

Poly(methyl acrylate-co-methyl methacrylate)/montmorillonite nanocomposites fabricated by soap-free emulsion polymerization

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Abstract The exfoliated poly(methyl acrylate-co-methyl methacrylate)/montmorillonite (MMT) nanocomposite latex solutions fabricated by soap-free emulsion polymerization were able to cast into a film. The films were transparent and ductile unless more than 5 wt% of MMT was incorporated. With the MMT content higher than 5 wt%, the inflammable residuals of nanocomposites after combustion could preserve their original film profile acting like an inflammable scaffold. Moreover, as 20 wt% MMT was incorporated, the yield strength of the films was increased up to 20 times and Young's modulus up to 2,000 times. However, the water vapor permeability coefficient of the films was only decreased down to its half value. This unexpected behavior of permeability was associated with the decrease of T_g as the content of MMT was increased, owing to the large difference of the reactivity ratios between methyl acrylate and methyl methacrylate monomers and their differential absorption to the MMT during copolymerization.

Keywords Nanocomposites · Montmorillonite · Poly(methyl acrylate) · Poly(methyl methacrylate) · Emulsion polymerization

Introduction

Exfoliated polymer/montmorillonite (MMT) nanocomposites have been widely investigated in recent years owing to their superior properties compared to the conventional composite materials [1–5]. Montmorillonite (MMT) is a natural clay, which is constructed of repeating triple-layer nanoplatelets composed of two tetrahedral silica layers fused into an edge-shared octahedral layer of alumina with a thickness of ~1 nm and a length of several hundred nanometers [6]. Stacking of the nanoplatelets creates a gap between the nanoplatelets called the interlayer or gallery. Isomorphic substitution within the layers, such as Si^{+4} by Al^{+3} or Al^{+3} by Mg^{+2} , generates negative charges that are counterbalanced by some cations, such as Na^+ in the gallery. Because of the weak interactions between the stacking layers, the cations inside the gallery can be easily exchanged by other cations. The maximum capacity for the cation exchange is known as the cation exchange capacity (CEC), which is expressed as meq/100 g. Thus, the exfoliated MMT nanoplatelets carry positive ions on the surface so that they can be considered as a two-dimensional electrolyte [7]. Researchers usually adopted certain organic modifications for MMT to explore the exfoliated nanocomposites. A few amount of the dispersed MMT in polymeric matrix can significantly improve the mechanical properties [8], thermal stability [9], and barrier properties [10]. Various polymers, processes, and characterizations associated with the polymer/MMT nanocomposites have been reported recently [11–15]. However, the adopted surfactants to organize the MMT are a small molecule that would degrade the thermal stability and durability of the fabricated nanocomposites.

Soap-free emulsion polymerization [16–19] is a clean and prevailing process to manufacture the polymeric latices.

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Recently, we have successfully adopted the soap-free emulsion polymerization to fabricate the exfoliated poly(methyl methacrylate) (PMMA)/MMT nanocomposite lattices [20]. During polymerization, the polymerizing chains were aggregated into a disk form inside the clay interlayer regions for micellation and exfoliated the MMT. The exfoliation of MMT was almost completed in the micellation stage. However, because PMMA has a glass transition temperature (T_g) of 105°C, the as-formed exfoliated PMMA/MMT nanocomposite latex particles are too rigid to form a film after casting. Therefore, their applications are limited.

In this work, in order to decrease the T_g , we fabricated the poly(methyl acrylate-co-methyl methacrylate) (P(MA-co-MMA))/MMT nanocomposite lattices through soap-free emulsion copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) monomers in various weight ratios. As the weight ratio of MA to MMA was increased to 3:1 or higher, the fabricated P(MA-co-MMA)/MMT nanocomposite latex solutions could be successfully cast into a film. Thus, the transparency, T_g , water vapor permeability and mechanical properties of the films were investigated and the results were associated with the reactivity ratios of monomers and the preferential adsorption of monomers to the MMT interlayer regions during emulsion copolymerization.

Experimental

Materials

MA and MMA monomers were purchased from Acros. Both were distilled under reduced pressure for purification before used. Potassium persulfate (KPS) purchased from Acros was used as the initiator without further purification. Montmorillonite (MMT, PK-802), with cationic exchange capacity (CEC)=114 meq/100 g, was obtained from PAI-KONG Nano Technology in Taiwan.

Preparation of polymer-clay latex solutions and films

To a two-neck flask that has been loaded with 125 ml deionized water was added 0.3852 g KPS and an allocated amount of MMT for preparation of P(MA-co-MMA)/MMT nanocomposite lattices containing 0, 1, 5, 10 and 20 wt% MMT, respectively. The weight ratios between MA and MMA monomers were set to 3/1, 4/1, and 5/1, respectively for copolymerization. The mixed monomers of 9.5 g were added to the flask with stirring and then heated to 70°C for copolymerization. After ~24 h until no further polymerization was detected, a few amount of the latex solution was removed for transmission electron microscopic (TEM)

observation. The remaining latex solutions after stirring homogeneously were poured into an aluminum foil rectangular mode with dimensions of 15×30 cm² and then dried at 50°C in an oven. After 24 h, the film was formed with a uniform thickness of ~0.2 mm. The P(MA-co-MMA)/MMT nanocomposite containing 1 wt% MMT was designated as P(MA-co-MMA)/1%MMT nanocomposite and so on.

Characterization

Morphology of the nanocomposite latex was investigated with a JOEL JSM-1230 TEM. X-ray diffraction patterns of the film and powder samples were recorded by using a Philip XRD-500 X-ray diffraction analyzer with nickel-filtered Cu K α radiation at 30 kV and 20 mA. Molecular weight of the P(MA-co-MMA) copolymers and the matrixes removed from their respective nanocomposite lattices by Soxhlet extraction were measured by gel permeation chromatography, which was carried out at 40°C with a Testhigh series III pump and a Testhigh ultraviolet-visible (UV-vis) detector model 500. One Phenol Gel 550A column and two Phenol Gel MXL columns in series were used with THF as a mobile phase (0.8 ml/min). The molecular weight and molecular weight distributions were estimated by referring to the polystyrene standard. The transmittance of the films was measured by Jasco model 555 UV-vis spectrophotometer. Glass transition temperature of the films was measured by a differential scanning calorimeter (DSC, TA Instrument model 2920) at a heating rate of 10°C/min under nitrogen atmosphere. Data were taken at the second run. Tensile properties of the films such as yield stress, Young's modulus, and elongation were measured by using a Tian-Siang tensile tester according to ASTM D-638 type IV with a cross-head speed of 1 mm/min at 30°C. At least five specimens were measured for each testing results.

Water vapor permeability of the films was measured by following ASTM E-96. The samples were dried at 80°C to a constant weight before testing. In general, ~150 ml deionized water was placed into a cylinder cup. The mouth of the cup was then sealed with a dried film specimen and then the cup was placed in an oven maintaining at 40°C and 39% relative humidity. The periodical weight was recorded until the change of weight with time was linear. The slope of the linear region was used to estimate the water vapor transmission δ , which was defined as the weight loss per unit time and unit area of the film specimen. Then, the permeability coefficient K_V of water vapor was estimated by using the following equation.

$$k_V = \frac{\delta d}{P_s(1 - R_h)} \quad (1)$$

where d is the thickness of film specimen, P_s is the saturated water vapor pressure at testing temperature, and

R_h is the relative humidity outside the testing cup expressed as a fraction.

Results and discussion

Morphology of the P(MA-co-MMA)/MMT nanocomposite latices and films

Typical TEM image of the exfoliated P(MA-co-MMA)/MMT nanocomposite latex is shown in Fig. 1. The polymerizing P(MA-co-MMA) not only exfoliated MMT but also adhered to the exfoliated MMT nanoplatelets so that no well defined P(MA-co-MMA) matrix was observed. Similar TEM images have also been observed for the exfoliated polyvinyl acetate/MMT nanocomposite latex prepared by the same method [21]. As the fabricated P(MA-co-MMA)/MMT nanocomposite latices were cast into films, their X-ray diffraction patterns have no diffraction peak contributed by the original interlayer d_{001} -spacing of neat MMT appeared at $2\theta \sim 7^\circ$ [20] as typically shown in Fig. 2, indicating that MMTs have been fully exfoliated and dispersed in the film. The number average molecular weight and polydispersity index (PDI) of P(MA-co-MMA) copolymers and their matrices removed from the nanocomposite latices prepared by various weight ratios of MA to MMA with various contents of MMT were summarized in Table 1. In general, the molecular weight was not substantially changed as the weight ratio of MA to MMA and the MMT content were changed. All the number average molecular weights were higher than 100,000.

The cast P(MA-co-MMA)/MMT nanocomposite films were transparent even though the films became blurring as the content of MMT exceeded 5 wt% owing to the light scattering from exfoliated MMT nanoplatelets. Figure 3 shows the typical photographs of the cast films. Their

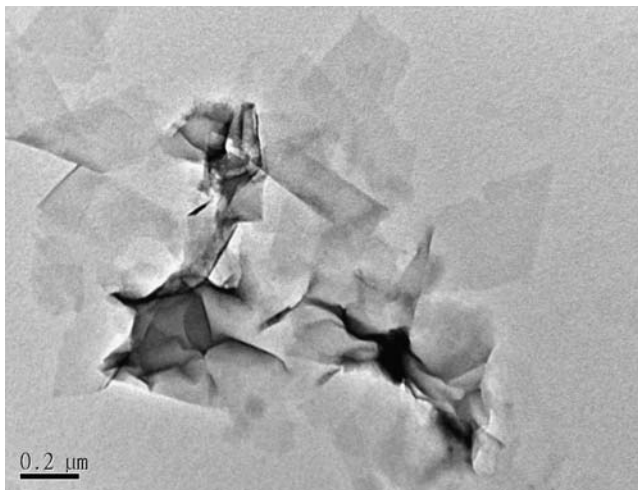


Fig. 1 TEM micrograph of P(MA-co-MMA)/10%MMT nanocomposite latex prepared by 3:1 weight ratio of MA to MMA

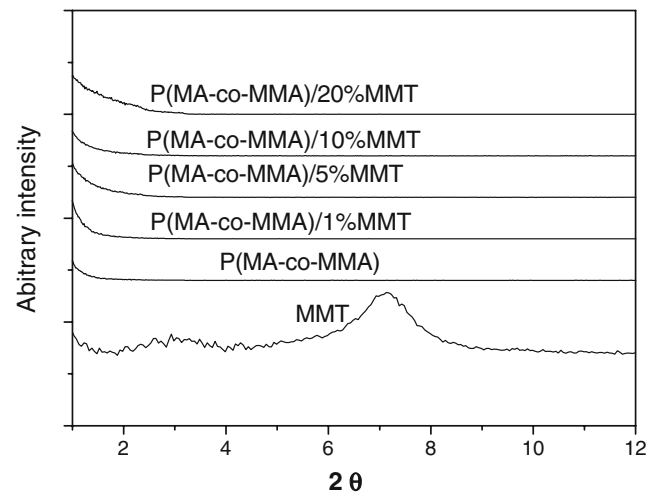


Fig. 2 X-ray diffraction patterns of P(MA-co-MMA)/MMT nanocomposite films with the indicated content of MMT prepared by 3:1 weight ratio of MA to MMA. That of the pristine MMT particles was also included for comparison

absolute transmittance measured by the UV-vis spectrophotometer was present in Fig. 4. Because of no absorption peak in the visible region of UV-vis spectra, the P(MA-co-MMA)/MMT nanocomposite films are transparent. As all the cast films were subjected to the combustion, the char residuals of P(MA-co-MMA)/MMT nanocomposite films with the MMT content higher than 5 wt% could preserve their original film profile. However, the neat copolymer films were immediately burned into black ashes as soon as they closed to the flame. Apparently, the films containing MMT performed a retarded burning speed. According to our previous study on the morphology of cast PVAc/MMT nanocomposite films prepared from the similar soap-free emulsion polymerization [21], the MMT nanoplatelets were dispersed evenly and flattened almost completely along the film surface. In other words, the exfoliated MMT nanoplatelets acted like a scaffold to preserve the film profile after burned. It is noteworthy that as combustion occurs, this scaffold would have a potential to block the flame transportation.

Properties of the nanocomposite films

The T_g measured from the DSC thermograms of the P(MA-co-MMA)/MMT nanocomposite films prepared by various weight ratios of MA to MMA with various contents of MMT were summarized in Table 2. Notably, T_g of PMMA is 105°C , whereas that of PMA is 6°C [22]. By using the Fox equation [23] to estimate the T_g of P(MA-co-MMA) copolymers,

$$\frac{1}{T_g} = \frac{W_{MA}}{T_{g,PMA}} + \frac{W_{MMA}}{T_{g,PMMA}} \quad (2)$$

where W_{MA} and W_{MMA} are the weight fractions of MA and MMA in the copolymer, and $T_{g,MA}$ and $T_{g,PMMA}$ are the T_g

Table 1 Molecular weight data of P(MA-co-MMA) matrices removed from their MMT nanocomposite latices

P(MA-co-MMA)/MMT latex with	MA/MMA=3:1 Mn×10 ⁵ PDI		MA/MMA=4:1 Mn×10 ⁵ PDI		MA/MMA=5:1 Mn×10 ⁵ PDI	
0% MMT	2.48	1.83	2.28	2.38	2.35	2.16
1% MMT	1.09	2.50	2.23	2.50	2.22	2.38
5% MMT	2.63	2.53	2.18	2.72	2.18	2.72
10% MMT	2.10	1.54	2.19	2.66	2.48	2.33
20% MMT	3.53	2.74	2.23	2.71	3.27	1.42

of PMA and PMMA. The T_g of copolymers with weight ratios of MA to MMA equal to 3:1, 4:1 and 5:1 will be 25.6, 21.4 and 18.7°C, respectively lower than those directly measured by DSC. It should be noted that the reactivity ratio r_1 of MA in MA/MMA copolymerization is 0.4, whereas r_2 of MMA is 2.15 [24]. The type of copolymerization is close to the ideal copolymerization, that is

$$\frac{d[\text{MA}]}{d[\text{MMA}]} = \frac{r_1[\text{MA}]}{[\text{MMA}]} \quad (3)$$

where [MA] and [MMA] are the concentrations of MA and MMA during copolymerization. Accordingly, the MMA monomers should be reacted about twice more than its fraction in the initial copolymerization. Because the conversion was only ~90%, most of the removed unreacted monomers at the final stage of emulsion polymerization should be MA. As a result, the estimated T_g of P(MA-co-MMA) is lower than the measured one. Interestingly, as MMT participated in the emulsion copolymerization, the T_g of fabricated P(MA-co-MMA)/MMT nanocomposites became close to the theoretical values or even lower (see Table 2). It is contradictory to the general observation that incorporating the exfoliated MMT would increase the T_g of

polymer matrix [21]. We have observed that micellation usually occurred in the interlayer region of MMT during emulsion polymerization of MMA under the presence of MMT and further polymerization exfoliated MMT [20]. Thus, it is rational to believe that MMT preferred to absorb MA monomer than MMA for copolymerization in micelles, resulting in the lower T_g for the fabricated P(MA-co-MMA)/MMT nanocomposites compared to the neat copolymers.

The water vapor permeability of fabricated P(MA-co-MMA)/MMT nanocomposite films was investigated at 40°C following the test method of ASTM E96. The results shown in Fig. 5 indicated that the permeability was decreased with decreasing the weight ratio of MA to MMA and increasing the content of MMT. The temperature of permeability test was higher than the T_g of testing specimens. It is conceivable that permeability is decreased with increasing the T_g of the samples owing to the fact that the free volume was decreased. However, the extent of decreased permeability for P(MA-co-MMA)/MMT nanocomposite films compared to the neat copolymers was not as great as the reported data for the cast PVAc/MMT nanocomposite films [21]. Apparently, it is due to the fact that T_g of the P(MA-co-MMA)/MMT nanocomposite films is lower than that of neat co-

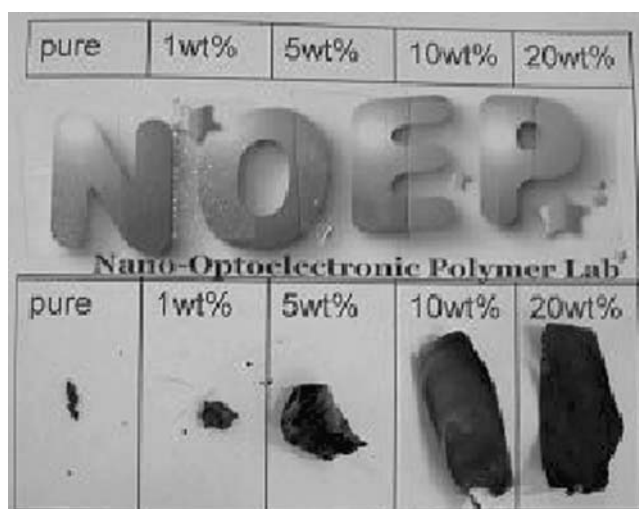


Fig. 3 Photograph of the P(MA-co-MMA)/MMT nanocomposite films prepared by 3:1 weight ratio of MA to MMA with the indicated MMT contents (*upper*), and their residuals after combustion (*lower*)

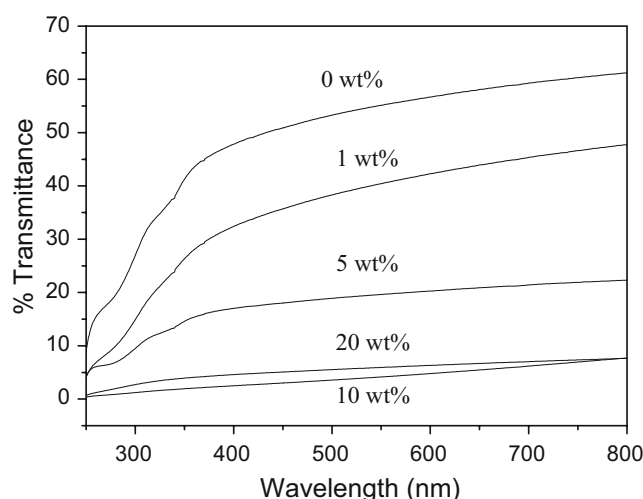


Fig. 4 Transmittance of the P(MA-co-MMA)/MMT nanocomposite films prepared by 3:1 weight ratio of MA to MMA with the indicated MMT contents

Table 2 Glass transition temperature of P(MA-co-MMA)/MMT nanocomposite films

P(MA-co-MMA)/ MMT film with	T_g , °C (MA/ MMA=3:1)	T_g , °C (MA/ MMA=4:1)	T_g , °C (MA/ MMA=5:1)
0% MMT	30	33.5	27
1% MMT	23	18.5	18.3
5% MMT	22	20	17.5
10% MMT	20	13.8	18.1
20% MMT	18	16.8	17.9

polymers, creating excess free volume for the water vapor to transport in the polymer matrix.

The tensile properties such as Young’s modulus, yield stress and elongation of P(MA-co-MMA)/MMT nanocomposite films prepared by various weight ratios of MA to MMA with various contents of MMT were shown in Fig. 6. It is surprising to find that Young’s modulus of the films was decreased as 1 wt% of MMT was incorporated. Further increase of the MMT content significantly increased the Young’s modulus of the films. The Young’s modulus could reach up to more than 2,000 times than that of the neat copolymer films as 20 wt% MMT was incorporated. The decrease of Young’s modulus by incorporating 1 wt% MMT to the copolymers might be due to the decrease of T_g , since the T_g of copolymer is close to the testing temperature and that of P(MA-co-MMA)/1%MMT nanocomposite films is about 10°C lower than the testing temperature(see Table 2). The yield strength of the films was increased with the content of MMT. As the content of MMT was increased to 20 wt%, the yield strength was increased up to 20 times higher than that of the copolymer. As to the elongation, it is surprising to find that for the P(MA-co-MMA) copolymer prepared by the 5:1 weight ratio of MA to MMA, the elongation was increased from 383 to 657% as 1 wt%

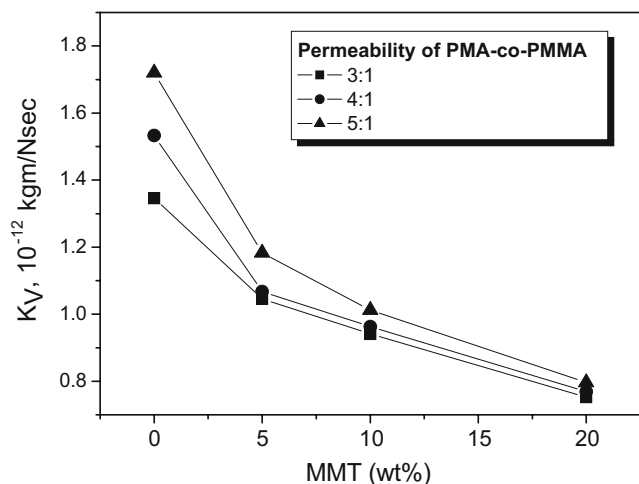


Fig. 5 Permeability coefficient K_V of the P(MA-co-MMA)/MMT nanocomposite films as a function of the MMT content, prepared by (square) 3:1, (circle) 4:1, and (triangle) 5:1 weight ratio of MA to MMA

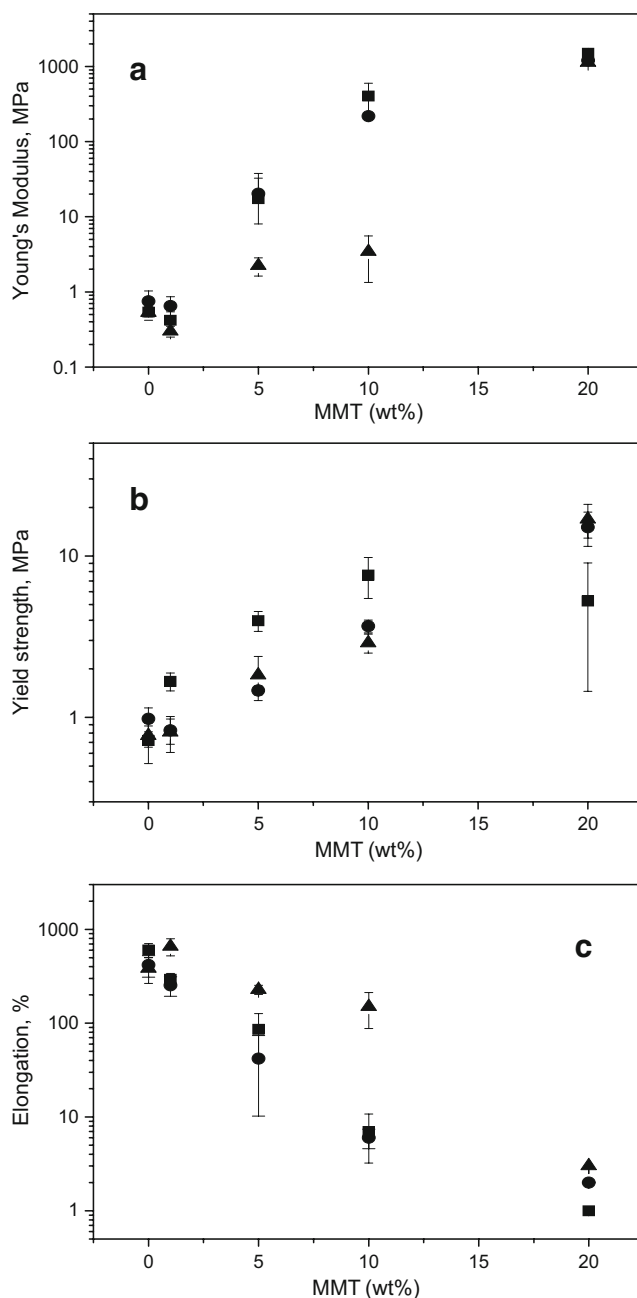


Fig. 6 a Young’s modules, b yield stress, and c elongation of the P(MA-co-MMA)/MMT nanocomposite films as a function of the MMT content, prepared by (square) 3:1, (circle) 4:1, and (triangle) 5:1 weight ratio of MA to MMA

MMT was incorporated. Further increase of MMT content decreased the elongation. However, the elongation still had 150% as 10 wt% MMT was incorporated. Again, in contrast to the T_g of copolymer close to the testing temperature, the T_g of the P(MA-co-MMA)/1%MMT nanocomposite films is about 10°C lower than the testing temperature so that the specimens became more ductile. Similar ductile behavior for the poly(2-methoxyethyl acrylate)/MMT nanocomposites with T_g of -34°C was also reported [25]. Notably, for the cast PVAc/1%MMT nano-

composite film with T_g slightly higher than the testing temperature, the elongation was significantly retarded by the exfoliated MMT nanoplatelets [21].

Conclusions

The exfoliated P(MA-co-MMA)/MMT nanocomposite lattices fabricated by soap-free emulsion polymerization were successfully cast into a transparent film. With the MMT content higher than 5 wt%, the inflammable residuals of nanocomposite films after combustion could preserve their original film profile acting like an inflammable scaffold. Owing to the large difference of the reactivity ratios between methyl acrylate and methyl methacrylate monomers and their differential absorption to the MMT during copolymerization, the T_g of P(MA-co-MMA)/MMT nanocomposite films was below room temperature and also lower than the T_g of copolymers, leading to more ductile for P(MA-co-MMA)/1%MMT nanocomposite films compared to neat copolymer. Besides, the water vapor permeability coefficient of the films was only decreased to its half value as 20 wt% MMT was incorporated. Nevertheless, the yield strength of the films was able to increase up to 20 times and Young's modulus up to 2,000 times as 20 wt% MMT was incorporated. Based on those superior properties of cast films, the P(MA-co-MMA)/MMT nanocomposite latex solutions should have great potential applications on the coating industries, especially for the fire-retardant coatings.

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