Synthesis of an Acrylate Elastomer with UV Stabilization and Its Application in Polyoxymethylene

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ABSTRACT: In this study, an acrylate elastomer with light-stable functional groups was synthesized by methyl methacrylate (MMA), butyl acrylate (BA), and a polymerizable UV stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxyl-proroxy) benzophenone (BPMA) via emulsion polymerization, and the product was poly[methyl methacrylate-*co*-butyl acrylate-*co*-2-hydroxy-4-(3-methacryloxy-2-hydroxylproroxy) benzophenone] [poly(MMA-*co*-BA-*co*-BPMA)]. The composition and characteristics of poly (MMA-*co*-BA-*co*-BPMA) were determined by using Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), and ultraviolet–visible absorption spectroscopy (UV–vis). Further, the obtained poly(MMA-*co*-BA-*co*-BPMA) was blended with polyoxymethylene (POM) to modify its photostabilization, as well as the mechanical properties of POM composite were tested before and after UV irradiation. The result showed that poly(MMA-*co*-BA-*co*-BPMA) can be dispersed well in the POM matrix, which could play a role of improving compatibility with and toughening for POM, and its light-stable functional groups could increase the UV resistance of POM composite. Mechanical properties of modified POM were kept well with higher impact strength and elongation at break than pure POM after UV irradiation. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2609–2615, 2012

Key words: UV stabilizer; acrylate elastomer; degradation; toughening; polyoxymethylene

INTRODUCTION

Polyoxymethylene (POM), being a highly crystalline material, is an important engineering resin widely used in industrial, transportation, agricultural, and construction because of its high strength, stiffness, and excellent chemical resistance. However, its poor anti-UV aging limits its applications, and mechanical properties declined seriously after UV irradiation, especially, the impact strength and elongation at break. Generally, improving photostabilization of such engineering resins is accomplished by adding a small amount of photostabilizers, but the compatibility between low molecular additives and POM matrix is not very good and the interfacial interactions are weak, which make the impact toughness of POM decrease further.[1–5] At the same time, problems such as migration, volatility, and solvent extraction will inevitably occur. To resolve such problems, many approaches have been developed, such as preparing reactive UV stabilizer and high-molecular weight UV stabilizer.[6–12]

In this study, we prepared a high-molecular weight UV stabilizer poly[methyl methacrylate-*co*-butyl acrylate-*co*-2-hydroxy-4-(3-methacryloxy-2-hydroxylproroxy) benzophenone] [poly(MMA-*co*-BA-*co*-BPMA)] by the copolymerization of a reactive UV stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxylproroxy benzophenone) (BPMA) with acrylic monomers [methyl methacrylate (MMA) and butyl acrylate (BA)] to ameliorate the compatibility between UV stabilizer and POM matrix. At the same time, POM was toughened by poly(MMA-*co*-BA-*co*-BPMA) for its elasticity.

EXPERIMENTAL

Materials

2, 4-Dihydroxybenzophenone (UV-0) (purity above 99.5%), provided by Jinchun Meibang Chemical (Wuhan, China), was used as received without further purification. Analytical reagent grade NaOH, Sodium dodecanesulfonate (SDS), alkylphenol polyoxyethylene(OP-10), Ammonium persulfate (APS), tetrahydrofuran (THF; analytical reagent), and calcium chloride (CaCl$_2$; analytical reagent) were provided by Kelong Chemical Reagent Factory of China (Chengdu, China). Methyl methacrylate (MMA; analytical reagent) and butyl acrylate (BA; analytical reagent), which were provided by Kelong Chemical

Reagent Factory of China, were distilled before application. UV stabilizer 2-hydroxy-4-(3-methacryloxy-2-hydroxylproroxy) benzophenone (BPMA) was synthesized according to patent.[13] Commercial polyoxymethylene copolymer (POM), with weight-average molecular weight (M_w) as 1.16×10^5 g/mol and melting temperature (T_m) as 165°C–167°C, was procured from YunTianHua Corp. of China. Water was deionized twice before use.

Preparation of poly(MMA-*co*-BA-*co*-BPMA), poly[methyl methacrylate-*co*-butyl acrylate] [poly(MMA-*co*-BA)]

Poly(MMA-*co*-BA-*co*-BPMA) was obtained through emulsion copolymerization of MMA, BA, and BPMA in a weight ratio (12 : 26 : 6). The process for preparation of poly(MMA-*co*-BA-*co*-BPMA) was shown as follows. First, BPMA (6 g) was dissolved in MMA (12 g) and BA (26 g). The mixture of MMA, BA and BPMA, SDS (1.6 g), OP-10 (0.4 g), and deionized water (130 mL) were placed in a four-necked round-bottom flask equipped with a thermometer, a stirrer, a ventilation pipe, and a refluxing condensation pipe to prepare poly(MMA-*co*-BA-*co*-BPMA) emulsion. APS (0.37 g) was dissolved in deionized water and then added to the emulsion. The reaction was carried out at 80°C for 3 h. After being coagulated with 5% CaCl$_2$ aqueous solution, poly(MMA-*co*-BA-*co*-BPMA) was purified by deionized water. The final product was dried under 70°C in vacuum drying oven. Poly(MMA-*co*-BA) was prepared by the same method without BPMA in the feed.

Preparation of POM/poly(MMA-*co*-BA-*co*-BPMA) composite, POM/poly(MMA-*co*-BA) + UV-0 composite

POM/poly (MMA-*co*-BA-*co*-BPMA) composite was prepared by the melt blending method. The poly (MMA-*co*-BA-*co*-BPMA) and antioxidant (Irganox 1010, Ciba, Switzerland) were melt-mixed with POM through a twin-screw extruder at 170°C–180°C. The test specimens for mechanical properties determination were prepared by injection molding. POM/poly(MMA-*co*-BA) + UV-0 composite was prepared by the same method.

UV irradiation of POM/poly(MMA-*co*-BA-*co*-BPMA) composite, POM/poly(MMA-*co*-BA) composite

POM samples containing 13 wt % poly(MMA-*co*-BA-*co*-BPMA) were placed in an exposure unit using two 500-W Ga–In source lamp with a maximum intensity at 365 nm. The intensity of irradiation was 5.41 W/m^2, measured using an UV irradiance meter model UV-A tester (Photoelectric Instrument Factory

of Beijing Normal University, Beijing, China). The irradiation test was taken at 55 ± 2°C with air circulation. Samples were removed at different intervals. The POM samples containing 12 wt % poly(MMA-*co*-BA) and 1 wt % UV-0 and the pure POM samples were measured by the same method.

Measurements and characterization

Fourier transform infrared measurement

Before the Fourier transform infrared (FTIR) measurements, poly(MMA-*co*-BA-*co*-BPMA) was Soxhlet-extracted with refluxing deionized water for 72 h. FTIR measurements of sample was carried out on a Nicolet 560 FTIR spectrometer (Thermo Nicolet Corp.). The measurement was performed in transmission.

High-resolution ^{1}H-NMR measurement

High-resolution ^{1}H-NMR spectrum was recorded on a Varian INOVA-400 spectrometer of 400 MHz. Deuterated chloroform was used as solvent, and tetramethylsilane was used as internal standard.

Ultraviolet–visible (UV–vis) measurement

The UV–vis absorption spectra of poly(MMA-*co*-BA-*co*-BPMA) was characterized with a T6 UV–vis spectrophotometer (PERSEE Corp., Beijing) in the range of 200–600 nm with THF as the solvent.

DSC characterization

For the DSC analysis, a TA Q200 with nitrogen as the purge gas was used. Powder samples scraped from the surface of POM composite were analyzed by heating from 50°C to 200°C at a rate of 10°C/min, and their heats of fusion (H_f) were derived to calculate the degree of crystallinity as below:

$$C = H_f/H_{f0}$$

where H_{f0} is defined as the heat of fusion of a 100% crystalline polyacetal (assumed to be 390 J/g, based on the standard enthalpy of POM in the database of Proteus Thermoanalysis Software provided by NETZSCH Co.).

Mechanical testing

The mechanical properties of the POM composites were characterized by a tensile test according to ISO 527-2: 1993 on a RGM-X010 test machine (Shenzhen Reger instrument Co., China) with 10-kN load cell. The crosshead speed was 50 mm/min, and average values of five measurements are reported. A UJ-40 tester (Chengde Testing Machine Factory, Hebei,
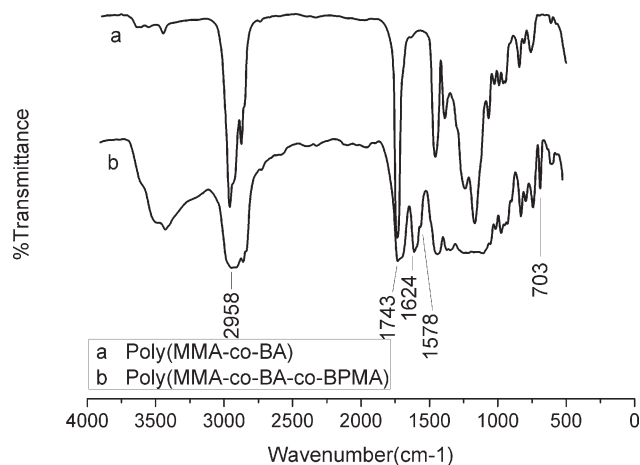
Figure 1 FTIR spectra of poly(MMA-*co*-BA-*co*-BPMA) and poly(MMA-*co*-BA).

China) was used for measuring notched Izod impact strength according to ISO 180:2000. All the tests were performed at 20°C and 65% relative humidity.

Scanning electron microscope observation

Scanning electron microscope (SEM) observation of a fractured surface after notched impact test was performed using a KYKY-2800 SEM. Prior to SEM investigation, specimens were immersed in THF for 24 h at room temperature to eliminate the poly (MMA-*co*-BA-*co*-BPMA) phase.

RESULTS AND DISCUSSION

FTIR analysis of the poly(MMA-*co*-BA-*co*-BPMA) elastomer

Research[11] shows that BPMA is easy to copolymerize with MMA, and they have a similar reactivity. It is attributed to the structure of BPMA because a 3-methacryloxy-2-hydroxylpropoxy group existed at 4-position of BPMA. The methacryloxy group is so far away from the benzophenone group that there is no steric hindrance effect in the copolymerization. Meanwhile, MMA, BA, and BPMA have a similar acrylate structure with high reactivity, and they can easily react with each other to prepare random copolymer.

   To confirm the polymerization of MMA, BA, and BPMA, FTIR measurement was used. The FTIR spectra of poly(MMA-*co*-BA-*co*-BPMA) and poly(MMA-*co*-BA) are shown in Figure 1. The absorption of the benzene ring of poly(MMA-*co*-BA-*co*-BPMA) at 1578, 1453, 756, and 703 cm^{-1} is shown in [Fig. 1(b)], whereas the absorptions at 1578 and 703 cm^{-1} cannot be found in the spectrum of poly(MMA-*co*-BA) [Fig. 1(a)]. The absorption of the carbonyl groups of poly(MMA-*co*-BA-*co*-BPMA) at 1744 and 1624 cm^{-1}

can be attributed to the carbonyl group (C=O) of BA and MMA and the ketone carbonyl group (C=O) of BPMA, respectively. However, the 1624 cm^{-1} absorption cannot be found in the spectrum of poly(MMA-*co*-BA). Also, the characteristic absorption bands of CH$_3$— at about 2957 cm^{-1} can be seen in Figure 1. According to the analysis of FTIR, it can be concluded that poly(MMA-*co*-BA-*co*-BPMA) was successfully synthesized through copolymerization of MMA, BA, and BPMA.

High-resolution ^{1}H-NMR of the poly(MMA-*co*-BA-*co*-BPMA) elastomer

The chemical structures of poly(MMA-*co*-BA-*co*-BPMA) were characterized by H^1-NMR, which is shown in Figure 2. The molecular structure of poly (MMA-*co*-BA-*co*-BPMA) is shown in Scheme 1. Hydrogen atoms of poly(MMA-*co*-BA-*co*-BPMA) are marked using a, b, c, and d. The peaks at $\delta = 0.94$–1.38 ppm and $\delta = 1.82$–2.11 ppm are ascribed to α-CH$_3$ and —CH$_2$—, respectively. The peaks at about $\delta = 3.59$ ppm are vested to —OCH$_3$ and $\delta = 3.92$–4.05 ppm pertaining to five protons of —CH$_2$—CH—CH$_2$—. The peaks at 7.50–7.63 ppm and $\delta = 6.34$–6.56 ppm are due to aromatic protons, and the peaks at $\delta = 12.60$–12.63 ppm are vested to —OH. These data help us prove that the structure of poly(MMA-*co*-BA-*co*-BPMA) is a copolymer.

UV–vis absorption spectroscopy analysis

In this study, the main purpose is to synthesize a high-molecular weight UV stabilizer to modify the photostability of POM. It is necessary to characterize the UV absorbance of poly(MMA-*co*-BA-*co*-BPMA). The UV–vis absorption spectra of poly(MMA-*co*-BA-*co*-BPMA) and poly(MMA-*co*-BA) are shown in Figure 3. Figure 3(a) shows absorption peaks of
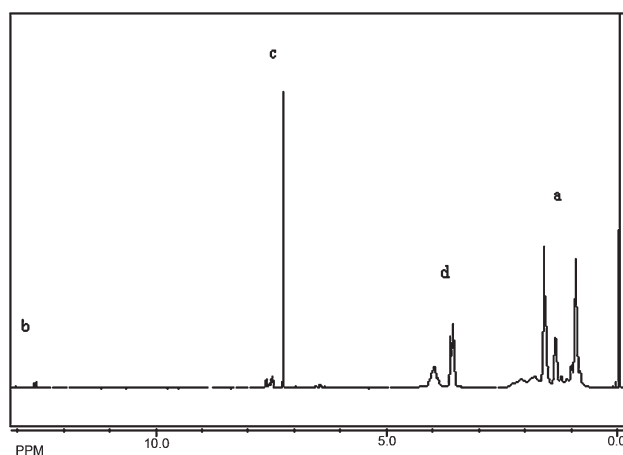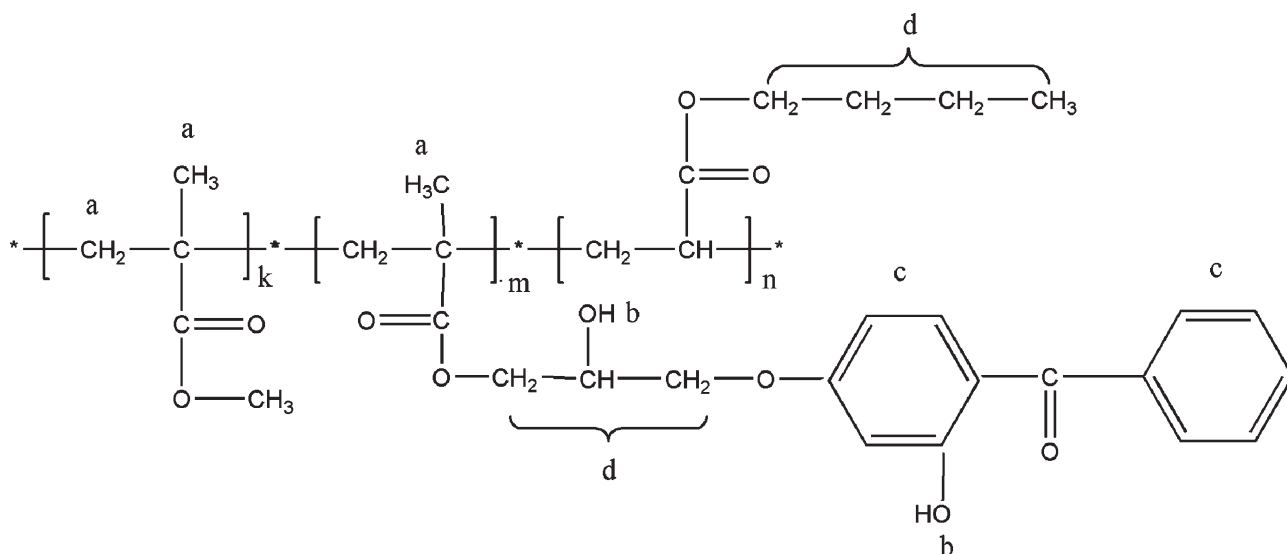

Figure 2 The ^{1}H-NMR spectrum of poly(MMA-*co*-BA-*co*-BPMA).

Scheme 1 Molecular structure of poly(MMA-co-BA-co-BPMA).

poly(MMA-co-BA-co-BPMA) at 295 and 322 nm that are due to the π→π* and n→π* transition, respectively, appears at the curve of PBPMA reported in previous research.[11] A peak at 246 nm ascribed to the n→π* transition of C=O group appears at the curve of poly(MMA-co-BA-co-BPMA), while the peak is shifted to 244 nm in poly(MMA-co-BA) [Fig. 3(b)] because of the addition of BPMA onto the polymer chains. However, the peaks at 295 and 322 nm do not exist in the UV absorption spectrum of poly(MMA-co-BA), which shows no UV absorbance in poly(MMA-co-BA). Therefore, it indicates that when BPMA was copolymerized with MMA and BA, the BPMA can retain its UV absorbance. The obtained copolymer has stronger UV resistance

at 295 and 322 nm, which is useful for protecting POM from UV degradation.

Morphological characteristic

The morphological structure of solvent etched fractured surface of POM/poly(MMA-co-BA-co-BPMA) blend is shown in Figure 4. The SEM micrograph for POM blend with 13 wt % poly(MMA-co-BA-co-BPMA) clearly demonstrates two-phase morphology as shown in Figure 4. The holes on the surface represent the poly(MMA-co-BA-co-BPMA) phase. As shown, a homogenous distribution of poly(MMA-co-BA-co-BPMA) phase in POM matrices can be achieved. On the basis of the micromorphology of
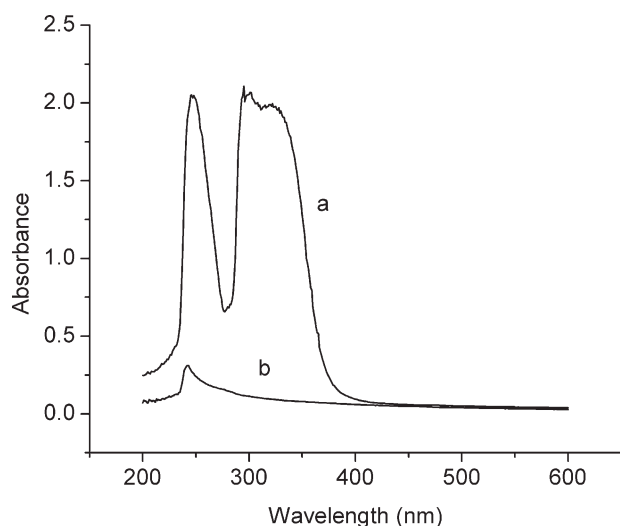

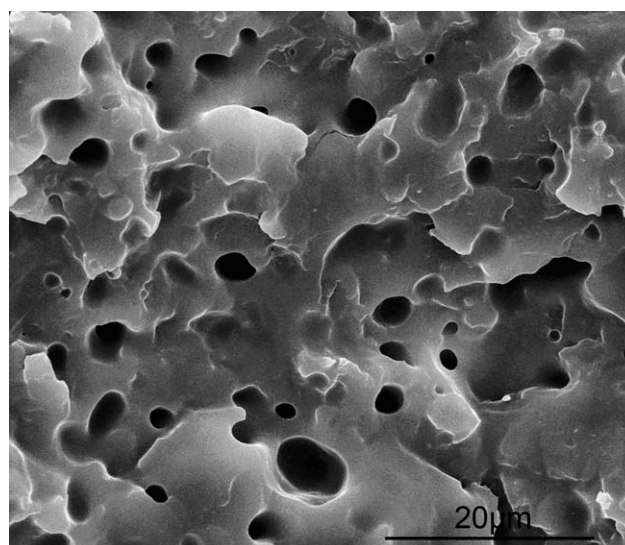**Figure 3** The UV–vis absorption spectra of poly(MMA-co-BA-co-BPMA) and poly(MMA-co-BA).

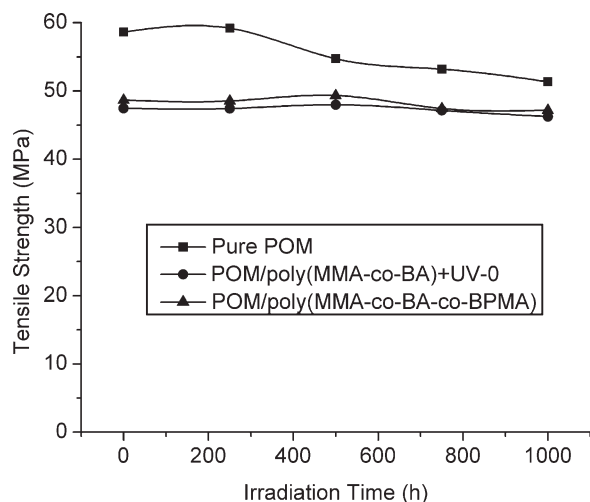**Figure 4** SEM micrograph of fracture surface of POM/13 wt % poly(MMA-co-BA-co-BPMA) blends.

Figure 5 Tensile strength of POM blends before and after UV irradiation, error bars show one standard deviation.

poly(MMA-*co*-BA-*co*-BPMA), particles are separated in the POM. It can be concluded that by means of melt-mixing, these particles can be dispersed well in the POM matrix.

Mechanical properties of POM modified by poly(MMA-*co*-BA-*co*-Bpma)

POM resin is sensitive to UV irradiation, resulting in degradation, especially in the wavelength of 280–400 nm, which will lead to the rapid deterioration of material performance. Especially, the impact strength and elongation at break of material decline seriously. Therefore, while toughening the POM effectively, improve that POM's resistance to UV irradiation, have already become an urgent issue. Poly(MMA-*co*-BA-*co*-BPMA) is a high-molecular weight UV stabi-
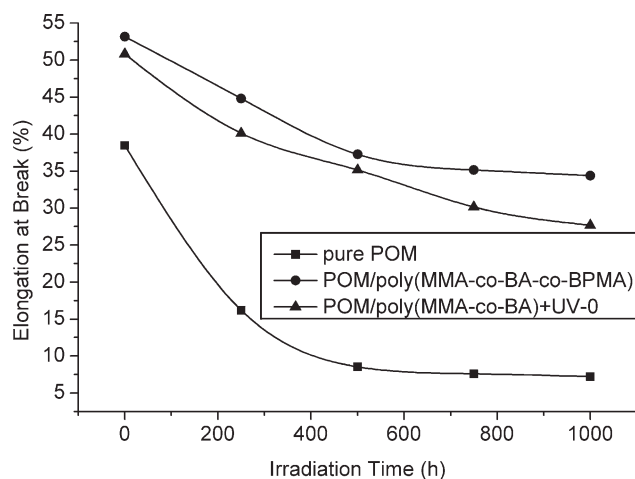
lizer prepared by copolymerization of MMA, BA, and BPMA and at the same time is a acrylate elastomer that can be used to improve the impact toughness of POM matrices.

The changes in mechanical properties of POM/13 wt % poly(MMA-*co*-BA-*co*-BPMA) blends before and after UV irradiation are shown in Figures 5–7. For comparison, pure POM and POM blend with same amount of poly(MMA-*co*-BA) and UV-0 instead of poly(MMA-*co*-BA-*co*-BPMA) were used. According to the curves in Figure 5, compared with that of pure POM, the tensile strength of POMs blend with acrylate elastomers decreased slightly before UV irradiation. However, all samples have a higher tensile strength after UV irradiation. At the same time, the POM/poly(MMA-*co*-BA-*co*-BPMA) composite has a higher tensile strength than POM/poly(MMA-*co*-BA)+UV-0, which can be attributed to poly(MMA-*co*-BA-*co*-BPMA) elastomer, which grafted light stability of function groups has better compatibility with POM than poly(MMA-*co*-BA) and UV-0. It is also found from Figure 5 that the tensile strength of pure POM after UV irradiation 200 h is higher than that of pure POM before UV irradiation, which conforms to our previous reports.[14] The main reason is that POM recrystallized under the UV irradiation and thermal oxidative environment in the early stage of aging. The tensile strength of modified POMs increased after about UV irradiation 500 h, which comes later compared with pure POM. This phenomenon is mainly due to the additives improve the light stability of POM to a certain extent.

Figure 6 illustrates the effect of poly(MMA-*co*-BA-*co*-BPMA) on the elongation at break in modified POM before and after UV irradiation. For pure POM, the elongation at break declined rapidly during the initial of aging, and then dropped smoothly
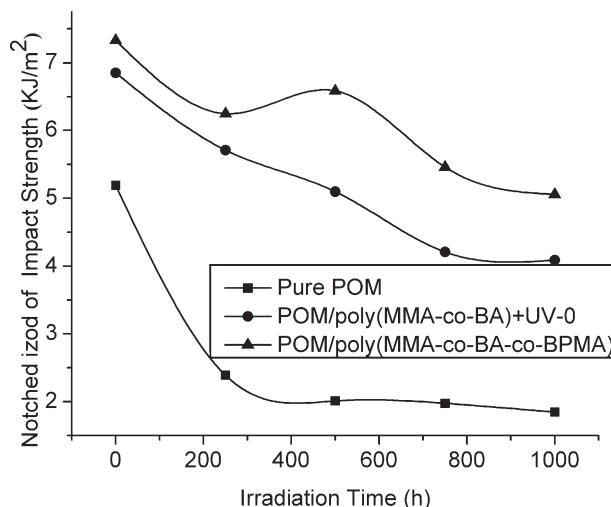

Figure 6 Elongation at break of POM blends before and after UV irradiation, error bars show one standard deviation.

Figure 7 Notched izod of impact strength of POM blends before and after UV irradiation, error bars show one standard deviation.
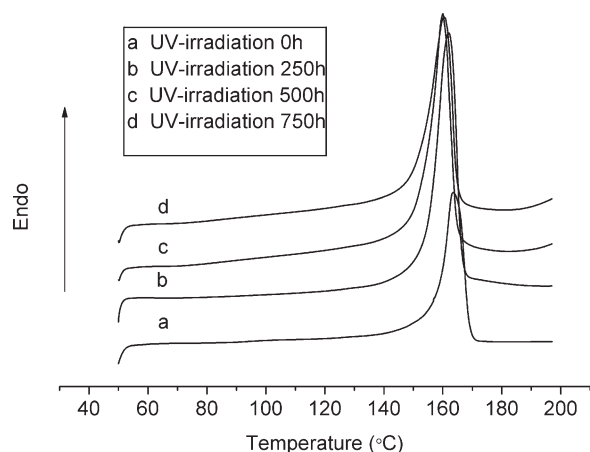
Figure 8 DSC curves of exterior part of POM/13 wt % poly(MMA-*co*-BA-*co*-BPMA) blend.

after 500-h UV irradiation, but only a 7.24% elongation at break was left. There was no longer yield phenomenon in tension, it belonged to brittle fracture. Because of the elastomer, the modified POMs remained higher elongation at break, which more than 25% after 1000-h UV irradiation, and the tensile fracture process was a ductile fracture. Before UV irradiation, the elongation at break of POM modified by poly(MMA-*co*-BA-*co*-BPMA) has reached 53%, which is almost the same as that of POM-modified by poly(MMA-*co*-BA) and UV-0. This illustrates that poly(MMA-*co*-BA-*co*-BPMA) plays a toughening effect on POM as a elastomer. After aging test, its retention rate of elongation was higher than that of elongation of POM modified by poly(MMA-*co*-BA) and UV-0. It can be attributed to that the UV stabilizer was grafted in acrylate elastomer by graft copolymerization to prepare a high-molecular weight UV stabilizer, also a light stabilizing acrylate elastomer, which not only improve the photostabilization of POM as a UV stabilizer but also increase the toughness of POM as a elastomer. At the same time, high-molecular weight UV stabilizer could improve the compatibility of small-molecule light stabilizer with POM and reduce the volatility and mobility of light stabilizer.

The notched izod impact strength of pure POM and these compositions before and after UV irradiation are shown in Figure 7. The major reason for pure POM failure is that its impact strength sharply decreased with the increase of irradiation time. Elastomer toughening has traditionally been the major system for POM to improve the impact strength. Commonly used elastomer is polyurethane elastomer. Acrylate elastomer and polyurethane elastomer have been used in toughening and modifying POM in our previous study.[15] We can easily see from Figure 7 that poly(MMA-*co*-BA-*co*-BPMA) had better toughening effect and light aging stability on POM

than poly(MMA-*co*-BA) and UV-0. For modified POM samples, the impact property declined during the initial of aging, then reached a maximum at 500 h. It can be inferred that the decrease of impact strength is not due to the photodegradation at an irradiation period of 250 h, but the increase of crystallinity resulting from the recrystallization of POM, which is in agreement with results above based on tensile strength tests. However, the impact strength of pure POM has been declining with UV irradiation time. This could be because the crystals have been destroyed in the early stages. However, at present, research on this aspect is very weak and lacks the corresponding theoretical analysis. The impact property of POM modified by poly(MMA-*co*-BA-*co*-BPMA) achieved 90% after 500-h UV irradiation and can still keep more than 70% within 1000-h UV irradiation. The impact strength of modified POM after 1000-h UV irradiation reached 97% of pure POM before UV irradiation, which proves it could satisfy the requirements of production used outdoor for long time.

Prior research[15] had shown that the crystallinity of unprotect neat POM increased, and the melting point decreased as the UV irradiation time increased. This can be attributed to scission of molecular chains of POM in the noncrystallines area exposed under UV irradiation. Figure 8 and Table I show the crystallinity and melting point of POM/13 wt % poly (MMA-*co*-BA-*co*-BPMA) blend. We found that the crystallinity of POM/13 wt % poly(MMA-*co*-BA-*co*-BPMA) blend increases with UV irradiation time. It reached a maximum at 500 h and then dropped down. These could be due to degradation and volatilization of amorphous molecules or the recrystallization of imperfect crystals in POM matrix. Because of lacking of experimental time and quantitative evaluation, we need to do more research in the future.

CONCLUSIONS

An acrylate elastomer with function on UV stability can be prepared by copolymerization of MMA, BA, and BPMA. As a high-molecular weight UV stabilizer, compared with small-molecule light stabilizer, poly(MMA-*co*-BA-*co*-BPMA) showed better compatibility with POM, which solved the problem of volatility and mobility of light stabilizer and can

TABLE I
DSC Data of POM/13 wt % Poly(MMA-*co*-BA-*co*-BPMA) Blend

	0 h	250 h	500 h	750 h
T_m (°C)	163.48	161.94	160.10	160.44
ΔH (J/g)	116.2	168.1	184.3	182.1
Crystallinity (%)	29.8	43.1	47.25	46.67

keep long-term and effective UV stability effect. Simultaneously, as an acrylate elastomer, mechanical properties of POM composite had been improved to some extent by addition of poly(MMA-*co*-BA-*co*-BPMA), especially the impact strength and elongation at break were improved in comparison to pure POM after UV irradiation.

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