain aspects of the mixing process as well as the interfacial adhesion between the shell polymer of the latexes and the matrix, which can be enhanced in presence of compatibilizer. Therefore, we also investigated the compatibilizing effect on the dispersibility of the core-shell latexes in aid of various compatibilizers, and thus a new modified PC blending material with high

impact toughness and good flame retardancy was developed based on recycled PC. In addition, it is surprisingly found that all the prices of two core-shell impact modifiers and three compatibilizers are lower than that of virgin PC. This means that, from the point of view of commercial applications, the use of recycled PC after toughening and flame retarding modifications is more economical than that of virgin PC because of the lower producing cost. Therefore, the reutilization of recycled PC based on this study would benefit the industrial ecosystems in terms of the cost savings.

EXPERIMENTAL

Materials

Recycled PC was received as pellets, which was obtained from water bottles, glazing, or roofing panels. Two types of core-shell latexes with commercial product names of Kane Ace® M-600 and MR-01 were kindly supplied by Kaneka Chemical Co. Kane Ace® M-600 is a kind of core-shell structured MBS latexes containing a polybutadiene rubbery core with a T_g of –60°C and a PMMA plastic shell, and it has a particle diameter of 200–300 nm. Kane Ace® MR-01 is a kind of core-shell structured poly(methyl methacrylate-co-methylphenyl siloxane-co-styrene) (MSiS) latexes having a ploy(methylphenyl siloxane) (PMPS) rubbery core with a T_g of –120 °C as well as a PMMA plastic shell, and it has the same particle size range with M-600. A random poly(styrene-co-maleic anhydride) (SMA) containing 8 wt % maleic anhydride with a number average molecular weight (M_n) of 120,000 was purchased from Zhengzhou Haizhu Technology and Trade Co. A solid epoxy resin (diglycidyl ether of bisphenol-A, DGEBA), EPI-CLON® 7050 with an epoxide equivalent weight of 1750–2100 g/equiv. was kindly supplied by Wuxi Bluestar Epoxy Co., China. Poly(hydroxyether of bisphenol-A) (Phenoxy) with an M_n of 18,000 was purchased from Beijing Chemical Reagents Co., China.

Preparation of PC blends

Recycled PC and the other additives were dried separately at 120 and 80°C, respectively, in a vacuum oven for 10 h. All components of the formulation were thoroughly premixed at room temperature and then were melt-blended using a twin-screw extruder (ZSK25-WLE, Werner & Pfleider, Germany). The screw speed was 200 rpm, and the temperatures at three zones of the barrel and at the die were 240, 250, 260, and 250°C, respectively. The extruded strings were cooled in a water bath and then pelletized. The pellets were dried again at 120°C before preparing the test bars for the measurement of combustion and mechanical properties.

Characterization

Measurements of mechanical properties

Notched impact, tensile, and combustion test bars were prepared via injection molding using a HFF120 × 2 screw injection machine; the barrel temperature was 275°C and the mold temperature was 65°C. Tensile properties were determined with a Jinjian XWW-20A universal testing machine using a 10,000 Newton load transducer according to the standard of ASTM D-638. Notched Izod impact strength was measured with a Sumitomo impact tester according to ASTM D256. The thickness of notched Izod impact specimens was 1/8 inch, and impact energy was 4 J. All the tests were done at room temperature and five measurements were carried out for each data point. The experimental error bars were also given to show a range of the data excluding the maximum and minimum values.

Measurements of flammability characteristics

The flammability of samples was first determined by limiting oxygen index (LOI) measurements using HD-2 oxygen index apparatus with a magneto-dynamic oxygen analyzer according to ASTM D2863 standard. The test bar with a size of 80 × 10 × 4 mm³ was clamped vertically in the center of the combustion chamber and ignited by a butane burner with a mixture of oxygen and nitrogen continuously going through with a flow rate of 171 mL/min. The flammability was determined by the minimum concentration of oxygen supplied for the combustion.

The flammability rating of samples was also determined through a vertical burning test in terms of the Underwriters Laboratory protocols for flammability of plastics (UL94) according to ASTM D3801 standard. The test bar with a dimension of 120 × 12.5 × 3 mm³ hung vertically over some surgical cotton was ignited by the Bunsen burner. Five test bars were tested for each sample. The sample achieves the UL94 classification of V-0 if total flaming combustion for each test bar stops within 10 s after two applications of 10 s each of flame to a test bar, and the cotton below the test bar is not ignited by the flaming drips.

Scanning electron microscopy

Scanning electron microscopy (SEM) was employed to observe the morphology of undeformed specimens. The injection-molded impact specimens were first broken in liquid nitrogen, and then were etched
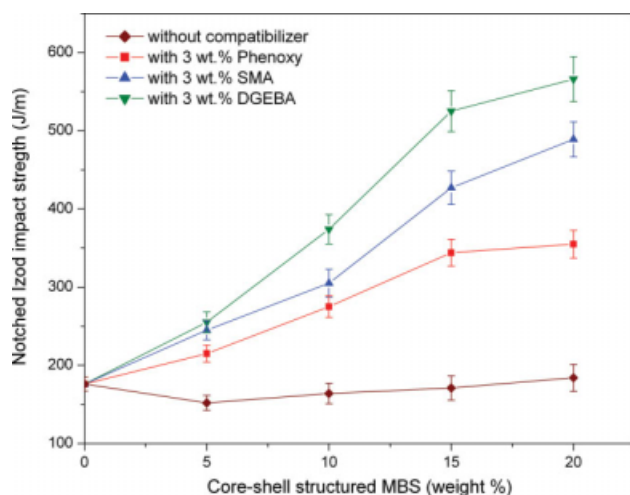
Figure 1 Notched Izod impact strength of the recycled PC blends with MBS and different compatibilizers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with boiled acetone to remove the core-shell latexes on the fracture surface. The cryogenic fracture surfaces were coated with a thin layer of gold-palladium and examined using a Hitachi S-4700 scanning electron microscope to observe the particle size and dispersion.

Transmission electron microscopy

The morphologies of the blends were also determined by transmission electron microscopy (TEM) using a Hitachi H-800 transmission electron microscope operating at an accelerating voltage of 200 kV. Ultrathin samples were obtained from molded specimens by microtoming perpendicular to the flow direction using a diamond knife at a temperature of –40°C. The microchips were stained using an aqueous solution of OsO_4 over a period of at least 9 h.

Thermogravimetric analysis

Thermal decomposition behavior was investigated by thermogravimetric analysis (TGA) using a Netzsch TG 209 F3 thermal analyzer. All measurements were performed under nitrogen with a heating rate of 20°C/min from 40 to 700°C. The sample weight was around 10 mg contained in aluminum sample cup.

RESULTS AND DISCUSSION

Impact resistance

The notched Izod impact strength of recycled PC and its blends with various amounts of core-shell impact modifiers and compatibilizers is presented in

Figures 1 and 2. It is well known that virgin PC has a high Izod impact strength of around 650 J/m.[34] However, recycled PC undertakes a great deterioration in impact toughness because of UV light, oxygen, and thermal aging, and its Izod impact strength only gains 172 J/m marked as a first data point in Figure 1. Therefore, the toughening of recycled PC is a major aim for its modification. However, when the core-shell structured MBS or MSiS as an impact modifier was introduced into recycled PC, the impact resistance was not improved significantly as expected. Even if the content of MBS rose to 20 wt %, the blends only showed a slight increase in Izod impact value. However, when 20 wt % MSiS was introduced into recycled PC, the impact strength decreased fairly. The overall variation trends of toughness against the MBS or MSiS content clearly show that the sole core-shell structured impact modifier cannot toughen recycled PC effectively. This result is a further indication of the failure to produce a toughness-improved material by this simple binary blending.

It is generally known that PC is immiscible with the PMMA shell of two impact modifiers, which may result in a poor interfacial adhesion between the two polymers, and thus, the phase separation between the recycled PC matrix and core-shell structured latexes. To improve the compatibility of recycled PC and the PMMA shell of two impact modifiers, DGEBA, SMA, and phenoxy as a compatibilizer were, respectively, incorporated into the binary blends. The molecular structures of these three compatibilizers are shown in Scheme 1 for understanding the rationality of their compatibilization between two polymers. Figures 1 and 2 clearly
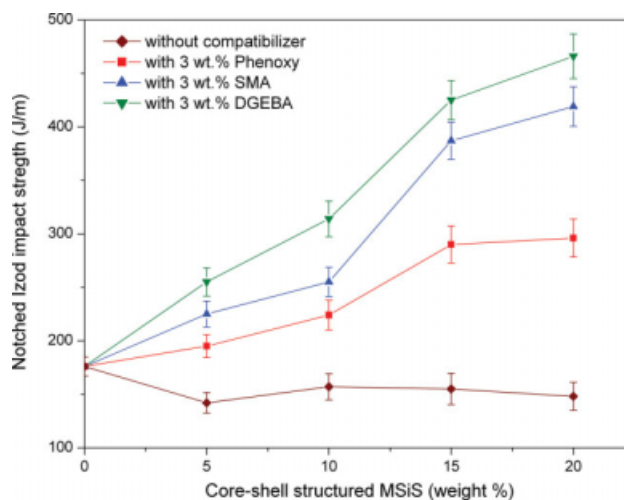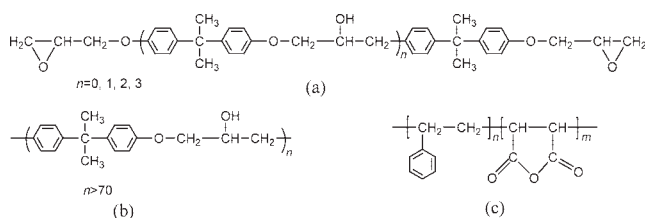

Figure 2 Notched Izod impact strength of the recycled PC blends with MSiS and different compatibilizers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 1 Schematic molecular structures of (a) DGEBA, (b) Phenoxy, and (c) SMA.

illustrate the effect of three compatibilizers on notched Izod impact strength of the recycled PC/MBS and recycled PC/MSiS binary blends, respectively. The results are fairly consistent with expectations. The recycled PC blends with MBS and MSiS achieved a significant improvement in impact resistance by addition of 3 wt % compatibilizer. It is evident that the presence of compatibilizer in the blends reduces the interfacial tension, introduces a steric hindrance to coalescence and can enhance the interfacial adhesion between PC phase and PMMA shell. Thus, the internal stress of the PC matrix transmits through the two phases more easily and the impact toughness of the compatibilized PC/MBS or MSiS blends is improved. Although three types of blends show much better toughness than the blends without compatibilizer, it is noticed that DGEBA exhibits an optimal compatibilizing effect for the recycled PC blends with MBS and MSiS among these three compatibilizers, which resulted in the most effective toughening of core-shell latexes for recycled PC. As shown in Scheme 1, DGEBA has a very similar structure with PC in their molecular chains, i.e. bisphenol-A segment, which makes the two polymers thermodynamically miscible. Meanwhile, many studies reported have indicated that DGEBA are thermodynamically miscible with PMMA[35–37]; therefore, DGEBA can generate a physically bridging effect between them. Furthermore, the polar hydroxyl and epoxide groups in DGEBA molecular chains can enhance the interaction between the molecules in blends. As a result, the compatibility of recycled PC and core-shell structured latexes was improved significantly. On the other hand, phenoxy has completely the same molecular structure with DGEBA, but a much longer molecular chain, so DGEBA has the much higher density of polar epoxide groups than phenoxy. Compared with Phenoxy, therefore, DGEBA can more effectively enhance the interaction between recycled PC and the PMMA shell of core-shell structured latexes, and consequently, the corresponding blends can achieve much better impact resistance. SMA also provides the strong enough interfacial adhesion and low enough interfacial tension between two polymers through the effectively physical interaction between the mol-

ecules in blends, so that it can enhance the toughening effect of core-shell structured latexes for recycled PC.

As is seen in Figures 1 and 2 the impact strength increases gradually with the increase of MBS or MSiS content with an aid of compatibilizers, and a weak ductile-brittle transition can be distinguished for the recycled PC blend containing 15 wt % impact modifier. It appears that there are three times as much as the notched Izod impact strength for the recycled PC/MBS blends in presence of compatibilizers, whereas there are only two times for the recycled PC/MSiS blends. It is obvious that the recycled PC blends with MBS show somewhat higher levels of toughness than the blends with MSiS, which is attributed to the fact that the rubbery core of MBS (i.e. PB) is more elastic than that of MSiS (i.e. PMPS). Figure 3 illustrates the effect of compatibilizer content on impact resistance for the recycled PC containing various core-shell structured impact modifiers, in which the first points mark the data of the blends without compatibilizers as a reference. It is found that the introduction of only 1 wt % compatibilizer could effectively enhance the compatibility of the recycled PC and the PMMA shell of the core-shell structured latexes, and thus, greatly improve the impact toughness of blends. Most of the blends exhibited maximal impact strength when 3 wt % compatibilizer was incorporated. This represents an optimal compatibilizing effect relative to the two components. However, three compatibilizers are rigid copolymers themselves, too much amount can increase the rigidity of blends. Therefore, there is a gradual decline as the compatibilizer increases continuously for three types of blends.
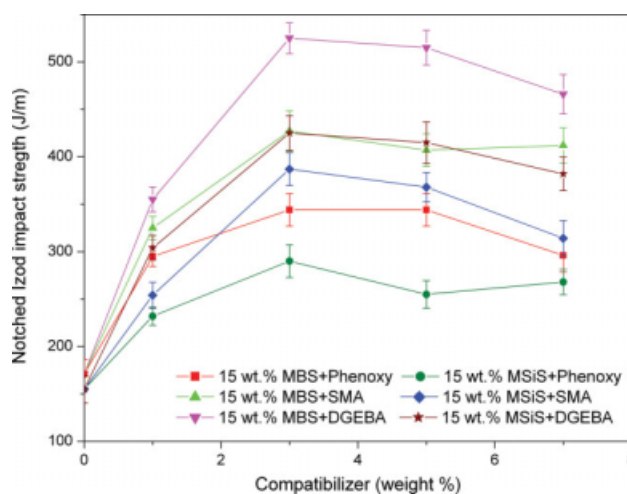

Figure 3 Notched Izod impact strength of the recycled PC/MBS and MSiS blends as a function of compatibilizer content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
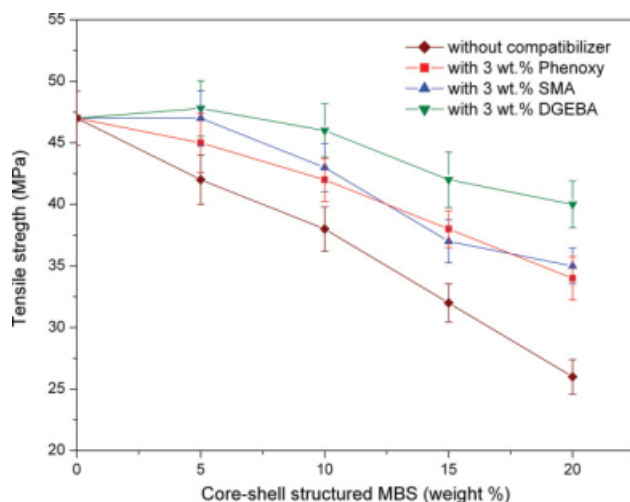
Figure 4 Tensile strength of the recycled PC blends with MBS and different compatibilizers. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Tensile properties

Tensile properties of the recycled PC blends containing various amounts of core-shell structured latexes and compatibilizers are shown in Figures 4–7 in which the first point mark the data of blends without any compatibilizers as a reference. Virgin PC is known for its high tensile strength of around 63 MPa; however, the recycled one suffers from deterioration in tensile strength (only about 47 MPa) as a result of a reduction in molecular weight because of aging and re-processing. Blending with core-shell structured latexes has potential advantages for improving impact resistance, but hopefully is not at the expense of losing the original tensile strength of
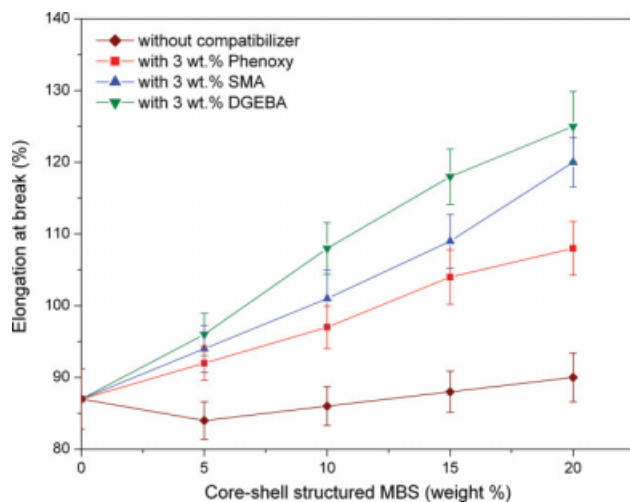
recycled PC. As shown in these figures, the tensile strength of recycled PC/MBS and MSiS binary blends decreases basically according to the addition rule of the amount of core-shell structured latexes, whereas the elongation at break is almost equal to that of recycled PC. In all cases, ternary blends containing compatibilizers show a smaller reduction in tensile strength compared with the binary ones without any compatibilizers. For example, Figures 4 and 5 show that the tensile strength of the recycled PC/MBS and MSiS blends is fairly affected by addition of 3 wt % compatibilizer, which leads to a significant increase in tensile strength. A reduction in tensile strength is to be expected by addition of core-shell structured latexes because of their soft rubbery cores. However, for the blends without any compatibilizers, the greater reduction noted is not expected just based on the dispersion of core-shell structured latexes alone but is more likely related to the interfacial adhesion of these impact modifiers in the PC matrix. It is obvious that the poor compatibility between two phases will lead to a greater loss in stiffness.

The recycled PC blends containing various compatibilizers exhibit very different tensile behaviors as shown in Figures 4–7. The blends containing DGEBA show a less loss in tensile strength and a significant improvement in elongation at break compared with the other two types of the blends, thus proving the interfacial adhesion imparted by compatibilizing effect of DGEBA is stronger than that of SMA and Phenoxy. An essential feature of the tensile properties (e.g. elongation at break) as a function of compatibilizer species is that experimental data in the interval DGEBA > SMA > Phenoxy are in accord with the impact toughness, which represent

Figure 5 Elongation at break of the recycled PC blends with MBS and different compatibilizers. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
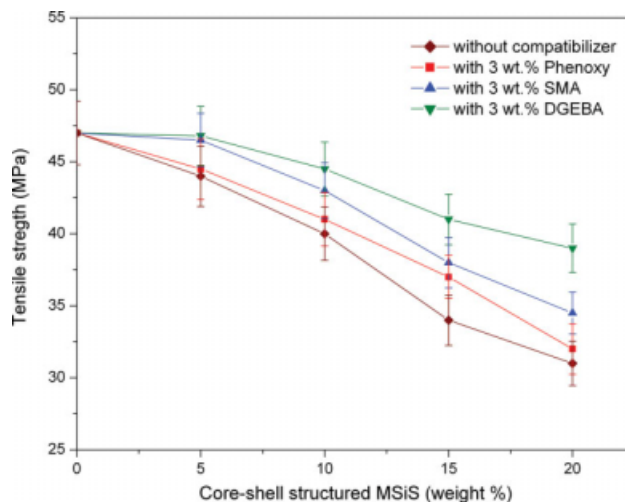

Figure 6 Tensile strength of the recycled PC blends with MSiS and different compatibilizers. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Figure 7 Elongation at break of the recycled PC blends with MSiS and different compatibilizers. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
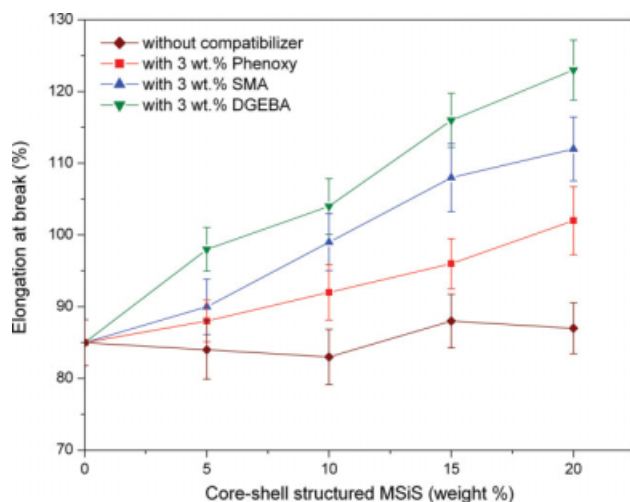
the compatibilizing effect by three compatibilizers. As impact strength can be correlated with the ability of polymer chains to execute segmental motion and hence dissipate the energy associated with crack propagation, an increase in elongation at break may also be responsible of the increase of impact strength.

Flame-retardant properties

Core-shell structured MSiS is not only an impact modifiers but also a flame retardant for the recycled PC because of its silicone-based rubbery core. It has

been reported that silicone-containing chemicals have a characteristic of high heat resistance and non-toxicity, which are considered to be "environment friendly" flame-retardant additives.[38-41] They release less amounts of toxic gasses in case of fire. Several types of silicone-containing additives have been proposed as flame retardants for PC, and some of them are of effective flame retardancy. The addition of relatively small amount of silicone-containing additive to PC can significantly improve its flame retardancy. Table I indicates the flame retardant properties of the recycled PC blends containing various amounts of MSiS and compatibilizers. It appears that recycled PC is a flammable material with a low LOI value of 25.5, and it only achieves a UL94 V-2 rating of flammability with flammable dripping. Incorporation of 3 wt % MSiS into the recycled PC resulted in an improvement in the LOI, but the blend still maintained the V-2 rating because of a few drips. As a result of an improvement in the LOI and a reduction of the total flaming time and maximum flaming time, the flame retardancy could be further enhanced with the increase of MSiS content, and thus the blend achieved a UL94 V-1 rating without any drips. It is found that the recycled PC blends with 10 wt % MSiS can achieve a UL94 V-0 rating. These results indicate that MSiS is able to provide good flame retardancy for recycled PC.

It appears that the silicone-based core of MSiS (i.e. PMPS) is an effective flame-retardant component in the current blending system, which provides non-flammability for recycled PC. There are some investigations on silicone derivatives as flame retardants for PC and its derivatives.[42-44] Iji et al. reported a

TABLE I
Flame-Retardant Properties of the Recycled PC and its Blends Based on MSiS

Sample	Composition (wt %)					Vertical burning test				
	Recycled PC	MSiS	DGEBA	SMA	Phenoxy	LOI (vol %)	UL94 rating	Flaming drips	Maximal flaming time (sec)	Total flaming time (sec)
1	100	–	–	–	–	25.5	V-2	Yes	22.5	109.8
2	97	3	–	–	–	26.1	V-2	Yes	18.8	74.0
3	95	5	–	–	–	27.9	V-1	None	13.2	64.3
4	93	7	–	–	–	28.5	V-1	None	11.4	45.8
5	90	10	–	–	–	29.7	V-0	None	7.2	28.5
6	94	3	3	–	–	27.5	V-1	None	16.6	61.0
7	92	5	3	–	–	28.2	V-1	None	11.3	48.8
8	90	7	3	–	–	30.2	V-0	None	7.1	35.9
9	87	10	3	–	–	31.5	V-0	None	4.2	18.1
10	94	3	–	3	–	27.6	V-1	None	14.0	67.8
11	92	5	–	3	–	28.4	V-1	None	11.6	51.3
12	90	7	–	3	–	29.8	V-0	None	9.2	43.5
13	87	10	–	3	–	31.2	V-0	None	4.3	21.6
14	94	3	–	–	3	27.2	V-1	None	15.2	70.4
15	92	5	–	–	3	28.1	V-1	None	12.5	50.2
16	90	7	–	–	3	29.2	V-0	None	8.6	45.3
17	87	10	–	–	3	30.4	V-0	None	6.5	30.2

special silicone with a branched structure, a phenyl-rich mixture of phenyl and methyl groups in the chain and methyl groups at the chain terminals to be effective in retarding the combustion of PC.[33] They proposed that the flame retardant effect of the branched silicone with methyl and phenyl was conducted by its rapid movement to the surface of PC to form the highly flame resistant char barrier during combustion. Hayashida et al. studied the flame retarding mechanism of PC with a trifunctional phenyl-rich silicone additive by pyrolysis-gas chromatography (PY-GC).[45] They suggested that the formation of the cross-linking structures between the PC substrates and the phenyl silicone additives might play an important role for the flame retardancy of the PC-silicone system. Only a very small degree of cross-linking results in heat release reduction that is sufficient enough to obtain a UL94 V-0 rating for recycled PC. The cross-linking also retards the dripping. A radical mechanism is described for the flame retarding process that occurs through homolytic Si–CH_3 bonds scission, which prevails at high temperatures and results in oligomers and methane release. Cross-linking of the macroradicals decreases the flexibility of the PMPS chain and hinders further splitting of cyclic oligomers. The thermal stability of this heavily cross-linked PMPS increases and reorganization of atomic bonds can take place with formation of black ceramic silicon-oxycarbide. Additionally, the molecular mechanism also implies Si–O bond scission that takes place at low temperature range and during slow heating, leading to the formation of cyclic oligomers. This process competes with oxidative cross-linking, which stabilizes the PC and also gives improvements in flame retardancy.

It is noteworthy from Table I that three types of compatibilizers (i.e. DGEBA, SMA, and Phenoxy) show a promise as a very effective adjunct for the flame retardancy of the recycled PC/MSiS blends. The MSiS when used in combination with these components can provide much higher LOI value and shorter total flaming time as well as maximum flaming time. It is discussed previously that the three compatibilizers can enhance the interfacial adhesion between recycled PC and the PMMA shell of MSiS and reduce the interfacial tension, and thus improve the dispersion of MSiS in the matrix. The superior flame retardant effect of MSiS obtained in this case is because of their excellent dispersion that leads to an accelerated migration toward the surface of PC during combustion, where they form a uniform and highly flame resistant barrier. The formation of highly flame-resistant char resulted from combination of polysiloxane and condensed aromatic compounds onto the surface of recycled PC. It is evident that the smaller the particle size of silicon-based component, the better sealing efficiency

the residual char has. For the recycled PC/MSiS blends without any compatibilizers, the aggregated MSiS has lower sealing efficiency of residual char because macro-sized component cannot cover on enough of the surface of the char. Therefore, the using level of MSiS is lower at about 7 wt % to obtain the V-0 rating in aid of compatibilizers. This loading level also preserves properties of recycled PC and in addition does provide impact resistance improvement while allowing the blends meeting UL 94 V-0 flame retardancy requirements.

Morphology

The degree to which core-shell structured latexes can be dispersed in the recycled PC matrix was examined using SEM described in the Experimental section. Figure 8 illustrates the morphology of the fracture surface of the recycled PC blends containing various amounts of MBS and compatibilizers, on which the holes left reflect the dispersion of MBS in the matrix after solution etching. Compared to the glossy surface of recycled PC as background [see Fig. 8(a)], the recycled PC/MBS binary blend shows a multiporous surface with nonuniform distribution of the hole size as shown in Figure 8(b). The MBS latexes have a particle size of around 0.2 μm. However, it is observed that the size of some holes is as large as around 2 μm, which is much larger than that of the MBS latexes. A very similar phenomenon can be observed for the recycled PC/MSiS binary blends as shown in Figure 9(a). This suggests that blends only based on MBS or MSiS have large aggregates of the latex particles because of the incompatibility between recycled PC and the PMMA shell of core-shell structured latexes. Incorporation of 3 wt % or more compatibilizer into the blends with MBS shows distinctly improved particle dispersion [see Fig. 8(c,e,f)]. It is clearly found that most of the MBS particles were monodispersed as individual latexes in the matrix from the half etched fracture surface as shown in Figure 8(d), and is also confirmed by the TEM images as shown in Figure 10. The SEM images of the fracture surface of the blends based on MSiS show quite similar morphological features to the corresponding composition of the recycled PC/MSiS as seen in Figure 9. However, the TEM images are unavailable because the rubbery core of MSiS does not contain any double bonds which can be stained for the observation by TEM.

The series of SEM images shown in Figures 8 and 9 give a visual impression of the degree of particle dispersion. It appears that the degree of particle dispersion is improved with the increase of compatibilizer content. Furthermore, the differences in particle dispersion for the blends containing different
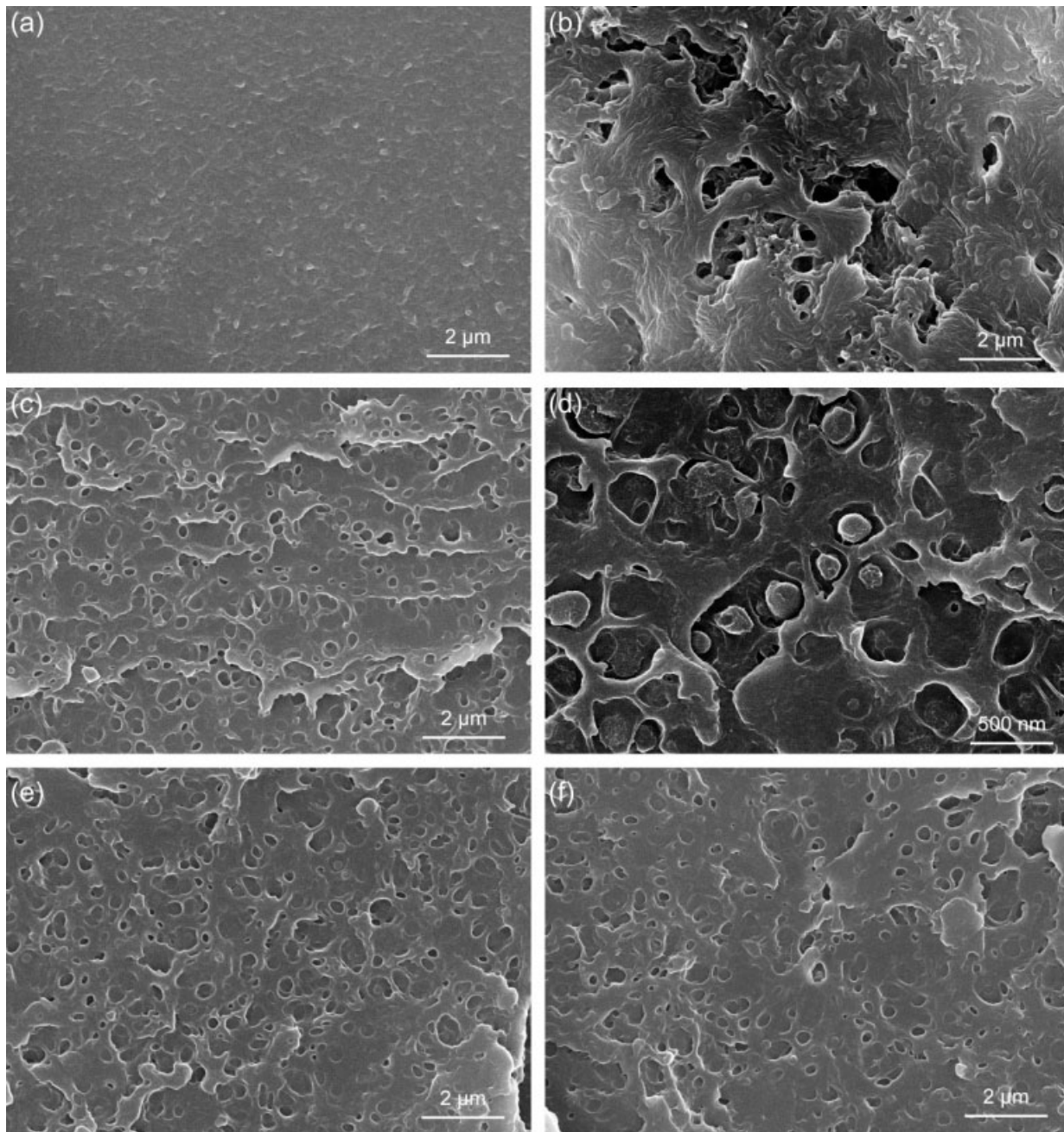
Figure 8 SEM images of the fracture surface of recycled PC and its blends with MBS and different compatibilizers: (a) neat recycled PC, (b) the blend with 15 wt % MBS, (c, d) with 15 wt % MBS and 3 wt % DGEBA, (e) with 15 wt % MBS and 3 wt.% SMA, and (f) with 15 wt.% MBS and 3 wt.% Phenoxy.

compatibilizer can also be noticeable. The recycled PC blends based on the impact modifiers and DEGBA show much better particle dispersion than the other two blending systems, while the blends with impact modifiers and Phenoxy still show a slight aggregation for the impact modifier particles, and thus achieve a least improvement in particle dispersion in three blending systems. As mentioned previously, the compatibilizing effect derived from the bridging combination of the recycled PC and

PMMA shell by DEGBA or Phenoxy. DGEBA contains a much higher concentration of polar epoxide groups than phenoxy because of its shorter molecular chains, and thus can lead to stronger interaction between two phases. Therefore, DGEBA provides much better compatibilizing effect for recycled PC/MBS or MSiS blends than Phenoxy. In addition, it is understandable that the more viscous the matrix, the larger the shearing stress that can be applied to aggregates of core-shell structured latexes for breaking
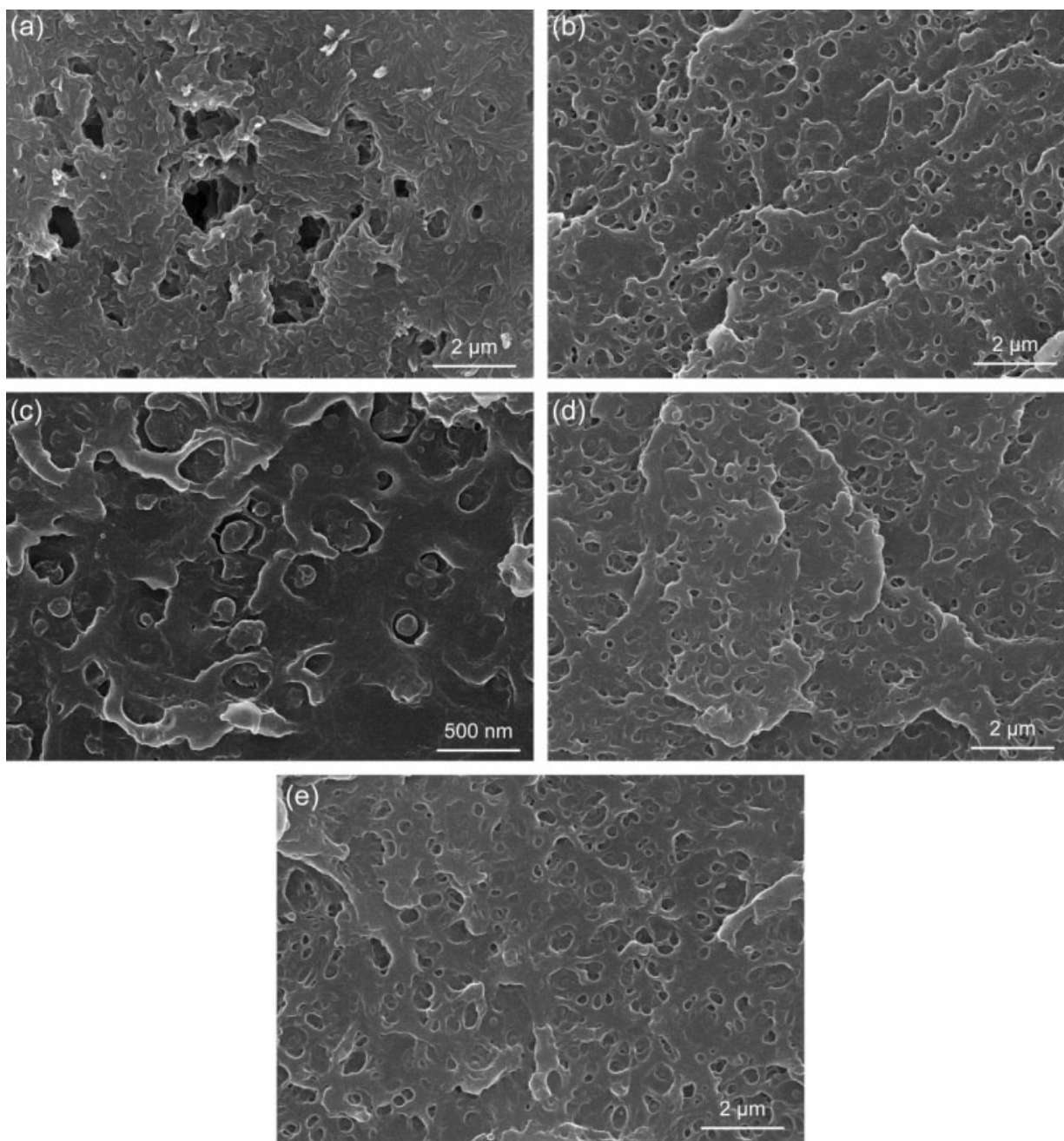
Figure 9 SEM images of the fracture surface of the recycled PC blends with MSiS and different compatibilizers: (a) the blend with 15 wt % MSiS, (b, c) with 15 wt % MSiS and 3 wt % DGEBA, (d) with 15 wt % MSiS and 3 wt % SMA, and (e) with 15 wt % MSiS and 3 wt % phenoxy.

them.[46–48] Thus, to some extent, the matrix viscosity is expected to play a role in the dispersion of core-shell structured latexes into PC assisted by SMA.

As is well known, impact resistance is very sensitive to the degree of the dispersion of impact modifier as well as the interfacial adhesion between two phases, and the higher toughness always correlates with the better dispersion of impact modifier. In the present study, the blends compatibilized with DGEBA achieved the good dispersion of core-shell structured latexes, and consequently they have supe-

rior impact strength compared to the other two blends. This result is in good agreement with the morphological observation. Furthermore, according to the morphological observation, the differences in particle dispersion for the blends containing the same compatibilizers are less evident when the compatibilizer content increases to 5 wt % or more, whereas, the impact strength is improvement continuously. This suggests that another contribution of compatibilizers to improving toughness is to enhance the interfacial adhesion.
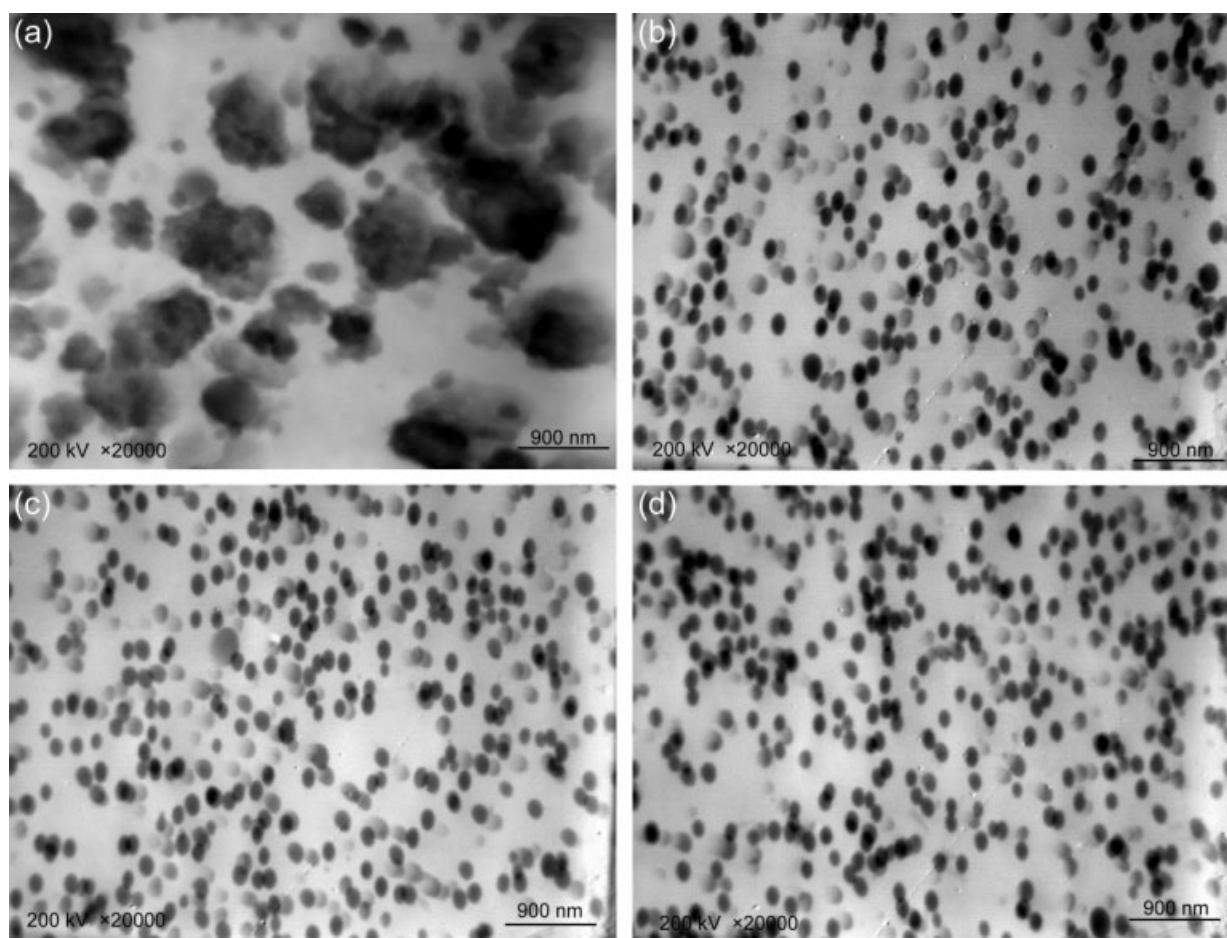
Figure 10 TEM images of the fracture surface of the recycled PC blends with MBS and different compatibilizers: (a) the blend with 15 wt %, (b) the blend with 15 wt % MBS and 3 wt % DGEBA, (c) with 15 wt % MBS and 3 wt % SMA, and (d) with 15 wt % MBS and 3 wt % phenoxy.

Toughening mechanism

Many reasons have been put forward to explain the toughening mechanisms in the core-shell structured impact modifier-toughened glassy polymers like PC, and it seems clear that there is no overriding mechanism responsible for these systems.[28] The presence of the core-shell structured impact modifiers in the PC matrix initiates a localized energy-absorbing mechanism from many sites rather than from a few isolated ones, in which recycled PC as a pseudoductile polymer can initiate cavitation as well as promote additional shear yielding during fracture process with relatively higher crack initiation energy but with a low crack propagation energy. The cavitation initiated by the core-shell structured latexes is to relieve the triaxial stress, i.e., inducing a transition from a plane strain condition to a plane stress condition around the crack tip. Once enough particle cavitation has occurred to relieve the triaxial stress, the yield region will extend, and the thus the impact energy can be dissipated by the matrix. Pitman et al.[49] have accounted for the phenomenon observed in PC in terms of a competition between shear yielding and crazing, with shear yielding promoting ductile behavior and crazing causing brittle fracture. Newman and Strella[50] suggested that the principal function of rubber particles is to produce sufficient triaxial tension in matrix so as to increase the local free volume and, hence, the shear yielding. A key issue in whether toughening occurs in plane stress or plane strain conditions is the relative size of the yield zone in the absence of impact modifier versus the size of the cavitation zone when modifier particles are present. Simple model calculations in the vicinity of a crack tip were performed to estimate the size of the yield and cavitation regions under both plane stress and plane strain conditions. Two modes of rubber-toughening mechanisms, localized and mass shear yielding, function simultaneously. The plane-strain localized shear yielding involves a volume much smaller than the plane-stress mass shear yielding. The single most important factor in determining the ductile-brittle transition is the strain at crack initiation, and any effort to
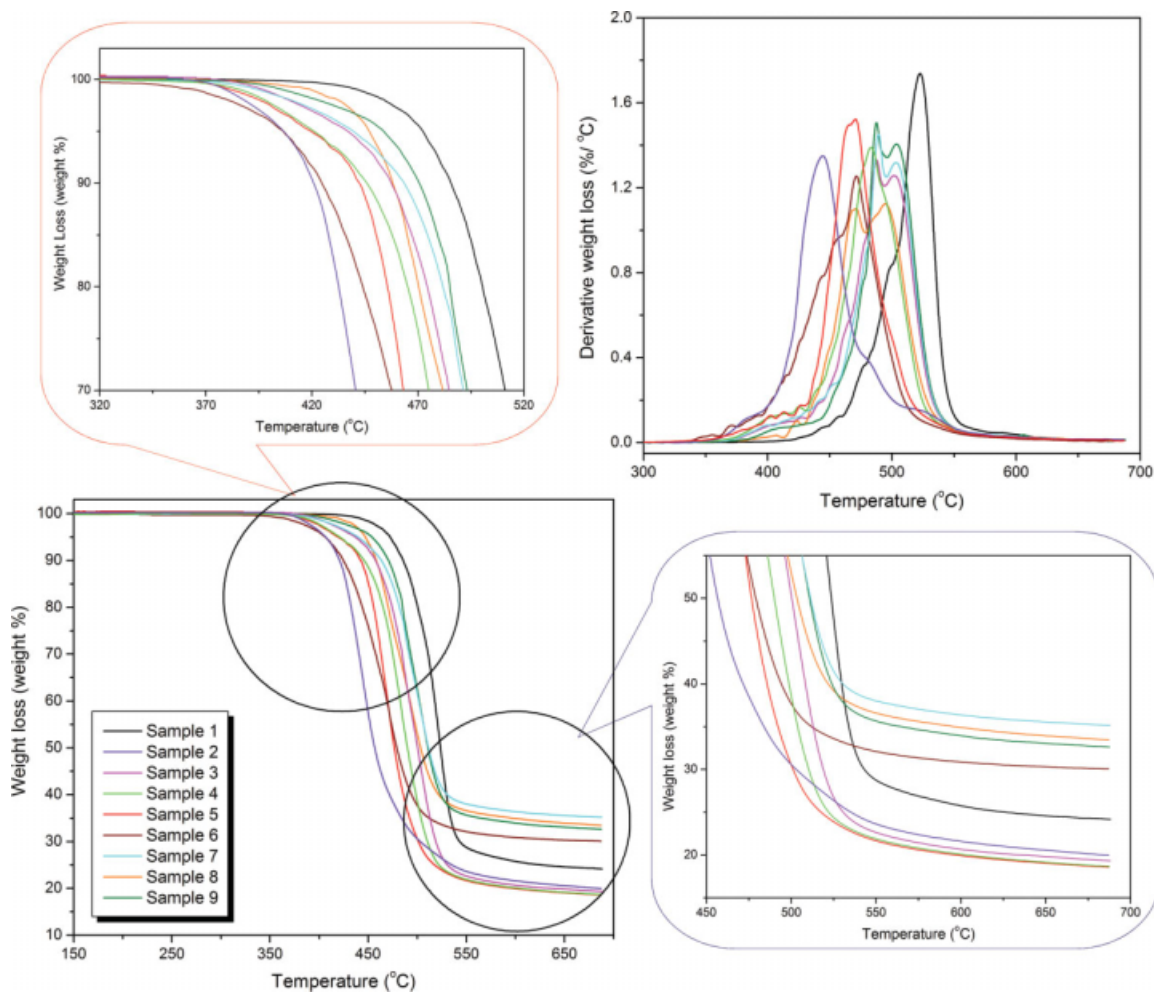
Figure 11 TGA and DTG of thermograms of recycled PC and its blends with different core-shell structured latexes and compatibilizers; the sample codes correspond to the compositions listed in Table II. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

toughen pseudoductile matrices is to delay or retard crack initiation for allowing the growth of the pre-crack plastic zone over its critical value.[11–13,16,51,52] In the case of the core-shell structured impact modifier-toughened PC, it is already concluded that while the cavitation of rubber particles does absorb energy, the enhanced plastic deformation of matrix is the major energy absorbing mechanism. This is not to say that the cavitation of rubber particles is unimportant. Rubber particles must cavitate before the

TABLE II
Thermal Properties of the Recycled PC and its Blends Obtained from the TGA Experiments

Sample	Composition (wt/wt/wt)	Temperature at characteristic weight loss (°C)		Temperature at rapid weight loss (°C)	Char yield at 600°C (wt %)
		2 wt %	10 wt %		
1	Neat recycled PC	454.3	485.6	522.5	24.2
2	Recycled PC/MBS (85/15)	388.2	420.9	444.3	19.9
3	Recycled PC/MBS/DGEBA (82/15/3)	409.3	457.4	487.9	19.3
4	Recycled PC/MBS/SMA (82/15/3)	397.9	445.7	483.2	18.7
5	Recycled PC/MBS/Phenoxy (82/15/3)	395.5	442.1	470.6	18.5
6	Recycled PC/MSiS (85/15)	380.7	424.7	471.2	30.0
7	Recycled PC/MSiS/DGEBA (82/15/3)	410.3	463.5	488.5	35.1
8	Recycled PC/MSiS/SMA (82/15/3)	432.6	458.2	471.3	33.5
9	Recycled PC/MSiS/Phenoxy (82/15/3)	423.1	470.2	487.5	32.6

stress state for brittle fracture of PC is reached in order to enhance the fracture toughness.[17]

Thermogravimetric analysis

Thermal degradation behaviors of the recycled PC blends containing various core-shell structured latexes and compatibilizers were evaluated by TGA with a temperature range from room temperature to 700°C. The TGA thermograms are shown in Figure 11, and the data obtained from TGA measurements are listed in Table II. The thermal decomposition of recycled PC is observed to occur at a higher temperature of above 500°C than those of many other polymers, indicating a good thermal stability even after processing and use. However, the TGA thermograms and obtained data of recycled PC/MBS and MSiS binary blends show a significant decline in decomposition temperatures at 2 wt %, 10 wt %, and rapid weight losses, indicating that these two core-shell structured impact modifiers have much lower thermal stabilities than recycled PC. Meanwhile, it is notable that the blend with MSiS degraded at a higher temperature than that with MBS, and also obtained a higher char yield at 700°C. This suggests its positive contribution to the flame-retardancy of recycled PC.

Some evident characteristic changes could be found from the TGA thermograms when the compatibilizers were incorporated into recycled PC/MBS and MSiS blends. All the blends containing the compatibilizers undergo a degradation process following the higher temperatures at characteristic and rapid weight losses than those without compatibilizers. It seems that the presence of compatibilizers thermally stabilizes these blends and thus results in an improvement in decomposition temperatures. Evidently, the addition of the compatibilizers is not a sample sum of the contributions from three components. Some interactions among these components during thermal degradation should be considered. The possibility of interactions is already supported by SEM observation. It is noteworthy that all the blends based on MSiS achieved higher char yields than recycled PC, and the amount of these thermal degradation residues increased with addition of compatibilizers. This suggests that an increase in carbonization leads to an improvement in flame retardancy of recycled PC/MSiS blends by incorporation of compatibilizers. In addition, Figure 11 shows the derivative TG (DTG) presenting a rate of weight loss as a function of the temperature in TGA. It is clearly illustrated that the maximum rates of the thermal decomposition decrease with introduction of compatibilizers, indicating that the high flame retardancy of recycled PC/MSiS blends is also resulted from the fast formation of char layer on the surface by slowly decomposing PC. These results are in good agreement with the previous study on flame retardancy.

CONCLUSIONS

Recycled PC cannot be effectively toughened by simple melt-blending with MBS or MSiS, since they fail to disperse uniformly in the PC matrix because of inadequate compatibility between PC and the PMMA shell of core-shell structured latexes. When DGEBA, SMA, and Phenoxy as compatibilizers were respectively incorporated into the blends, notched Izod impact strength can be improved significantly. The presence of compatibilizers in the blends reduces interfacial tension, introduces a steric hindrance to coalescence, and can enhance the interfacial adhesion between PC phase and the PMMA shell. With the aid of compatibilizers, the dispersion of core-shell structured particles in the PC matrix is improved greatly. Thus, the ternary blends achieve a good impact resistance when cavitation of the particles relieves the triaxial stress and promotes massive shear yielding of the matrix, and then enables the matrix to fracture by the plane stress ductile tearing mode. In addition, MSiS also plays a role as a flame retardant in recycled PC. The blends containing 7 wt % MSiS and 3 wt % compatibilizer can achieve a UL94 V-0 rating in vertical burning test. The good flame retardancy obtained is attributed to the fine dispersion of the MSiS particles in the PC matrix, which results in a rapid migration of MSiS to the surface of PC during combustion, where they form a uniform and highly flame resistant char barrier.

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