

Enhanced Ultraviolet Resistance of Polypropylene Random Copolymer Filled by ZnO-supported Mesoporous Zeolite*

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Abstract To enhance the ultraviolet resistance of ZnO based polymer materials, ZnO-supported mesoporous zeolite (M-ZnO) was prepared and characterized by atomic absorption spectroscopy and scanning electron microscopy. The ultraviolet resistance, crystallization behavior and melting characteristics of ZnO and M-ZnO filled PPR composites were compared by FTIR spectra and differential scanning calorimetry. The ultraviolet resistance of M-ZnO filled PPR composites is higher than that of ZnO filled PPR composites, indicating higher ultraviolet resistance of M-ZnO than that of ZnO. The crystallization temperatures of mesoporous zeolite filled PPR were higher than those of M-ZnO and decreased with increasing UV-irradiation time. But the crystallization temperatures of M-ZnO filled PPR composites were not influenced by UV-irradiation time. The ZnO supported on the surface of zeolite is effective in enhancing the ultraviolet resistance of ZnO based polymer materials.

Keywords: Polypropylene random copolymer (PPR); ZnO; Mesoporous zeolite; Photo-oxidation degradation.

INTRODUCTION

Ultraviolet (UV) irradiation is a frequently encountered factor that can induce photo-oxidation degradation of polymers. There are a great number of studies on the photo-oxidation degradation for polypropylene (PP) and its composites^[1–19]. The exposure of PP to ultraviolet irradiation generally resulted in the reduction in molecular weight and the build-up of chemical groups like carbonyls groups (mainly ketones, esters and acids) and hydroxyls (mainly hydroperoxides and alcohols)^[3, 14]. For the filled PP composites, the presence of fillers generally accelerates the photo-oxidation degradation of PP. Li *et al.*^[14] found the photo-oxidation degradation of PP/CaCO₃ and PP/SiO₂ nanocomposites was much more susceptible than that of unfilled PP. Addition of MMT, boehmit, hydrotalcite, and so on, speeds up the rate of photo-oxidation degradation of PP^[10, 11, 16–19].

However, it was observed that addition of zinc oxide (ZnO) can improve the ultraviolet resistance of PP. Zhao and Li^[20] found that ZnO nanoparticles play an important role in stabilizing the PP molecules and delay the photo-degradation process by acting as screens. The dominant screening mechanism is that the ZnO nanoparticles absorbed the UV radiation and hence reduced the UV intensity that can promote the oxidation of the PP chains. Both Vigneshwaran *et al.*^[21] and Pandey *et al.*^[22] also found that the presence of ZnO reduced the photo-oxidation degradation of PP. However, it has been little reported on enhancing the ultraviolet resistance of ZnO in its filled polymer materials with ZnO supported on the surface of inorganic particles.

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In our previous studies, we prepared ZnO-supported microporous zeolite with ZnO supported on the surface of microporous zeolite and found the antibacterial properties and ultraviolet resistance of ZnO-supported microporous zeolite filled polypropylene random copolymer (PPR) materials^[23, 24]. In order to further prove this effect, ZnO-supported mesoporous zeolite (M-ZnO) was prepared and its filled PPR composites were fabricated in this article. The photo-oxidation degradation, crystallization behavior and melting characteristics were compared for ZnO and M-ZnO filled PPR composites by UV-irradiation. The ultraviolet resistance of M-ZnO filled PPR composites higher than that of ZnO filled PPR composites was observed. ZnO supported on the surface of mesoporous zeolite is effective in enhancing the ultraviolet resistance of ZnO based polymer materials.

EXPERIMENTAL

Materials

PPR (R200P, MRI = 0.23 g/10 min at 230 °C and 2.16 kg, the content of ethylene is 3.8%, $M_n = 72.2 \times 10^4$ g/mol, $M_w/M_n = 4.5$ and the density is 0.91 g/cm³) was provided by Hyosung Corporation. Mesoporous zeolite (M) with average particle size about 11.8 μm and porediameter about 3.5–4.5 nm was supplied by Tianjin Kaimei Technology Company, China. Zn(NO₃)₂ (AR) and concentrated nitric acid (GR) were bought from Guangzhou Chemical Factory, China. ZnO with average particle size of (30 ± 10) nm was supplied by Aladdin Chemistry Co. Ltd.

Preparation of ZnO-supported Mesoporous Zeolite

Mesoporous zeolite of 10 g was thermally treated at 400 °C in a muffle furnace for 3 h. Then it was transferred into a three-neck flask. As the system was evacuated to 0.063 MPa and kept for 0.5 h, then 50 mL 20 wt% Zn(NO₃)₂ solution was added. The mixture was stirred for 1 h and then dried at room temperature. In order to change Zn(NO₃)₂ into ZnO, the prepared mixture was heated from room temperature to 550 °C in muffle furnace and the prepared mesoporous zeolite was denoted as M-ZnO.

Preparation of Filled PPR Composites

PPR composites were prepared with an HL-200 internal mixer (Jilin University Science and Education Instrument Factory, China) at 170 °C and 50 r/min for 7 min. The PPR composites filled by M and M-ZnO with 1, 3 and 5 phr were denoted as 1M, 3M, 5M and 1M-ZnO, 3M-ZnO, 5M-ZnO, respectively. The ZnO filled PPR composites containing the same ZnO content as 1M-ZnO, 3M-ZnO and 5M-ZnO were denoted as ZnO₁, ZnO₃ and ZnO₅, respectively. The ZnO contents in filled PPR composites are listed in Table 1.

Table 1. ZnO contents in filled PPR composites

Samples	1M-ZnO and ZnO ₁	3M-ZnO and ZnO ₃	5M-ZnO and ZnO ₅
ZnO (phr)	0.42	1.26	2.10

The PPR and its composites films for photo-oxidation degradation experiments were pressed on XLB 50-D plate vulcanizing press (Zhejiang Shuangli Group Huzhou Xingli Rubber Machinery Manufacturing Company, China) at 180 °C and 10 MPa.

Characterization

Content of zinc oxide in the ZnO-supported mesoporous zeolite

The prepared M-ZnO of 5 mg was dissolved in concentrated nitric acid and diluted by deionized water, the ZnO contents in the M-ZnO were characterized on a Japan Hitachi Z-2000 atomic absorption spectrometer (AAS). The analytical line was 213.9 nm and the ZnO contents were calculated following the formula (1):

$$W_{\text{ZnO}} \% = \frac{c_{\text{Zn}} \times V \times M_{\text{ZnO}}}{M_{\text{Zn}} \times m_s} \times 100\% \quad (1)$$

In which, W_{ZnO} is the mass content of ZnO in M-ZnO, c_{Zn} ($\mu\text{g/mL}$), V (L) and m_s (g) are the concentration, volume and mass of the sample, respectively. M_{ZnO} and M_{Zn} are the molar mass of ZnO and Zn, respectively.

Morphology of ZnO-supported mesoporous zeolite

The morphologies of M, M-ZnO and ZnO particles were observed with a scanning electron microscope (SEM S4800, Hitachi, Japan). The samples were observed under an acceleration voltage of 10 kV and a current of 10 μA .

Photo-oxidation degradation

Photo-oxidation degradation of PPR and its composite films with thickness of 20 μm was carried out under a UV lamp of 300 W (The UV irradiation wavelength is 300–400 nm). The temperature of sample surface is $(80 \pm 2)^\circ\text{C}$ and the vertical irradiation distance is 20 cm. The film samples subjected to UV irradiation for 0, 6, 12, 24, 36 and 48 h, respectively were characterized by FTIR analysis. The FTIR measurements (model Nicolet Nexus 670) were carried out with the scanning range of 4000–500 cm^{-1} and resolution ratio of 4 cm^{-1} at transmission mode using 32 scans. The carbonyl groups formed due to the photo-oxidative degradation of samples under UV irradiation was used to calculate the carbonyl index by the equation (2)^[20, 21].

$$\text{Carbonyl index} = \frac{A_c}{A_R} \quad (2)$$

And A_c is the area of a carbonyl adsorption band between 1700 and 1800 cm^{-1} and A_R is the area of a reference band between 2700 and 2750 cm^{-1} in the infrared spectrum of samples^[25].

Crystallization and melting behaviors of UV-irradiated samples

The crystallization behaviors and melting characteristics of PPR and filled PPR composites films before and after UV irradiation were studied on a TAQ20 differential scanning calorimeter under nitrogen atmosphere. Sample of 5 mg was heated from room temperature to 200 $^\circ\text{C}$ at the rate of 10 K/min and kept for 5 min. After cooling to room temperature at the rate of 10 K/min and kept for 1 min, the samples were reheated to 200 $^\circ\text{C}$ at the rate of 10 K/min. The crystallinity was determined by $X_c\% = (\Delta H / \Delta H_0) \times 100\%$, in which ΔH and ΔH_0 were the melting enthalpy of the samples and 100% crystalline PPR, respectively, $\Delta H_0 = 209 \text{ J/g}$ ^[26].

The crystal structure of PPR and filled PPR composites

The crystal structure of the PPR and filled PPR films were studied by wide angle X-ray diffraction (WAXD) measurements. It was conducted by using a Rigaku Geigerflex Model D/Max-IIIa rotating anode X-ray diffractometer with Cu $K\alpha$ radiation. The scanning rate used was 0.02 ($^\circ$)/min and the scanning angle was from 5 $^\circ$ to 40 $^\circ$.

RESULTS AND DISCUSSION

The Content and Morphology of ZnO-supported Mesoporous Zeolite

The ZnO content in the prepared M-ZnO characterized by AAS was 41.9%. And the morphology observed by SEM also showed the formation of ZnO supported on the surface of zeolite. It can be seen from Fig. 1 that the surface of zeolite is smooth, while the M-ZnO is wrapped by a layer of ZnO. The size of ZnO supported on the surface of zeolite is lower than that of pure ZnO as shown in Fig. 1(e, f), which indicated that the specific surface area of ZnO supported on the surface of zeolite is higher than that of pure ZnO. So we can inference that the M-ZnO has stronger ultraviolet resistance than pure ZnO.

The Photo-oxidation Degradation of Filled PPR Composites

Infrared spectrometry is a powerful tool to study the photo-oxidation degradation of PP^[20, 21, 27]. Similarly, it can be used to study the photo-oxidation degradation of PPR and its composites. Figure 2 shows the infrared spectra of PPR and its composites after UV irradiation for 48 h. It can be seen that the UV irradiation significantly increased the intensities of carbonyl band between 1650 cm^{-1} and 1800 cm^{-1} for PPR and 1M. The intensity of

carbonyl band of 1M is stronger than that of PPR, indicating that addition of zeolite can accelerate the photo-oxidation degradation of PPR. A great number of investigations have demonstrated that the presence of fillers can accelerate the photo-oxidative degradation of PP^[6, 10, 11, 14–18]. It is attributed to the preferential interactions between the antioxidant and the polar fillers, resulting in the decreased antioxidant activity.

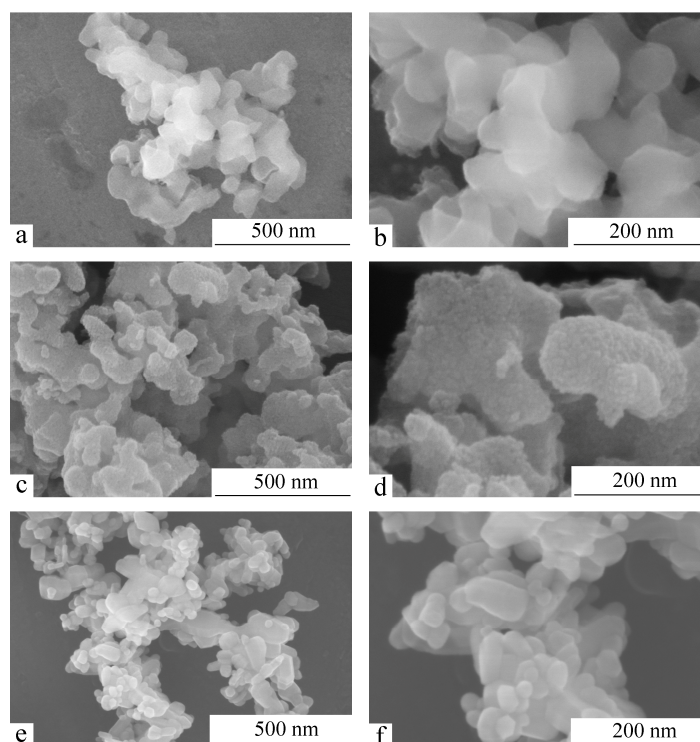


Fig. 1 SEM morphologies of M (a, b), M-ZnO (c, d) and pure ZnO (e, f)

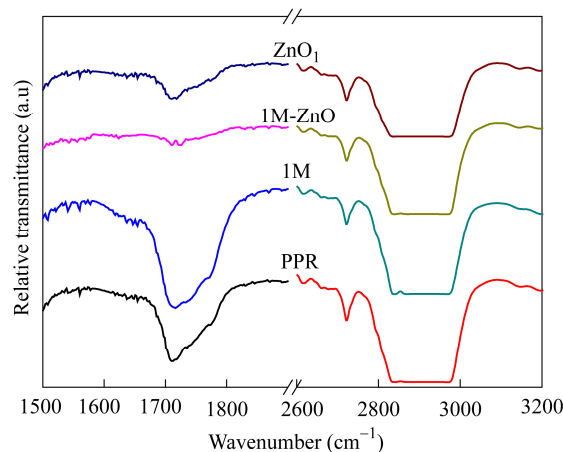


Fig. 2 FTIR spectra of 1500–2000 cm^{-1} and 2600–3200 cm^{-1} for PPR, 1M, 1M-ZnO and ZnO_1 after UV irradiation treatment for 48 h

However, no significant change was observed in the intensities of carbonyl band between 1650 cm^{-1} and 1800 cm^{-1} for 1M-ZnO and ZnO_1 . It indicated that ZnO particles play an important role in stabilizing the PPR molecules and delay the photo-degradation process because the ZnO particles absorbed the UV radiation acting as screens^[20]. It should be pointed out that the intensities of carbonyl band for 1M-ZnO composites are lower

than those of ZnO₁ composites, indicating the higher ultraviolet resistance of M-ZnO than that of ZnO. In order to quantitatively analyze the photo-oxidation degradation behavior of PPR and its composites, the changing of carbonyl index of PPR and its composites was investigated with the UV irradiation time. Carbonyl index values as a function of UV irradiation time for PPR and its composites are shown in Fig. 3. It can be observed that the carbonyl index of all samples increased with increasing UV irradiation time. The carbonyl index of 1M composites is higher than that of PPR in the different UV irradiation time. It is further proved that the presence of zeolite can accelerate the photo-oxidation degradation of PPR. While the carbonyl index of 1M-ZnO and ZnO₁ composites is significantly lower than that of PPR, indicating the reduced photo-oxidation degradation of PPR in the presence of ZnO and M-ZnO.

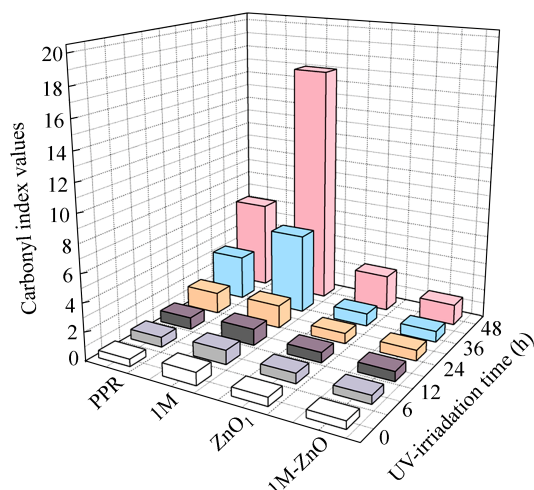


Fig. 3 Carbonyl index values as a function of UV-irradiation time for PPR and its composites

However, it can be observed from Fig. 3 that the carbonyl index of 1M-ZnO composites is lower than that of ZnO₁ composites, especially for UV irradiation time above 36 h. This experiment result clearly demonstrated that the higher ultraviolet resistance of M-ZnO than ZnO. Although addition of zeolite can accelerate the photo-oxidation degradation of PPR, the ultraviolet resistance of PPR is distinctly increased in M-ZnO filled PPR composites. This observation also proved that the surface of zeolite was completely coated by ZnO in the M-ZnO, which offset the influence of zeolite on the photo-oxidation degradation of PPR.

According to the photo-oxidative degradation mechanism of polypropylene^[28], it is suggested that UV-irradiation induced the broken of macromolecular chains to result in the formation of alkyl radicals R $\cdot$, shown in Fig. 4. The peroxide radicals (ROO $\cdot$) produced by reaction between alkyl radicals and O₂ can react with PPR macromolecular chains to form chemical species with hydroperoxide groups (ROOH), which can react quickly with O₂ to form organic compounds of low molecular weight such as ketones, acids, alcohols and esters

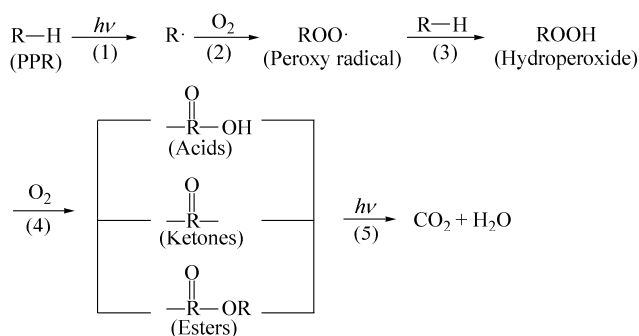


Fig. 4 The photo-oxidative degradation mechanism of PPR

due to the unstable hydroperoxide compounds. Photo-oxidative degradation of organic compounds with low molecular weight finally forms CO_2 and H_2O during UV-irradiation for long time. The largely enhanced ultraviolet resistance of the M-ZnO filled PPR composites higher than ZnO filled PPR composites is attributed to the larger specific surface of ZnO supported on the surface of zeolite due to the smaller size of ZnO as is shown in Fig. 1.

Influence of Filler Content on the Photo-oxidation Degradation of PPR Composites

In order to study the filler content on the photo-oxidation degradation of PPR, the infrared spectra of PPR composites with different filler contents were measured. It can be observed from Fig. 5 that the intensities of carbonyl band between 1650 cm^{-1} and 1800 cm^{-1} increased with increasing filler contents in zeolite filled PPR composites. However, the intensities of carbonyl band decreased with increasing filler contents in M-ZnO and ZnO filled PPR composites. It can be seen clearly from Fig. 6 that the carbonyl index of zeolite filled PPR composites increased with increasing filler contents and the UV irradiation time. However, the carbonyl index of M-ZnO and ZnO filled composites decreased with increasing filler contents. And the UV irradiation time has little effect on the carbonyl index of ZnO and M-ZnO filled PPR composites, especially for the M-ZnO filled PPR composites. The higher ultraviolet resistance of M-ZnO filled PPR composites than that of ZnO filled PPR composites is attributed to the higher specific surface area of ZnO in the M-ZnO (as is shown in Fig. 1).

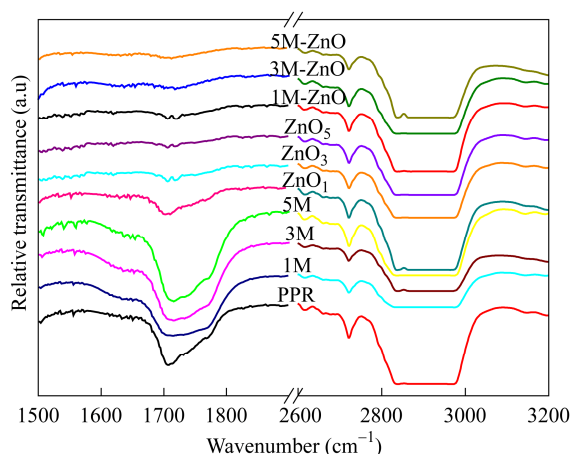


Fig. 5 FTIR spectra in the range of $1500\text{--}2000\text{ cm}^{-1}$ and $2600\text{--}3200\text{ cm}^{-1}$ for PPR, M-ZnO or ZnO filled PPR composites after UV irradiation treatment for 48 h

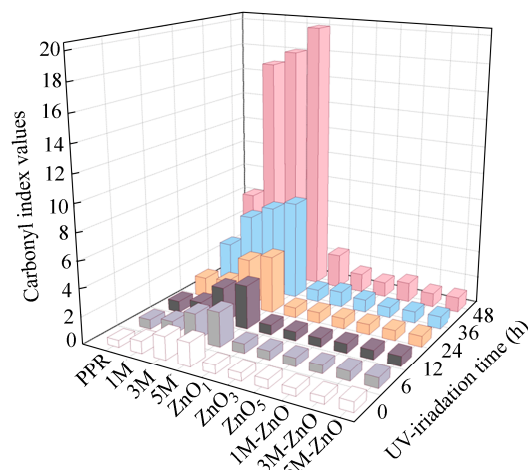


Fig. 6 Carbonyl index values as a function of UV irradiation time for PPR and M-ZnO or ZnO filled PPR composites after UV irradiation treatment for 48 h

Crystallization and Melting Behaviors of UV Irradiated PPR Composites

The photo-oxidation degradation of PPR resulted in the change of its macromolecular structure, which would influence its crystallization. The investigation on the crystallization and melting behaviors of UV irradiated PPR and its composites would benefit understanding the effect of M-ZnO on the photo-oxidation degradation behaviors of PPR.

The DSC melting behavior of UV irradiated PPR and its composites can reflect the change of crystal lamellar perfection of PPR. It can be observed from Fig. 7 and Table 2 that the melting peak temperatures (T_m) of PPR and zeolite filled PPR composites firstly increased then decreased with increasing UV irradiation time. It is suggested that the increased T_m are similar to thermal annealing to be benefit of improving the crystal perfection of PPR in the initial stage of UV irradiation. The T_m decreased sharply when the UV irradiation time above 24 h. It is considered that the photo-oxidation degradation happened not only in amorphous region but also crystalline region, resulting in the decreased crystal lamellar size of PPR. However, no significant change of T_m was observed in the M-ZnO and ZnO filled composites as the UV irradiation time was up to 48 h. This indicated that the UV irradiation did not seriously destroy the molecular chain structure in crystalline region of

PPR in the M-ZnO and ZnO filled PPR composites. The thermal annealing has the benefit of improving the crystal perfection of PPR matrix in M-ZnO and ZnO filled PPR composites during long time UV irradiation, which leads to the shoulder melting peak during DSC experiments^[29]. When the defect content increases, the ability to form the second, more stable phase during the DSC experiment is reduced, hence the shoulder melting peak would become less evident for PPR and 1M after long time UV irradiation.

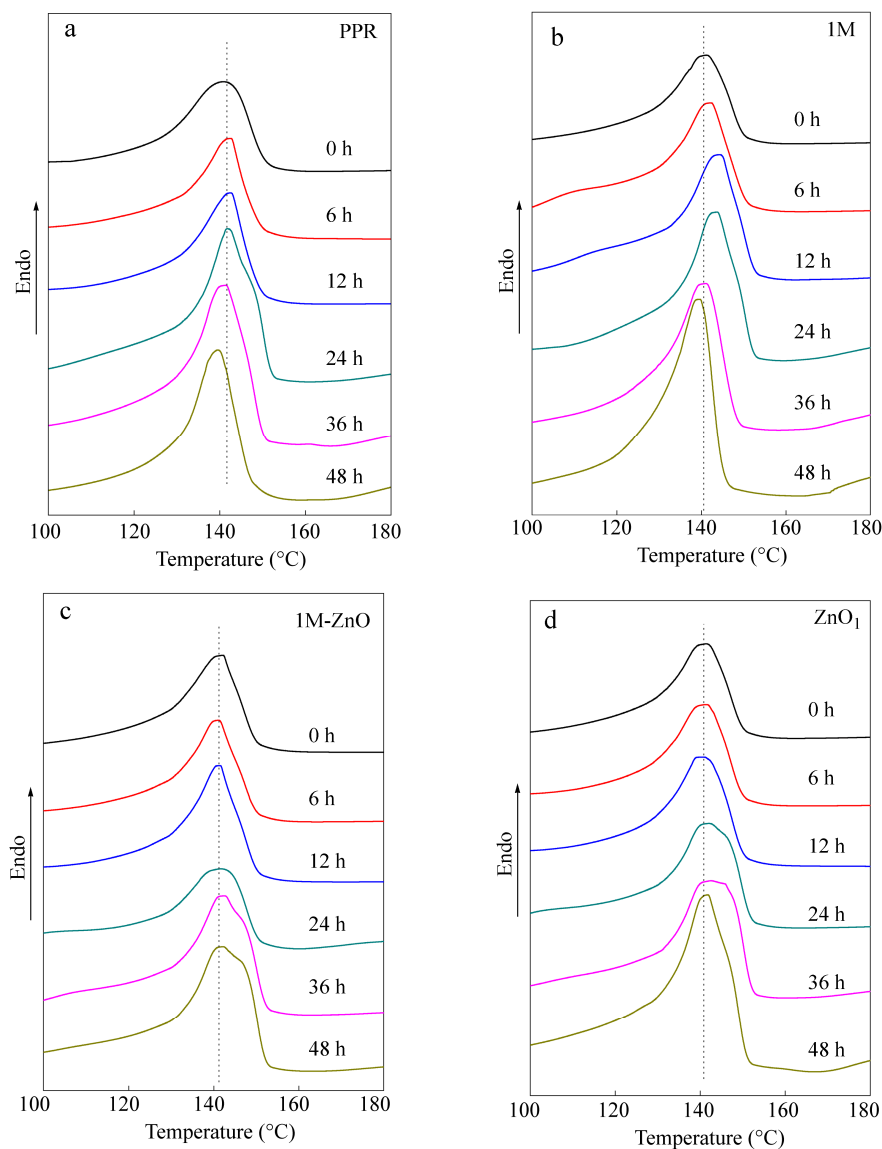


Fig. 7 First melting curves of UV irradiated PPR and its composites

Table 2. DSC melting data of UV irradiated PPR and its composites

Sample	PPR		1M		ZnO ₁		1M-ZnO	
Time (h)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
0	140.9	59.8	141.3	57.5	140.4	59.0	141.1	62.2
6	142.6	68.7	142.3	68.5	140.4	72.9	141.2	62.5
12	142.5	74.7	144.4	73.4	140.5	75.9	141.6	68.8
24	141.8	93.2	143.4	87.5	141.5	76.0	141.8	70.2
36	141.4	100.7	141.1	93.5	142.5	91.9	142.5	76.3
48	139.6	107.7	139.5	106.6	141.4	107.4	142.2	80.9

It can be seen from Fig. 8 that the crystallinity of PPR and its composites increased with increasing UV irradiation time due to the chemical-crystallization in amorphous region^[30–32]. It is generally suggested that the chain scission caused by photo-oxidation degradation in amorphous region of crystalline polymers can release the entanglement of molecular chains and produce more freed segments to move into the original crystals or form new crystalline structure in the original amorphous zone to result in the increased crystallinity. The crystallinities of M-ZnO filled PPR composites are lower than those of ZnO filled PPR composites. It is considered that the chemical-crystallization is lower in the M-ZnO filled PPR composites due to the higher ultraviolet resistance of M-ZnO than that of ZnO.

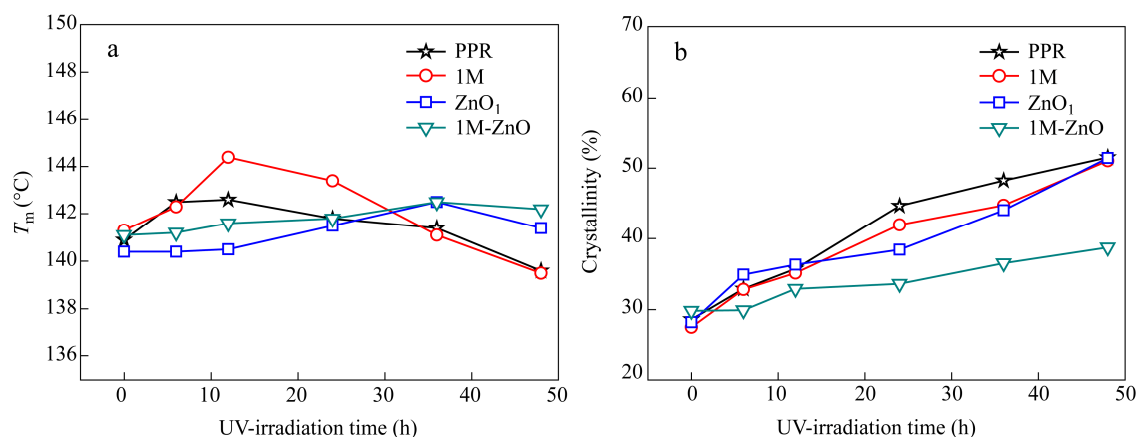
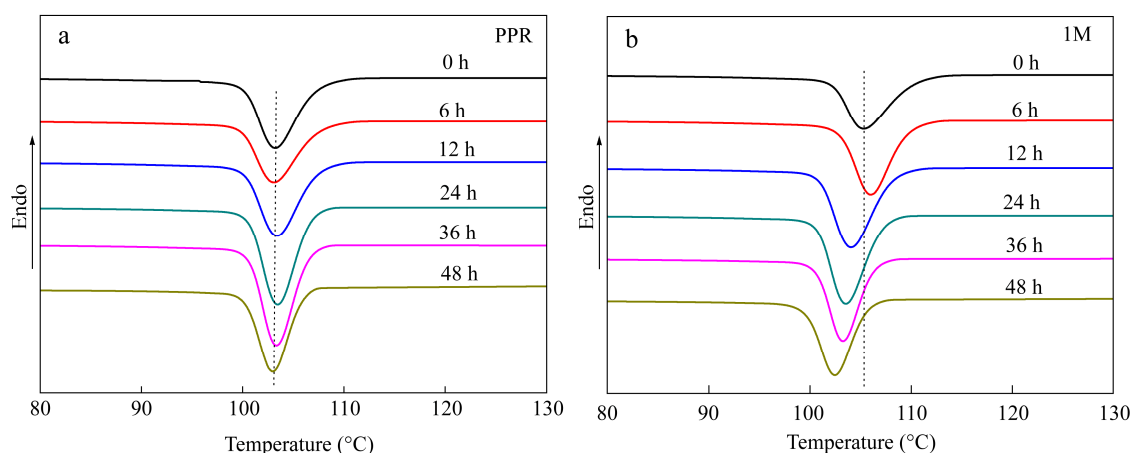


Fig. 8 Melting temperature and crystallinity of UV irradiated PPR and its composites as a function of UV irradiation time

Figure 9 is the crystallization curves after melting of UV irradiated PPR and its composites and the corresponding DSC data is summarized in Table 3. It can be observed that the UV irradiation time has no significant effect on crystallization peak temperatures (T_c) of PPR. Although the zeolite filled PPR composites have higher T_c due to the heterogeneous nucleation of zeolite, its T_c apparently decreased with prolonging UV irradiation time. It is attributed that the presence of zeolite accelerated the photo-oxidation degradation of PPR, resulting in the decreased regularity of PPR molecular chain^[29]. For ZnO₁ and 1M-ZnO composites, the T_c of PPR first increased at the UV irradiation time below 24 h. It was attributed to the heterogeneous nucleation of ZnO and M-ZnO. At the UV irradiation time above 36 h, the degradation of PPR decreased the crystallization ability of PPR, resulted in the decreased T_c of PPR.



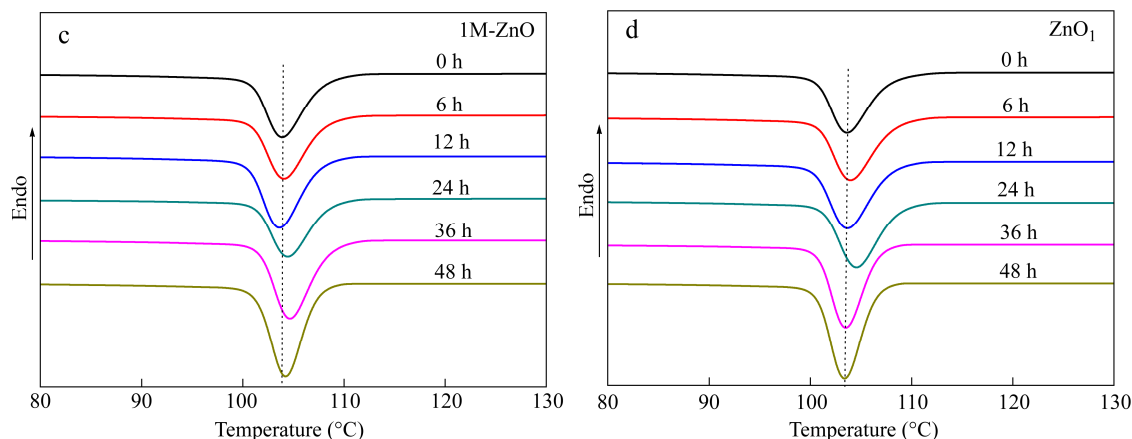


Fig. 9 Crystallization curves of UV irradiated PPR and its composites

Table 3. DSC crystallization data of UV irradiated PPR and its composites

Sample	PPR		1M		ZnO ₁		1M-ZnO	
Time (h)	T_c (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_c (J/g)
0	103.0	58.5	105.3	60.9	103.5	63.4	104.0	58.9
6	103.1	59.7	106.1	65.0	103.6	66.3	104.1	59.7
12	103.4	68.3	104.1	68.4	103.7	68.0	104.3	62.3
24	103.5	74.6	103.6	71.5	103.8	68.5	104.5	68.3
36	103.3	71.6	103.3	64.8	103.5	68.9	104.7	71.4
48	103.2	67.5	102.5	60.2	103.4	71.3	104.2	73.3

It can be observed from Fig. 10 that the T_c of 1M-ZnO and ZnO₁ is lower than that of 1M, but higher than that of PPR. The UV irradiation has no influence on T_c of ZnO and M-ZnO filled PPR composites. It is attributed that the heterogeneous nucleation of ZnO and M-ZnO is lower than that of zeolite, which also indicated that the surface of zeolite was coated by the ZnO in the M-ZnO.

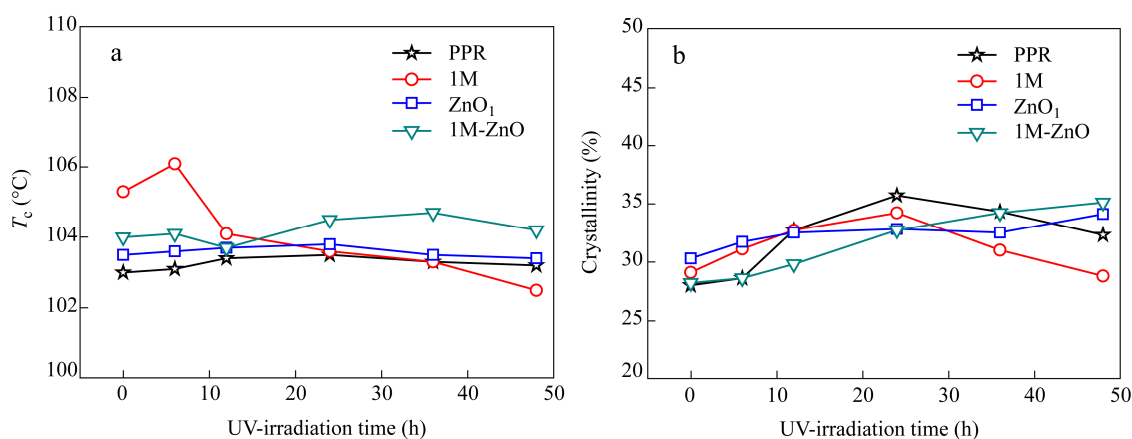


Fig. 10 Crystallization temperature and crystallinity of UV irradiated PPR and its composites

The crystallinities of PPR and 1M first increased then decreased with prolonging UV irradiation time as shown in Fig. 10. The increased crystallinity of PPR is attributed to the formation of a little polar chains produced in the initial photo-oxidation degradation of PPR as heterogeneous nucleation to accelerate crystallization of PPR^[33], while the serious polymer degradation with increasing UV irradiation time resulted in the decreased regularity of molecular chain and crystallinity of PPR^[34]. However, the crystallinities of 1M-ZnO

and ZnO₁ composites increased with prolonging UV irradiation time, especially for 1M-ZnO composites. This indicated that no serious photo-oxidation degradation of PPR took place due to the high ultraviolet resistance of M-ZnO and ZnO and the formation of a little polar chains as heterogeneous nucleation to accelerate the crystallization and increased crystallinity of PPR.

The re-melting behavior of PPR and its composites crystallized from melt of samples UV irradiated with different time significantly reflect the change of the regularity of PPR molecular chain. It can be observed from Figs. 11 and 12 that the UV irradiation time has little influence on T_m of PPR below 12 h. At the UV irradiation time of 24 h, two melting peaks, T_{m1} and T_{m2} , were observed and the intensity of T_{m1} is higher than that of T_{m2} . It is suggested that the UV irradiation induced the change of the regularity of PPR molecular chains due to the photo-oxidation degradation, resulting in the different crystallization and melting behavior of PPR. The T_{m1} is attributed to the melting of crystallized PPR with poor regularity and T_{m2} is due to the melting of crystallized PPR with high regularity.

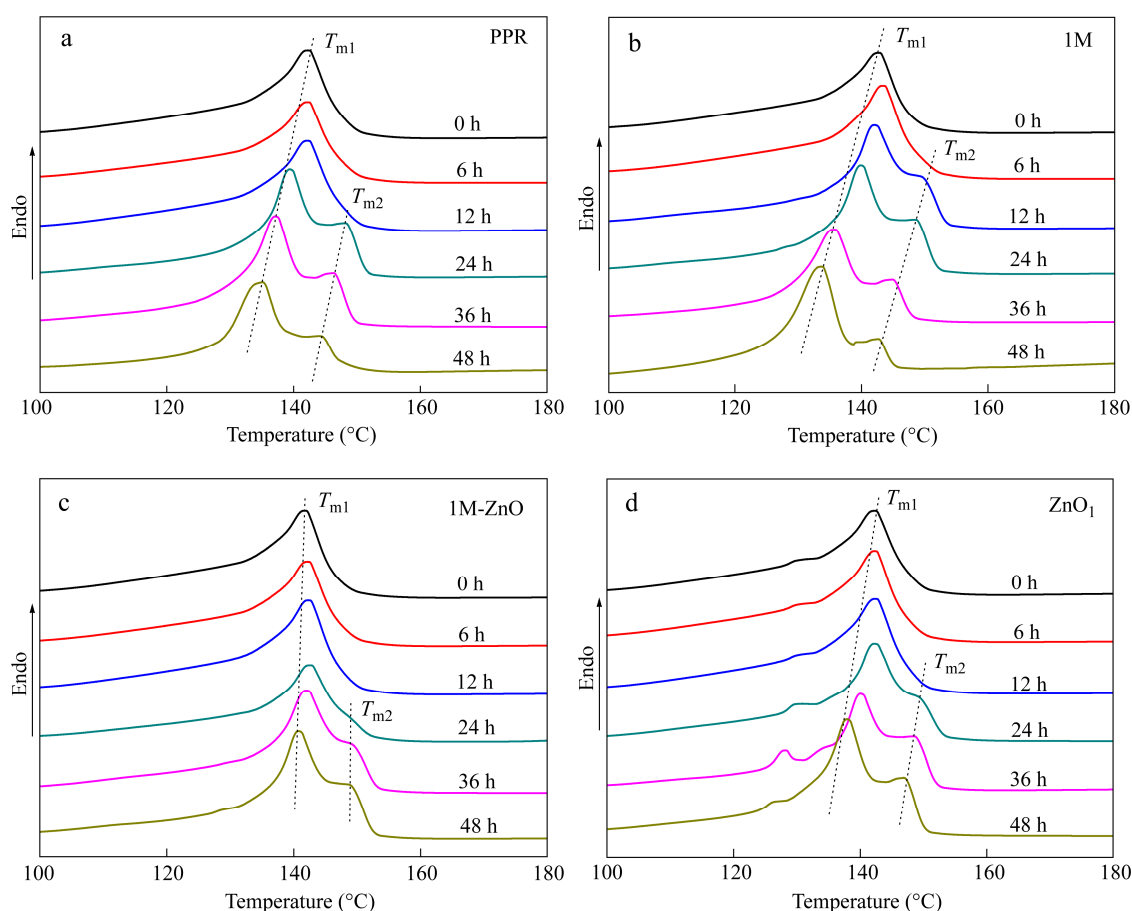


Fig. 11 Re-melting curves of UV irradiated PPR and its composites

For the zeolite filled PPR composites, the double melting peaks were observed at the UV irradiation time of 12 h. The T_m also decreased with increasing UV irradiation time and was lower than those of PPR at the UV irradiation time above 24 h. It is attributed that the presence of zeolite can speed up the photo-oxidation degradation, resulting in the reduced regularity of PPR molecular chains. For the 1M-ZnO and ZnO₁ composites, the UV irradiation time, in which double melting peaks appear, could be 36 h and 24 h, respectively. In addition, the lower temperature peak around 120–130 °C of ZnO₁ composites is attributed to the melting of β crystals, which is approved by WAXD. Figure 13 shows the WAXD curves of PPR and filled PPR before UV-irradiation.

For PPR, 1M and 1M-ZnO, only α crystals can be found. However, a small peak can be observed at $2\theta = 16.2^\circ$ for ZnO₁, indicating the presence of β crystal form. It is attributed to the weak β -nucleation of ZnO nanoparticles to develop a small amount of β crystals in PPR composites filled by ZnO nanoparticles^[20]. For 1M-ZnO filled PPR composites, only α crystals can be found due to the reduced β -nucleation of ZnO supported on the surface of zeolite. The T_m of 1M-ZnO and ZnO₁ composites are higher than those of zeolite filled PPR composites as can be seen in Table 4. The decreased T_m is less than those of PPR and zeolite filled PPR composites with increasing UV irradiation time. It should be pointed out that the T_m of 1M-ZnO are higher than those of ZnO₁ and the intensity of T_{m2} of 1M-ZnO is lower than that of ZnO₁. All the results indicated that the ability of ultraviolet resistance is as follows: M-ZnO > ZnO > M.

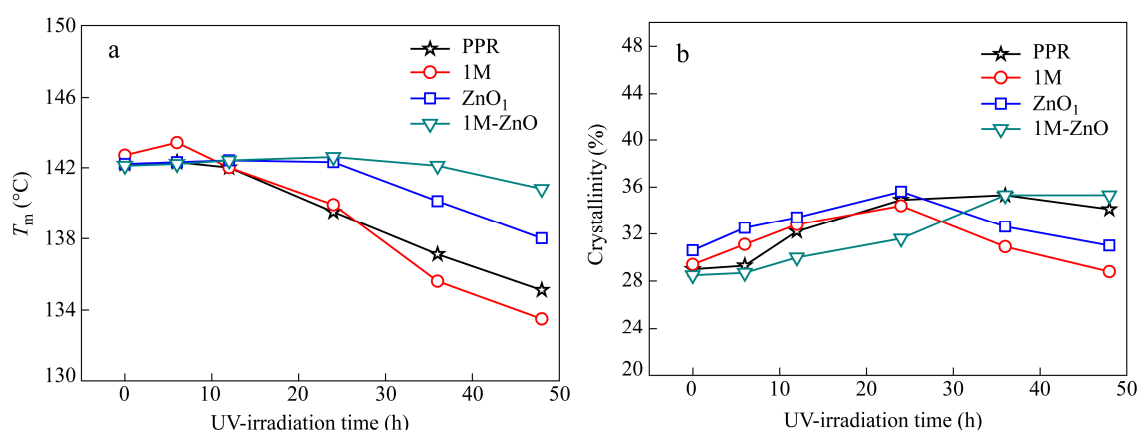


Fig. 12 Melting temperatures and crystallinity of UV- irradiated PPR and its composites on second melting process

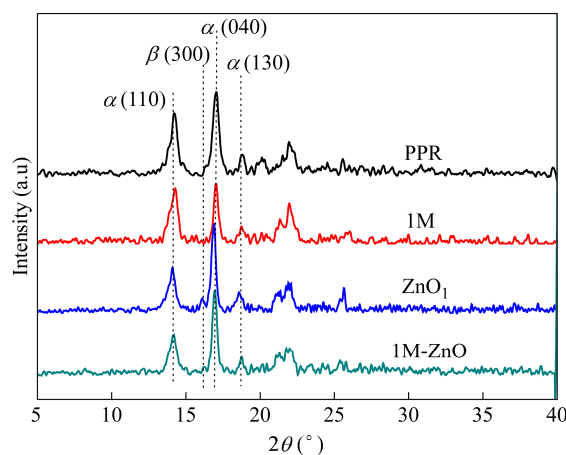


Fig. 13 The WAXD patterns of PPR and filled PPR before UV-irradiation

Table 4. DSC re-melting data of UV irradiated PPR and its composites

Sample	PPR		1M		ZnO ₁		1M-ZnO	
Time (h)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
0	142.2	60.7	142.7	61.4	142.2	63.9	142.1	59.6
6	142.3	61.3	143.4	65.1	142.3	68.0	142.2	59.9
12	142.0	67.4	142.0, 149.4	68.6	142.4	69.8	142.4	62.6
24	139.5, 147.9	72.9	139.9, 148.6	71.9	142.3, 148.9	74.3	142.6	66.0
36	137.1, 146.2	73.8	135.6, 144.6	64.5	140.1, 148.3	68.1	142.1, 148.7	73.8
48	135.1, 144.1	71.2	133.5, 142.5	60.1	138.0, 146.7	64.7	140.8, 148.6	73.7

CONCLUSIONS

ZnO supported on the surface of mesoporous zeolite (M-ZnO) can be prepared with mesoporous zeolite and $\text{Zn}(\text{NO}_3)_2$ solution. The presence of zeolite accelerated photo-oxidation degradation of PPR. Addition of ZnO and M-ZnO increased the ultraviolet resistance of PPR. The lower carbonyl index of M-ZnO filled PPR composites than that of ZnO filled PPR composites indicated that the ultraviolet resistance of the prepared M-ZnO is stronger than that of ZnO. The ultraviolet resistance of zeolite filled PPR composites decreased with increasing filler contents, but the filler contents have less influence on ultraviolet resistance of M-ZnO filled PPR composites. The heterogeneous nucleation of zeolite is higher than that of M-ZnO. However, the crystallization temperatures of zeolite filled PPR composites decreased with prolonging UV irradiation time and the crystallization temperatures of M-ZnO filled PPR composites were little influenced by UV irradiation time. The ability of ultraviolet resistance is as follows: M-ZnO > ZnO > M.

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