



Poly(methyl methacrylate-*co*-butyl acrylate)/ Organophosphate-modified Montmorillonite Composites

Sanit Sirapanichart^{1,2}, Pathavuth Monvisade^{1,3*}, Punnama Siriphannon^{1,4},
and Jiti Nukeaw^{1,2}

(1) College of KMITL Nanotechnology, King Mongkut's Institute of Technology
Ladkrabang, Bangkok 10520, Thailand

(2) Thailand Center of Excellence in Physics, Bangkok 10400, Thailand

(3) Polymer Synthesis and Functional Material Unit, Department of Chemistry,
Faculty of Science, King Mongkut's Institute of Technology Ladkrabang,
Bangkok 10520, Thailand

(4) Department of Chemistry, Faculty of Science, King Mongkut's Institute of
Technology Ladkrabang, Bangkok 10520, Thailand

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A B S T R A C T

Poly(methyl methacrylate-*co*-butyl acrylate)/tetrabutylphosphonium modified montmorillonite (P(MMA-*co*-BA)/P-MMT) composite films were prepared by simple solution casting technique. P(MMA-*co*-BA) was synthesized through solution polymerization in the presence of benzoyl peroxide (BPO) as an initiator. After modification via cation exchange reaction by tetrabutylphosphonium bromide, the organoclay was dispersed in toluene and added into P(MMA-*co*-BA) solution. The well-dispersed mixture was cast by doctor blade technique to obtain the composite films. The P-MMT content in the composites was varied (i.e., 1, 2, 3 and 6 wt%) in order to study its effects on thermal stability, mechanical properties and UV shielding ability. The structure of P-MMT in the composites was investigated by XRD technique. The composites containing 1 and 2 wt% of P-MMT showed the d_{001} peak slightly shifted to lower 2θ , indicating mainly intercalated structure occurred with some agglomerations of particles. The intercalated structure of P(MMA-*co*-BA)/P-MMT 2% composites was observed by TEM technique. The TGA results showed that degradation of the composites occurred at higher temperatures compared to that of their virgin polymer and the degradation point increased with P-MMT content. Tensile strength and Young's modulus of composites were higher than those of their original copolymer. By addition of 1-3 wt% of P-MMT, it could be seen that the higher the P-MMT loading, the higher would be the tensile strength and Young's modulus. The P(MMA-*co*-BA)/P-MMT composite films showed their screening ability in UV region, especially in the UV-B range, which is rather higher than that in the visible region.

Key Words:

montmorillonite;
organoclay;
organophosphate;
poly(methyl methacrylate-*co*-butyl
acrylate);
solvent casting.

INTRODUCTION

Poly(methyl methacrylate), PMMA, is one of the most widely used type of acrylate polymers. It is often preferred on account of its moderate properties, especially its clarity and outstanding outdoor weathering resistance, easy handling and processing, and low cost. These impressive properties make PMMA to be preferred economically to polycarbonates

(PC) when a high strength quality is not critical.

However, PMMA usually behaves in a brittle manner when loaded, resulting in its restricted application. Thus, there are two solutions suggested to surpass its original application. The first common solution is the copolymerization of MMA with other monomers, which their polymers

(*) To whom correspondence to be addressed.

E-mail: kmpathav@kmitl.ac.th

have glass transition temperature (T_g) below room temperature, e.g., butyl acrylate polymers (PBA). Generally, the PBA is considered as a colourless transparent rubbery polymer at ambient temperature, thus, it is commonly used in copolymer systems to alleviate the brittleness of the final product [1].

In other attempts, for the second approach, various types of inorganic nanoparticles have been added into PMMA matrix [2,3]. Among inorganic nanoparticles, montmorillonite (MMT) clays have received considerable interest because of their structural stiffness, strength and dimensional stability in two dimensions, rather than one, to produce the composites with various polymers, e.g., acrylate polymers [4,5], NBR/PVC [6], PP/EPDM [7] and PVC [8]. The efficiency of MMT to modify the properties of the polymer depends primarily on the degree of its dispersion in the polymeric matrix.

In order to achieve good dispersion and dispersion stability of the inorganic nanoparticles into the polymer, it is necessary to modify them to be more organophilic and compatible with polymer matrix. Most commercially available organo-MMTs are produced by exchange of alkali or alkali earth cations in the interlayer space of MMT with alkyl ammonium salts. However, the alkyl ammonium modified MMTs, e.g., cetyltrimethylammonium [9], hexadecylammonium [10], dimethyl dehydrogenated tallow quaternary ammonium [11] are thermally unstable above 250°C. For this reason, to improve thermal stability of MMT, organophosphonium salts, e.g., tetrabutylphosphonium bromide, hexadecyl tributylphosphonium bromide, tetraphenylphosphonium bromide [12], butyltriphenylphosphonium bromide [13], and/or tributyl tetradecylphosphonium chloride [14] have been alternatively used to modify the MMT.

There are some reports of using phosphonium modified MMTs in polymer nanocomposites such as epoxies [10,15], styrenic polymers [16-19], poly(vinyl chloride) [11], polyesters [20-22], and PMMA [23-25]. However, almost organophosphonium salts which were used in those works containing phenyl groups and/or long alkyl chains that are normally more expensive compared to phosphonium salts with shorter alkyl chains. Besides, according to Patel et al. [12] tetrabutylphosphonium MMT is as

stable as tetraphenylphosphonium MMT due to the high thermal stability of tetrabutylphosphonium cation. Therefore, polymer/clay composites which involve tetrabutylphosphonium cation will possess not only reasonable high thermal stability but also higher cost feasibility.

As it is stated above, the objective of this work was to improve some properties of PMMA by copolymerization with butyl acrylate (BA) monomer along with incorporation of the stable and economical short-alkyl-phosphonium modified MMT into the copolymer matrix. Thus, in this work we used tetrabutylphosphonium salt as an intercalating agent for modification of MMT. Composite films made of poly(methyl methacrylate-co-butyl acrylate) and tetrabutylphosphonium intercalated montmorillonite (P(MMA-co-BA)/P-MMT) were prepared by simple solution casting technique. The composite films were characterized by various techniques. Thermal stability, mechanical properties and UV shielding ability were investigated for these composites.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na-MMT) was supplied by Thai Nippon Chemical Industry Co. Ltd., Thailand, under the trade name of Mac-gel (CEC of ~100 meq/100 g). Methyl methacrylate (MMA) and butyl acrylate (BA) monomers were commercially available and used as supplied without further purification. Tetrabutylphosphonium bromide (TBPB) was purchased from Fluka, Switzerland. Toluene and methanol of analytical grade were purchased from Fisher Scientific Co., UK. Benzoyl peroxide (BPO) was purchased from Carlo Erba Reagenti, Italy.

Preparation of Tetrabutylphosphonium-modified Montmorillonite

First, Na-MMT was dispersed in de-ionized water for 2 h under sonication (ULTRASONIK, Fisher Scientific Worldwide, USA) and dried at 100°C, followed by grinding to pass a 400 mesh sieve. Two grams of screened MMT was dispersed in 800 mL of de-ionized water under sonication for 1 h. To obtain P-MMT, 20 mL of 0.36 M of TBPB was slowly added

into screened MMT suspension under sonication for 1 h. P-MMT was then separated from the suspension and washed several times with distilled water until the testing of the mother liquor with 0.1 M of AgNO_3 showed clear solution, without any white precipitation. Then, it was dried overnight at 110°C and ground to pass a 400 mesh sieve. Crystalline structure and apparent interlayer spacing (d -spacing) of starting MMT and modified MMT were characterized by powder X-ray diffractometer (XRD, Bruker AG, D8 Advance, Germany). Chemical composition of the MMTs was obtained by X-ray fluorescence spectrometer (XRF, Bruker AG, SRS 3400, Germany).

Synthesis of Poly(methyl methacrylate-co-butyl acrylate)

Samples of MMA (9.0 g) and BA (1.0 g) monomers were dissolved in 40 mL of toluene in presence of 0.1 wt% of BPO (with respect to total weight of monomers) as the initiator. This solution was purged with nitrogen gas for 15 min and then polymerized at 85°C in water bath for 24 h. White precipitate of P(MMA-co-BA) was obtained by precipitation in methanol.

The weight average molecular weight (\overline{M}_w), number average molecular weight (\overline{M}_n) and molecular weight distribution (MWD) of the P(MMA-co-BA) were measured by gel permeation chromatography (GPC, Milipore, Waters e2695, USA) using polystyrene standard method and tetrahydrofuran as mobile phase. The results show that \overline{M}_w 140,000 g/mol, \overline{M}_n 72,000 g/mol and MWD 1.9.

Preparation of P(MMA-co-BA)/P-MMT Composite Films

P-MMT was dispersed in toluene under sonication for 30 min and added into P(MMA-co-BA)/toluene solution (30 wt%). The amount of P-MMT was varied as 1, 2, 3 and 6 wt% with respect to the weight of P(MMA-co-BA). The mixture was stirred vigorously by a magnetic stirrer for 24 h. The obtained P(MMA-co-BA)/P-MMT suspension was degassed by using sonication technique for 30 min and cast into films by using doctor blade technique to obtain the P(MMA-co-BA)/P-MMT composites with 100 ± 20 μm thickness.

Characterization of Composite Films

The basal spacing of the composite films was characterized by XRD technique. Thermal stability of neat P(MMA-co-BA) and composite films were determined by thermogravimetric analysis (TGA, Perkin Elmer, Pyris 1 TGA, USA) at a heating rate of $5^\circ\text{C}/\text{min}$. The UV-Vis transmission spectra of the neat copolymer and the composite films were recorded by UV-Vis spectrophotometer (Thermo Electron Corporation, Helios, UK). The morphology of the film was observed by a Jeol transmission electron microscope (JEM-2100, Japan). The mechanical properties of the neat polymers and the composite films were determined by universal testing machine (LLOYD Instrument, LR5K, UK), following the ASTM D 882 method.

RESULTS AND DISCUSSION

Characterization of MMTs

The basal spacing (d_{001}) of the MMTs was determined by the XRD. The XRD patterns of Na-MMT and P-MMT are shown in Figure 1. The crystalline peak corresponded to 001 plane of Na-MMT is at $2\theta = 6.12^\circ$, indicating the basal spacing of 14.2 \AA . After modification, the d_{001} peak shifted to lower angle of $2\theta = 5.64^\circ$ ($d_{001} = 15.7$ \AA) in P-MMT due to the cation exchange between Na^+ ions and TBPB ions. The intercalating TBPB ions into the layers of Na-MMT brought about the expansion of the basal spacing of the MMT. Furthermore, the presence of the intercalating TBPB ions in the layers of P-MMT was confirmed by XRF technique as shown in Table 1. The exchangeable sodium (Na) ions in 001 plane

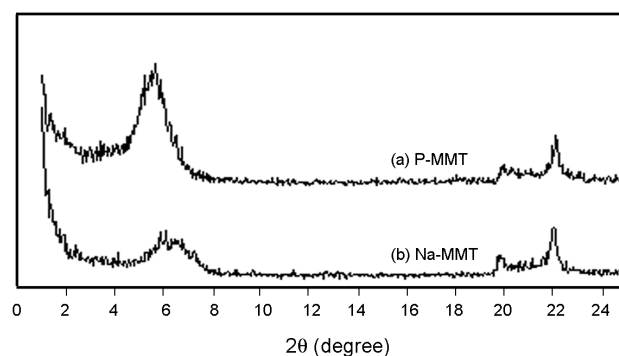


Figure 1. XRD Patterns of: (a) P-MMT and (b) Na-MMT.

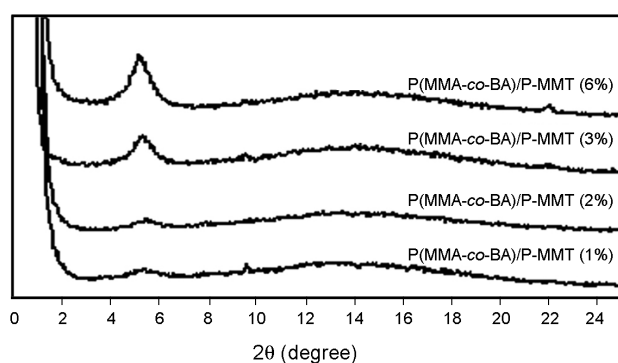
Table 1. Composition of Na-MMT and P-MMT.

Sample	Composition (wt%)								
	Al	Si	P	Na	Mg	Ca	K	Fe	O
Na-MMT	8.1	32.2	-	2.9	2.5	1.6	0.9	2.3	49.5
P-MMT	8.5	32.8	1.5	-	2.6	1.4	0.8	1.8	50.6

could be detected in the Na-MMT. After intercalation with TBPB, the presence of phosphorus (P) concomitant with the absence of Na are observed in P-MMT.

Characterization of P(MMA-co-BA)/P-MMT Composite Films

The XRD patterns of P(MMA-co-BA)/P-MMT composites with 1, 2, 3 and 6 wt% of P-MMT loading are shown in Figure 2. For the P(MMA-co-BA)/P-MMT containing 1 and 2 wt% of P-MMT, the crystalline peak of 001 plane is observed at $2\theta = \sim 4-6^\circ$ with very low intensity, implying that the intercalation of the P(MMA-co-BA) into the P-MMT layers caused the expansion of the 001 plane. In addition, those very small d_{001} peaks of the composites also indicated some agglomerate of P-MMT. The higher the amount of P-MMT content (3 and 6 wt%), the stronger intensity of the d_{001} peak was observed without significant change of their peak positions compared to those of the composites containing 1 and 2 wt% of P-MMT. These results indicate the penetration of the copolymer chains into the 001 plane of the P-MMT, forming the intercalated structure along with more agglomeration of particles

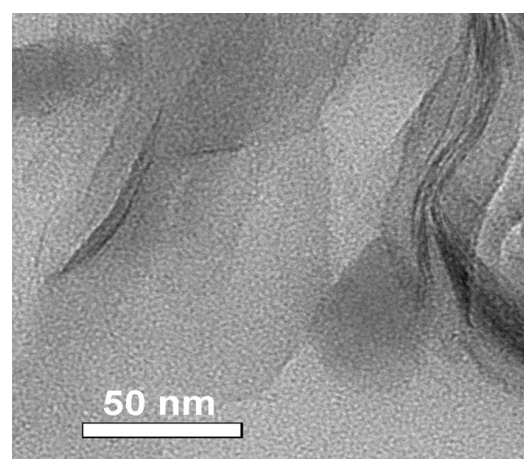
**Figure 2.** XRD Patterns of P(MMA-co-BA)/P-MMT composites with P-MMT contents of 1, 2, 3, and 6 wt%.

of P-MMT. However, the penetration of the copolymer chains is cumbersome due to their high molecular weight containing steric butyl side-chains, making the exfoliation unlikely to happen. Therefore, at this point, the suitable concentration of P-MMT addition might be suggested at 2 wt%, however, the properties of these composite films were also investigated to figure out the optimum concentration of P-MMT.

Figure 3 shows TEM micrograph of P(MMA-co-BA)/P-MMT 2% composites where the dispersion of P-MMT tactoids can be seen in the P(MMA-co-BA) matrix. The loosely packed structure of P-MMT tactoids is observed as the delaminating striation of P-MMT layers. This morphology represents the intercalated structure of the P(MMA-co-BA)/P-MMT composites, supporting the previous XRD analysis.

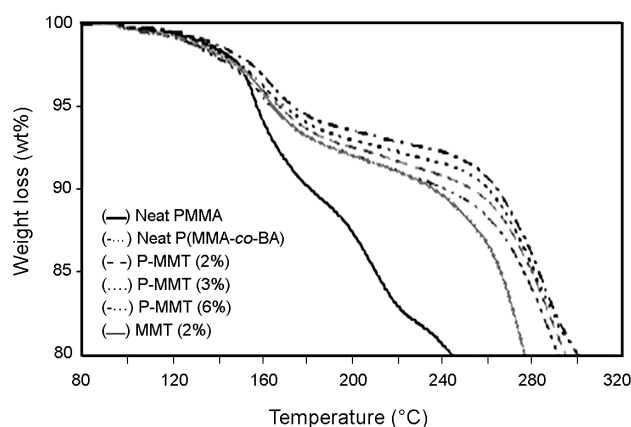
Thermal Properties of P(MMA-co-BA)/P-MMT Composite Films

The decomposition temperature at 10% ($T_{d-10\%}$) and

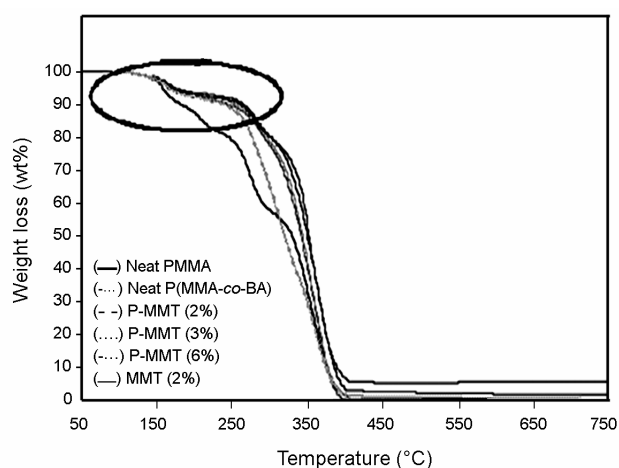
**Figure 3.** TEM Micrograph of P(MMA-co-BA)/P-MMT 2% composite.

50% ($T_{d-50\%}$) weight loss data evaluated by TGA for the neat polymers and the P(MMA-co-BA)/P-MMT composites are illustrated in Figure 4 and listed in Table 2. In case of neat PMMA and neat P(MMA-co-BA), there is an increase in thermal stability. The neat P(MMA-co-BA) exhibits $T_{d-10\%}$ at 241°C that is 60°C higher than that of the neat homopolymer. This increment could be regarded as the stabilizing effect of BA units in the copolymer structure [26], bringing about the increase of T_d values of P(MMA-co-BA).

Moreover, for the composites, it is seen that T_d of composites with unmodified MMT (MMT 2%) is lower than those of the neat P(MMA-co-BA) and those of the composites with 2 wt% of P-MMT loading. This is due to the incompatibility between the unmodified MMT and P(MMA-co-BA) matrix



(a)



(b)

Figure 4. TGA Curves of PMMA, P(MMA-co-BA) and composites of P(MMA-co-BA) matrix shown (a) decomposition at 80-320°C and (b) decomposition at 50-750°C.

Table 2. Decomposition temperature of PMMA, P(MMA-co-BA) and composite films.

Sample	Decomposition temperature ^a	
	$T_{d-10\%}$ (°C)	$T_{d-50\%}$ (°C)
Neat PMMA	181	363
Neat P(MMA-co-BA)	241	365
P-MMT 2%	253	367
P-MMT 3%	260	375
P-MMT 6%	264	374
MMT 2%	236	320

(a) As measured by TGA: $T_{d-10\%}$ and $T_{d-50\%}$ are the decomposition temperature values at 10% and 50% weight loss, respectively.

leading to more agglomeration of the unmodified MMT, implying less possibility for the intercalation of polymer chains into the interlayer spaces of the unmodified MMT layers.

In addition, as seen in Figure 4, the presence of the unmodified MMT could slightly enhance the thermal stability of the neat copolymer at the earlier stage of decomposition until about 5% weight loss where $T_{d-5\%}$ of P(MMA-co-BA) and P(MMA-co-BA)/MMT 2% are 163°C and 166°C, respectively. This could be attributed to the presence of clay which is a highly thermal stable inorganic substance. However, the clay not only acts as a thermal barrier but also as heat storage. Hence, the agglomeration of unmodified MMT causes the larger heat sink in the polymer matrix. Besides, the agglomeration of unmodified MMT particles could also increase the continuity of the polymer matrix in the composites. With more continuity of the polymer matrix, the faster thermal decomposition of the polymer matrix would be observed with less interference by the MMT particles. Therefore, the presence of the larger heat sink and the higher continuity of the copolymer matrix could accelerate the thermal decomposition of the P(MMA-co-BA) as there is more decomposition observed beyond 5% weight loss. Consequently, the decomposition temperature of the P(MMA-co-BA)/MMT 2% composite could be lower than that of the neat copolymer.

Besides, it is also seen that the T_d of the P(MMA-co-BA)/P-MMT composites is higher than that of the

pristine P(MMA-co-BA), indicating the enhancement of thermal stability of the composites. This shows that P(MMA-co-BA) is more compatible with P-MMT compared with the unmodified MMT, and hence, it may be suggested that there is some intercalations occurred between P-MMT and the polymer matrix. Moreover, this phenomenon can be attributed to the presence of P-MMT, which is a high thermally stable nanoscale-inorganic substance thus it can act as a barrier for heat transmission and preventing the out-diffusion of the volatile decomposition product. Moreover, it is also seen that the thermal stability of the composites is increased with the increase of P-MMT content, e.g., the composites containing 6 wt% of P-MMT could increase $T_{d-10\%}$ up to 264°C that is 23°C higher than that of its pure copolymer.

Mechanical Properties of P(MMA-co-BA)/P-MMT Composite Films

The mechanical properties, including tensile strength, elongation-at-break and Young's modulus of the neat polymer and composite films are illustrated in Figure 5. The tensile strength and the Young's modulus of the P(MMA-co-BA) are decreased compared to those of the PMMA. This is the effect of the presence of BA in the copolymer molecules that can make the final product to be softer. However, those fading properties could be alleviated with the presence of P-MMT. It was found that tensile strength and Young's modulus of the composites increase beyond those of the pristine PMMA.

At 1-3 wt% P-MMT content, it can be seen that with higher P-MMT loading, higher tensile strength and Young's modulus composites are obtained. The tensile strength and Young's modulus of P(MMA-co-BA)/P-MMT 3% composites are significantly increased from its neat copolymer; i.e., from 45.6 to 61.5 MPa for the tensile strength and from 1090 to 1770 MPa for the Young's modulus. Besides, the elongation-at-break of the P(MMA-co-BA)/P-MMT composites is not significantly changed from that of the neat P(MMA-co-BA). Due to the rigidity of the intercalated P-MMT nanoparticles, they could tolerate external stress better than the polymer matrix but could not be distorted during deformation process, causing stress localization in nano-scale dispersed in polymer matrix, which could distribute the applied

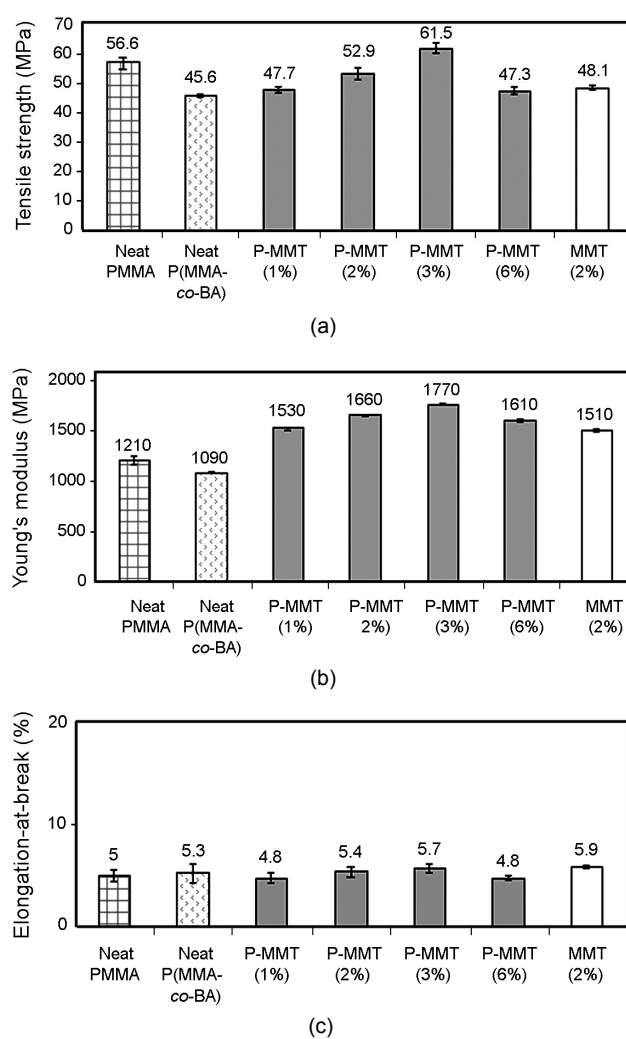


Figure 5. Mechanical properties of PMMA, P(MMA-co-BA) and composite films of P(MMA-co-BA) matrix: (a) tensile strength, (b) Young's modulus, and (c) elongation-at-break.

stress and delay the fracture of the intercalated composites. Nevertheless, tensile strength and Young's modulus of the composites dropped at 6 wt% loading of P-MMT. This result can be explained as such that at higher concentration of clay loading, the greater stress localization would result, causing lower resistance to the applied force. Although, those mechanical properties of the composites at 6 wt% loading of P-MMT are faded, they are still higher than those of its original polymer.

Comparing the composite films containing 2 wt% of P-MMT and unmodified MMT, tensile strength and Young's modulus of the former are higher than those of the latter. This was due to the incompatibility of the unmodified MMT and P(MMA-co-BA) leading to

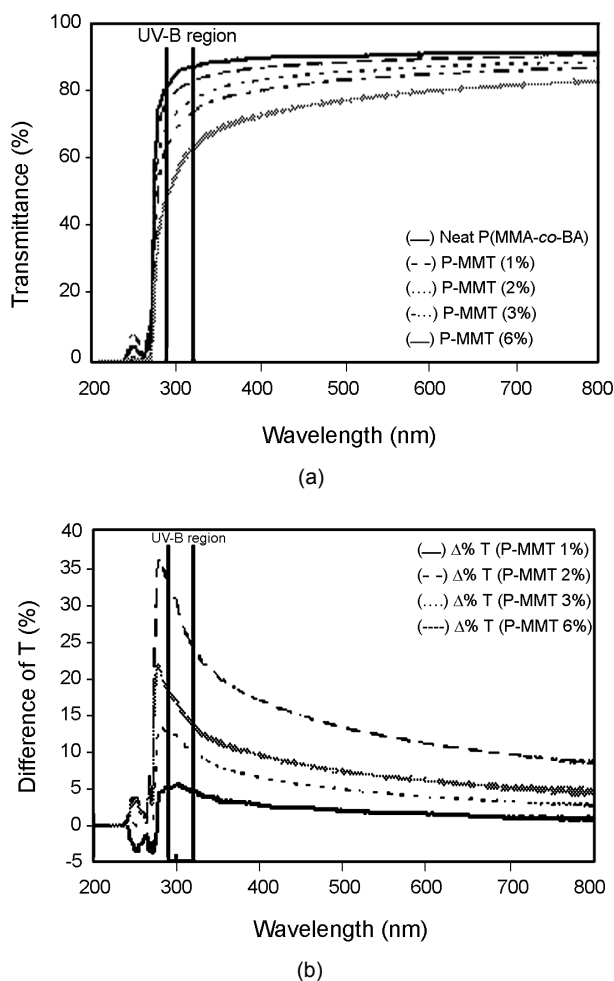


Figure 6. Optical property: (a) UV-Visible transmittance of P(MMA-co-BA) and P(MMA-co-BA)/P-MMT composite films and (b) the difference of UV-Visible transmittance between pure copolymer and its composites.

lower possibility for the polymer chains to intercalate into the interlayer spaces of MMT, and resulting in bad dispersion of MMT. Therefore, the localized stress magnitude would be larger causing more defects in the polymer matrix, and consequently, the unmodified MMT composite film is probably easier to break down than the intercalated MMT composite film. Furthermore, the tensile strength and Young's modulus of the composites with unmodified MMT are still higher than those of the neat copolymer. This might be attributed to the effect of the inorganic addition as it is already discussed.

UV-Visible Spectrophotometry

The transmittance spectra of the neat P(MMA-co-

BA) and P(MMA-co-BA)/P-MMT composite films measured by UV-Vis spectrophotometer and the difference of percentage of transmittance between the pure copolymer and its composite films are demonstrated in Figure 6. These films are highly transparent in the visible range and they show the intense energy absorption for wavelengths lower than 320 nm (UV-B range). When the P-MMT was added into the copolymer matrix, it was found that at higher P-MMT loading in the composites, the lower was the transmittance of UV and visible lights as shown in Figure 6a. Although the presence of P-MMT in the composites resulted in the decreases of both UV and visible lights transmittance, the reduction of UV transmittance was relatively higher than that of the visible light as demonstrated by the curves of the percentage difference of transmittance ($\Delta\%$) between pure copolymer and its composite films in Figure 6b.

From the above results, the preparation of optically transparent P(MMA-co-BA)/P-MMT composite films could be successfully performed with enhancement of thermal stability, mechanical properties and UV screening ability.

Consequently, at this point, the optimum concentration of P-MMT addition was suggested to be 3 wt%, because it showed better mechanical and thermal properties than those of the neat polymers and the other composite films.

CONCLUSION

P(MMA-co-BA)/P-MMT composite films were successfully prepared by simple solution casting technique. The composites containing 1 and 2 wt% of P-MMT showed mainly intercalated structure along with some agglomerate particles. The intercalated structure of P(MMA-co-BA)/P-MMT 2 wt% composites was observed by TEM micrograph. Thermal stability of P(MMA-co-BA) was increased and it was dependent on P-MMT loading. The tensile strength and Young's modulus of the composite films were enhanced without any change in their ductility properties. The higher the P-MMT loading, the higher tensile strength and Young's modulus were achieved, but dropped at 6 wt% loading due to higher stress localization. In addition, the composite

films retained their high transparency and UV screening ability, especially in the UV-B region. P(MMA-co-BA)/P-MMT composites showed better thermal and mechanical properties compared to P(MMA-co-BA)/unmodified-MMT composite films. In agreement with the resulting properties, 3 wt% of P-MMT addition would be recommended for preparation of P(MMA-co-BA)/P-MMT composite film.

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SYMBOLS AND ABBREVIATIONS

MMA	: Methyl methacrylate
BA	: Butyl acrylate
PMMA	: Poly(methyl methacrylate)
PBA	: Poly(butyl acrylate)
P(MMA-co-BA)	: Copolymer of methyl methacrylate and butyl acrylate
MMT	: Montmorillonite
P(MMA-co-BA)/P-MMT	: Composite of poly(methyl-methacrylate-co-butyl acrylate) and tetrabutylphosphonium intercalated montmorillonite
P-MMT	: Tetrabutylphosphonium intercalated montmorillonite
Na-MMT	: Sodium-montmorillonite
TBPB	: Tetrabutylphosphonium bromide
XRD	: X-ray diffractometry

GPC	: Gel permeation chromatography
XRF	: X-ray fluorescence spectrometry
TGA	: Thermogravimetry analysis
TEM	: Transmission electron microscopy
T_d	: Decomposition temperature
d_{001}	: Interlayer space between 001 plane
\overline{M}_w	: Weight average molecular weight
\overline{M}_n	: Number average molecular weight
MWD	: Molecular weight distribution

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