

Phosphonium-adapted turkish bentonite in polyurethane acrylate based uv-cured materials

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The effect of phosphonium salt adapted Turkish bentonite, which was synthesized through the reaction of between allyl phosphonium bromide and bentonite, was studied on the properties of polyurethane acrylate based materials such as physical, mechanical and thermal properties, especially flame retardancy. The effects of phosphonium adapted bentonite content and neat bentonite in polymer matrix studied as well. Chemical and morphological structures of the composites were characterized by FTIR, XRD and SEM analysis. XRD and SEM images confirmed which the adapted bentonite was exfoliated in the polymer structure due to its good dispersion. Moreover, thermal, flame retardant, mechanical and optical properties of urethane acrylate based materials results showed that the materials containing phosphonium adapted bentonite pointed out higher modulus, better thermal properties due to increasing the crosslinking density as compared with the UV-cured materials which contained pure bentonite. In addition to this, the existed of the phosphonium compound advanced the flame retardancy of the urethane acrylate based materials.

Key words: Polyurethane acrylate, Na-Bentonite, Phosphonium salt, Flame retardant, UV-curing.

Introduction

Owing to their mechanical, thermal, chemical resistance and good conductivity properties, bentonite-polymers materials (BPMs) have been used extensively in a broad range of applications during the past two decades, including many industrial applications such as, rechargeable batteries, electronic, photochemical cells, sensors and anticorrosion coatings etc. [1-3]. BPMs are environmentally friendly and cheap and have high chemical resistance [3]. Particularly, in the case of nano-composites composed of layered materials as an inorganic host, silicate layers play an important role in novel nano composite properties such as decreased thermal expansion coefficient [1, 4-6]. Polyurethane acrylate (PUA) is known as one the most important leading polymers because of its potential commercial applications in, for example, high abrasion resistance, tears strength, excellent shock absorption, flexibility, and elasticity [2, 5, 7].

The main purpose of bentonite modification is to render the layered silicates miscible with polymer matrices like polyurethane acrylate, by lowering the surface energy, improving the wetting characteristics of the polymer matrix, and enlarging the interlayer spacing of bentonite. Natural bentonite commonly is an alumina-silicate based mineral with sodium hostage

ions (e.g. exchangeable ion) present between the bentonite layers [8-9].

The literature contains many studies about modification of bentonite and adapted PUA-bentonite materials investigated to improve the mechanical performance of polyurethane acrylate. Generally, the modification is employed by ion-exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkyl ammonium [4, 10] or alkyl phosphonium cations [11-12] or by intercalation in bentonite of hydrophilic polymers, such as polyethylene oxide (PEO) [8, 13], or polyvinyl alcohol (PVA) [8, 14]. The bentonite adapted with phosphonium salts have an appreciably higher thermal stability than the ammonium salts adapted bentonite and may be potentially useful materials for melt processing of polymer layered silicates nano-composites [11-12, 15]. Up to now, there are few study has been used modification of PUA-bentonite with UV-curing technique [16-21]. It has more advantage than classical thermal polymerization processes. For example, low energy consumption, cost efficiency, high reactivity and curing speed, excellent adhesion, flexibility and good rheological behavior. Hence, UV-curable polymeric materials are also used in a variety of applications [21-23].

Since the early 1800s, Boric acid and borate salts, phosphorus, halogen, and other elements have been used as flame retarding agents. When phosphorus containing compounds were compared with these agents, it was discovered to bring about less toxic gases and smokes during combustion [1, 21]. In order to increase the flame retardance of a polymeric material generally high

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charging of the additives are demanded. But that state can negatively impact the mechanical, psychical, optical properties and etc. of these materials. Reduction in the properties of the polymeric materials incorporated with phosphorus-containing chemicals, which are highly efficient to develop the flame retardancy, does not occur [6, 16, 24].

The aim of the present study was to explore the mechanic and psychical (e.g. thermal, flame retardant, tensile stress-strain) properties of phosphonium salt adapted bentonite (PSMB) containing polyurethane acrylate resin (PUA). For this purpose, PUAs were prepared with 1, 3, 5 and 7 wt% PSMB charging and the structures of the UV-curable materials were enlightened by FT-IR spectrum. The morphology of materials was examined by using Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). What is more, the effect of PSMB on the thermal properties and flame retardancy of PUA based materials were studied in conditions of TGA and LOI. Mechanical properties of photocured materials were determined by standard tensile stress-strain tests method. Additionally, its optical properties were examined by UV Spectroscopy.

Materials and Methods

Materials

Aliphatic urethane acrylate (CN9009), Ethoxylated-20-trimethylolpropane triacrylate (TMP20EOTA) and 1,6-hexanediol diacrylate (HDDA) were supplied from Sartomer, USA. Photoinitiator, 2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxide (Darocur[®] TPO), was provided by Ciba Specialty Chemicals. Allyl bromide and Triphenyl phosphine were supported from Sigma Aldrich. Hydrochloric acid, diethyl ether and toluene were provided from Merck, Germany. Deionized (DI) water was used (TKA, Germany) all experiments.

Sodium bentonite was obtained from Gemas Company, Turkey. The composition of the sodium bentonite is given in Table 1.

Characterization

The chemical structures were identified by FTIR spectra recorded on a Perkin-Elmer Spectrum 100 ATR-FTIR spectrophotometer. The transition mode

was used and the wavenumber range was set from 4000 to 400 cm^{-1} . SEM imaging of the materials was performed on JEOL JSM 7000F. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a platinum coating. Thermogravimetric analyses (TGA) of the UV-cured free films were performed using a Perkin-Elmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 to 750 $^{\circ}\text{C}$ with heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. X-ray powder diffraction (XRD) data were obtained using a PANalytical X'Pert Powder Multipurpose Diffractometer in Bragg-Brentano geometry (Cu-K α radiation). Mechanical properties of the UV-cured free films were determined by standard tensile stress-strain tests to measure modulus (E), ultimate tensile strength (δ), and elongation at break (ϵ). Standard tensile stress-strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S apparatus, using a cross-head speed of 5 mm/min. The contact angles of 3-5 mL of distilled water, which was applied to the surface by a syringe, were performed by using a Kruss DSA-2 goniometer meaning of sessile drop test method in which drops were created by using a syringe. The image of the liquid drop was captured on a video camera and transferred to a computer screen. Optical properties of UV-cured films were examined by using a UV spectrometer (UV2600 Shimadzu).

The limiting oxygen index (LOI) test was used for determining the flame retardance of the UA based materials. The LOI values of these materials were measured with an FTT (Fire Testing Technology) instrument on test specimen bars of 120 \times 60 \times 3 mm^3 dimensions, according to ASTM D2863-08.

Synthesis of allyl phosphonium salt

Phosphonium salt was synthesized similar to the reported by Zeytuncu *et al.* [15]. Firstly, triphenyl phosphine and allyl bromide at the same molar ratio (1 : 1) were dissolved in 80 ml of dry toluene and were loaded into 500 mL round-bottom flask. The reaction mixture was then heated to reflux at 110 $^{\circ}\text{C}$ for 2 h, and then cooled to room temperature. A white powder product was obtained. The phosphonium salt was filtered and washed several times with diethyl ether. Finally, it was dried for 2 h at 45 $^{\circ}\text{C}$ in vacuum oven.

Preparation of adapted bentonite

Adapted Bentonite was prepared according to the reported process in Ref. [21]. 2 g of bentonite was vigorously stirred in 100 mL deionized water for 5 h at room temperature. On the other side, phosphonium salt of 2 g was dispersed in 25 mL deionized water with 1 mL 2 M HCl and then added into the bentonite suspension and stirred continuously overnight. The resulting product was filtered and washed with distilled water for several times and then dried for 24 h at 50 $^{\circ}\text{C}$ in vacuum oven.

Table 1. Composition of sodium bentonite used in the study.

Compounds	Wt.,%
SiO ₂	65.90
Al ₂ O ₃	21.50
Fe ₂ O ₃	4.46
CaO	1.63
MgO	2.82
Na ₂ O	2.69
K ₂ O	0.56
Other oxides	0.44

Table 2. Composition of the formulations.

Samples	UA (g)	HDDA (g)	TMP20EOTA (g)	Darocur [®] TPO (g) ^a	Unadapted bentonite (Wt.,%)	Adapted bentonite (Wt., %)
CF	3	1.5	0.5	0.15	0	0
F0	3	1.5	0.5	0.15	3	0
F1	3	1.5	0.5	0.15	0	1
F2	3	1.5	0.5	0.15	0	3
F3	3	1.5	0.5	0.15	0	5
F4	3	1.5	0.5	0.15	0	7

^aDarocure TPO was added at 3 wt% of the total weight.

Preparation of photocured materials containing adapted bentonite

The composition of all UV-curable materials is listed in Table 2. The neat polymer matrix, which is named as control formulation (CF), was prepared by mixing the calculated amounts of aliphatic urethane acrylate resin (UA), HDDA as reactive diluents, TMP20EOTA as a crosslink agent and Darocur[®] TPO as a photo initiator. The formulations (Fn, n:0,1,2..) were prepared at room temperature for 30 min mainly from the CF and four different amounts (i.e. 1, 3, 5, and 7% ,w/w) of adapted bentonite and 3 wt.% of neat bentonite to investigate the influence on material properties, especially flame retardant property. Free films were prepared by applying the formulations on to a glass coated mold (10 mm × 50 mm × 1 mm). In order to prevent the inhibiting effect of oxygen, resin in the mold was covered by transparent polyester film before irradiation with a high pressure UV-lamp which was applied for 240 s.

Results and Discussion

FT-IR characteristics

To identify the synthesized phosphonium salt, sodium bentonite and adapted bentonite, ATR-FTIR analysis was used and the spectra were given in Figure 1. As seen from Figure 1a, the peak observed at 3032 cm⁻¹ indicated the C-H aromatic stretching bond. The absorption band at 2860 cm⁻¹ due to C-H alkane stretching peak and C=C double bond stretching peak appeared at 1628 cm⁻¹, P-Ar stretching peaks at about 1430-1485 cm⁻¹ and at around 1100 cm⁻¹ and C-C aromatic multiple bond stretching peak about 1586 cm⁻¹

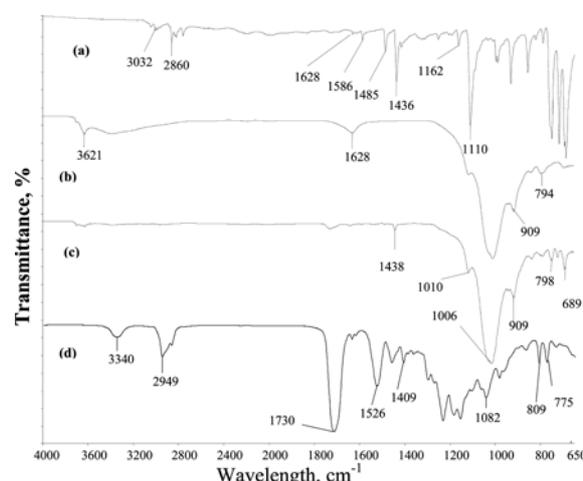


Fig. 1. FTIR spectra of a) phosphonium salt, b) Na-bentonite, (c) Adapted bentonite, and d) F2 material.

were found, respectively [25-26]. FTIR spectrum of pure bentonite (Fig. 1b) showed the peaks at 3600 and 1000 cm⁻¹ attributed to the hydroxyl (OH) groups which are related to typical peaks of Na-bentonite. The main peak of the aromatic ring at 1438 cm⁻¹ (stretching of C-C bonds) was also present in adapted bentonite as seen from Figure 1c [15]. FTIR spectra of the UV-cured materials can be seen in Figure 1d. The allyl and the acrylate bands at 1630 cm⁻¹ were disappeared after curing, since the crosslinking occurred exactly and the interaction was completed among the materials.

Morphology of the coatings

The morphology of the UV cured materials was

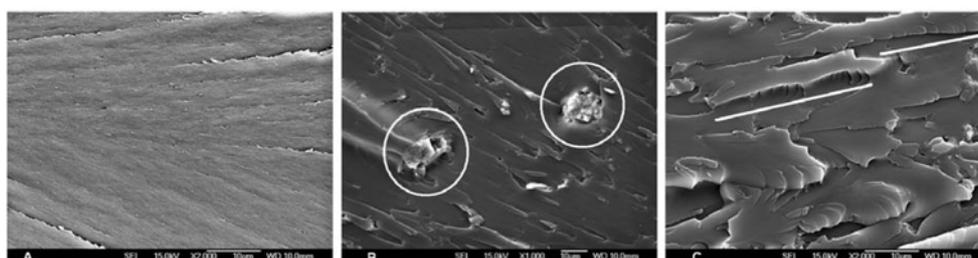


Fig. 2. SEM images of A) CF material X2000, B) F0 material X2000, and C) F2 material X2000.

determined by SEM from a fractured surface. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating. The SEM images were shown in Figure 2. It can be seen from the images that stratification formed as addition bentonite to the structure. The neat formulation CF containing just polymer matrix had a smooth surface without any cracks. While bentonite was added into the formulation, it exhibited that it didn't disperse in the structure and a rough surface morphology was obtained. On the other hand, adapted bentonite showed a good distribution in the polymer matrix and a layered surface was achieved owing to the exfoliated nature. These results supported the XRD measurement, as well.

XRD analysis

The X-ray diffraction patterns of the bentonite and phosphonium salt adapted bentonite were shown in Figure 3. The X-ray diffraction patterns of the UA based adapted materials with 1, 3, 5 and 7 wt% phosphonium adapted bentonite containing were given in Figure 4. As seen in Figure, it is understood from the absence of the peaks that the amorphous structures were formed into the polymer composites owing to

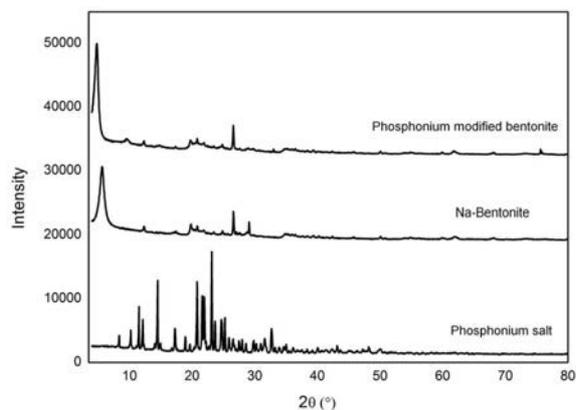


Fig. 3. XRD patterns of phosphonium salt, bentonite and phosphonium salt adapted bentonite.

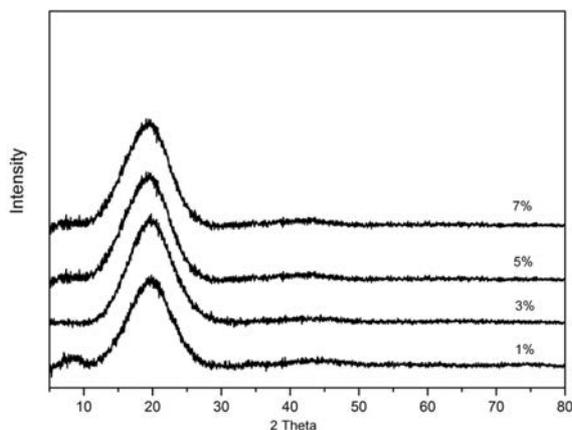


Fig. 4. XRD patterns of (a) 1 wt%, (b) 3 wt%, (c) 5 wt% and (d) 7 wt% adapted bentonite containing materials.

being of the adapted bentonite [19, 27-28].

Thermal properties

The thermal properties of UA based materials were investigated by thermogravimetric analysis. Figure 5 shows the TGA thermograms of UA based materials from 30 to 750 °C in inert atmosphere (N₂). The analysis data are collected in Table 3. 5% weight loss temperature and the maximum weight loss temperature of CF were found as 274 and 385 °C, respectively. The complete decomposition of the based formulation, CF, occurred at

Table 3. Thermal properties of bentonite containing UV-cured films.

Sample	T _{5%} (°C)	Max. weight loss (°C)	Final weight loss (°C)	Char yield (%)
CF	274	385	465	0
F0	278	400	468	1.75
F1	284	403	468	0.83
F2	287	401	465	2.27
F3	288	402	462	2.42
F4	291	405	462	2.80

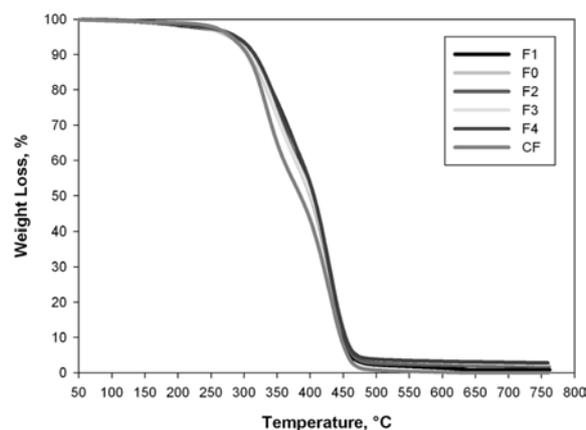


Fig. 5. TGA spectra of bentonite containing materials.

465 °C with no residual. On the other hand, the 5% weight loss temperature of F1 which contains neat bentonite was altered to 278 °C. When phosphonium adapted bentonite was added into the urethane acrylate resin, the 5% weight loss temperature slightly increased to 284 °C and the maximum weight loss temperature also achieved 403 °C. As the amount of adapted bentonite was increased in the UV-cured UA materials, the temperatures increased slightly. It can be said in accordance with these results, the enhanced thermal stability of these UV-curable materials is related to the interactions between bentonite and polymer matrix because of the additional crosslinks. Moreover, the char yields at 750 °C increased by depending on the increasing of the adapted bentonite amount. While no residue was observed for the neat polymer composition, the addition of phosphonium adapted bentonite caused approximately 2-3 percent

char yield [8, 11-12]. Consequently, it can be said that the phosphonium group covers the surface of bentonite and delays its degradation by preventing it from heat, thus increasing the char yield of the UV-cured materials.

Flame retardant properties

The flame-retardant properties of UA based materials were tested by measuring the limiting oxygen index (LOI). The LOI value, the minimum oxygen concentration in an oxygen/nitrogen mixture that will just support the combustion, can be used as an indicator to assess the flame retardancy of materials. Figure 6 shows the LOI values of the UA based photo-cured materials. The values increased from 16 to 27 with increasing the content of phosphonium salt adapted bentonite that delayed the ignition and yielded a heat bound. Moreover, it is obvious that the bentonite adapted with phosphonium salt is more accomplished to increase the LOI of the UA based materials than the non-adapted bentonite [6-8, 15-16, 21].

Mechanical properties

The mechanical properties of urethane acrylate (UA) based materials were examined and the obtained data as Young's modulus, tensile strength and elongation at break are given in Table 4. According to data, the modulus of UA materials increased with increasing amount of bentonite. When adapted bentonite was added in the formulation, the modulus value of F2

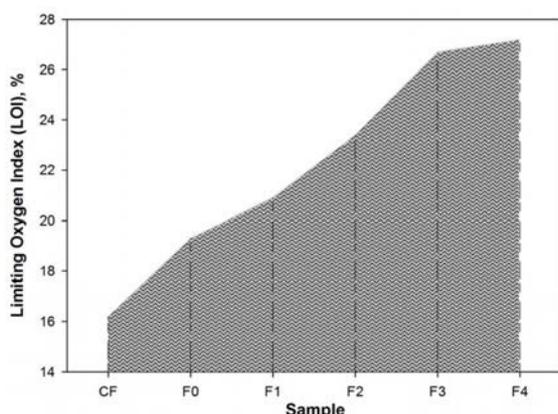


Fig. 6. Effect of phosphonium salt adapted bentonite content on limiting oxygen index (LOI).

containing 3 wt% phosphonium adapted bentonite increased by 16%. It is related to the development of crosslinking density of UA based materials in view of allyl groups. By increasing amount of bentonite, tensile strength of the UA based materials also increased. The elongation at break values decreased as the amount of adapted bentonite increased. Additional of crosslinks restricted the movement of the polymer chains, so the elongation at break values reduced [14, 18, 29]. As understood from the results, it can be noted that the bentonite adapted with phosphonium salt depending on the dispersion into the polymer matrix made UA based materials be stronger and a bit brittle.

Surface wettability properties

The contact angle, which is very sensitive to the surface composition changes, is the angle at which a liquid interface meets the solid surface. The wettability characteristics of the UA materials containing phosphonium adapted bentonite were investigated by measuring the contact angles with water; results are shown in Table 3. The contact angle of CF was found as 70°. After addition of neat bentonite, the contact angle value decreased because of its hydrophilic nature. Yet, at the beginning of adding adapted bentonite the contact angle values increased, then decreased by depending on the concentration of phosphonium adapted bentonite in polymer matrix. It might be related to poor dispersion of adapted bentonite at higher concentration [15]. There are three different images in Figure 7 that were taken from the Kruss software. As observed from the results, gloss values of polymer/bentonite materials

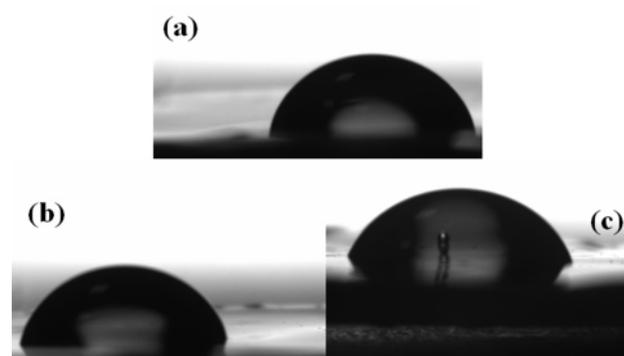


Fig. 7. Contact angle images of water drop on (a) CF, (b) F0, and (c) F2.

Table 4. The physical and mechanical properties of UV-cured materials.

Sample	Young's modulus (N/mm ²)	Tensile Strength (N)	Elongation at break (%)	Contact Angle (°)	UV Transmittance (%) at 600 nm
CF	116	78	36	70	86
F0	143	108	33	61	76
F1	155	162	24	66	75
F2	166	164	24	65	73
F3	169	206	18	62	67
F4	174	212	8	62	64

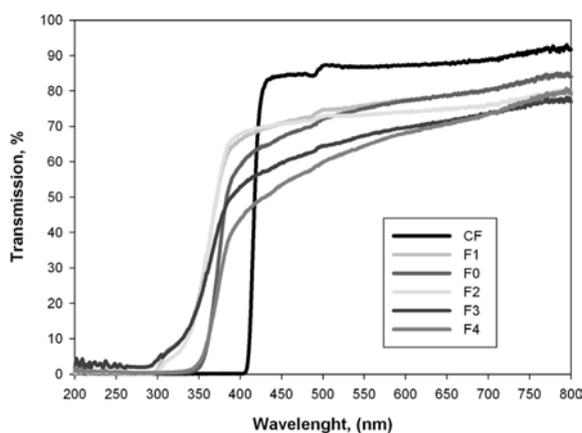


Fig. 8. Transmission spectra of UA materials containing adapted bentonite.

generally decrease due to the rough surface of these composites.

Optical properties

UV-transmittance property of UV-cured materials was investigated in the range between 300 and 800 nm and the spectra were given in Figure 8. The values at 600 nm were given in Table 4, as well. As seen from Figure and table, addition of 3 wt% bentonite into the formulation decreased the light transmission of the materials as 1 wt% of adapted bentonite did. Due to completion of exfoliation, the dispersion of adapted bentonite in the polymer matrix improved [8]. Furthermore, by increasing the concentration of adapted bentonite, the optical transmittance of UA based materials lessened greatly because of the scattering of light by phosphonium adapted bentonite particles in the UA based materials [15].

Conclusions

In this study, it was aimed to prepare phosphonium salt adapted Turkish bentonite and examine its effects on the properties of UV-curable UA based materials. The allyl phosphonium bromide was reacted with the bentonite by ion-exchange reaction. Then, 1-7 wt % adapted bentonite containing UV curable materials were prepared. XRD results show that intensity was increased with increasing the amount of phosphonium salt adapted bentonite. In addition, the evident from XRD results, the adapted bentonite was good mixed and well dispersed in the polymer matrix. When compared to neat bentonite containing materials, the addition of adapted bentonite enhanced the mechanical and thermal properties, as well as the flame retardancy of the materials to some extent. The development of the mechanical, thermal and fire retardancy properties was ascribed to the increased crosslinking density and the existed of allyl phosphonium content.

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