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Influence of Alkylphosphonium Modified Montmorillonite to the Tensile Properties of PMMA Composites

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Considering its excellent thermal stability, alkyl phosphonium surfactant: tri-isobutyl(methyl)phosphonium (TIBMP) was used in this research as an intercalant for surface modification of Na^+-MMT via ion exchange process forming organomontmorillonite (OMMT). The OMMT was then used as filler in poly(methyl methacrylate) (PMMA) via melt intercalation technique. OMMT decomposed at a higher temperature than commercial alkyammonium modified MMT. Exfoliated and intercalated types of nanocomposites are obtained from PMMA/OMMTs at low and high content of OMMT loading, depending on the space of those clay platelets had to disperse in PMMA. The ability of OMMT to carry a certain load applied in PMMA matrix enhances the tensile strength in all composites. TIBMP are compatible with PMMA matrix, and significantly improves the tensile properties of PMMA composites.

Keywords: montmorillonite, alkylphosphonium, functionalized montmorilonite, nanocomposite

I. INTRODUCTION

Clays are hydrous silicates or alumino silicates and fundamentally contains silicon, aluminium or magnesium, oxygen and hydroxyl with various associated cations. These ions and OH groups are organized into two dimensional structures as sheets. Among the different types of clay minerals, montmorillonite(MMT) is the most commonly used in the preparation of polymer clay nanocomposites MMT consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers [1]. MMT layers retained in the platelet structure with a regular gap between them and each layer of clay is stacked together to form a flipping book-like structure.

Due to the hydrophilic properties of layered silicate clay in nature, hydrophobic polymers are unlikely to interact and tend to agglomerate when added into polymeric matrix. This phe-

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nomenon is due to higher surface energy of MMT than polymeric matrix which tends to create a stronger cohesive interaction between clay particles [2]-[5]. Therefore, surface modification of clay mineral is essential to allow MMT to disperse and separate into individu al layers (exfoliated). This is crucial to weaken the interlayers′ cohesive energy, creating a better compatibility and interfacial interactions between layered silicate and polymeric matrix [6].

Physical adsorption of organic ion can alter the nature of the clay minerals′ surface and improve the physical and chemical properties of the surface. The advantage of physical attachment is that the structure of the clay mineral is not altered. Alkyl ammonium surfactant, which is commonly used in modification of montmorillonite are reported to be thermally unstable, hence the resulted organoclay could suffer decomposition following the Hofmann elimination reaction during the melt processing [7]-[8]. Triisobutyl(methyl) phosphonium (TIBMP) was used in this study due higher thermal stability compared to alkylphosphonium which was reported by previous researchers [9].

Recently, melt compounding has become the mainstream in preparing polymer-clay nanocomposite, as it has several advantages over other preparation routes. Melt processing is more environmental friendly because no solvents are required when preparing polymer-clay nanocomposite. In addition, this approach is simpler and economical for industries as it does not need the polymer production line dedicated to the sole product [10]. In this study, the MMT will undergo cation exchange reaction before being melt compounded with PMMA. The influences of TIBMP to the organoplilicity of MMT, as well as the tensile properties of the PMMA composites were investigated.

II. EXPERIMENTAL PROCEDURE

A. Modification of Na$^+$-MMT

Na-montmorillonite Kunipia-F was purchased from Kunimine, Japan. CEC 119meq/100g surfactant used was triisobutyl(methyl) phosphonium tosylate CYPHOS IL 106 was purchased from Ionic Liq Tech. Poly(methyl methacrylate) (PMMA) with density of 1.18g/cm^3 was supplied by Lucite International Company.

Na$^+$-MMT have been swollen by first adding 25.00g of Na$^+$-MMT in two litres of hot distilled water by using a mechanical stirrer with speed of 60-70 rpm for about an hour. An aqueous solution of the surfactant which is equivalent to CEC with ration of 1:1.2 was added drop wise into the MMT suspension and constant stirring was continued for an hour to complete the ion exchange reaction and thus forming white precipitate. The produced organophilic montmorillonite (OMMT) precipitate was filtered and washed by using hot distilled water. The precipitate was then dried in an oven at 110°C for two days. Then, this dried precipitate was grinded using mortar to obtain fine powder organoclay prior it was sieved in 100 μm size particle siever.

B. Preparation of PMMA/MMT composite

PMMA/OMMT composites were prepared by using melt intercalation technique in an internal mixer, at 130 rpm rotor speed, 15 mins resident time at 175 °C. PMMA was melt-mixed with OMMT at 1 to 5 weight %. The dumbbell shape of tensile specimen was prepared using Haake Mini Jet II injection moulding machine with the cylinder temperature of 240 °C, injection pressure of 50 bars with the mould temperature of 130 °C. Tensile test was carried out by using Universal testing instrument Instron 3366 with a tensile speed of 10 mm/min. This test was conducted with five times repetition to obtain the average reading. The tensile strength, tensile modulus and elongation of the composite were determined.

C. Characterization and measurements

The presence of TIBMP resulted from the surface treatment on MMT was investigated using Fourier Transform Infrared (FTIR) spectrophotometer within the wavelength range of 4000-400cm^{-1}. Elemental analyses of total carbon, nitrogen, hydrogen, nitrogen and sulphur were performed using CHNS Elemental Analyser to attain some idea of the composition of TIBMP (i.e., to distinguish between MMT and OMMT, based on total organic carbon). The clay samples were characterized using KBr pressed disk technique. The d001 value of the Na^{+}-MMT, OMMT (both in powder form) and the obtained composites were examined via powder x-ray diffractometer (PXRD). The scan range involved was 3-15° for each composite with scan rate of 2 °/min. Thermogravimetric analysis was done using Pyris Perkin Elmer Thermogravimetric analyser. Each data was recorded by using a heating rate 10°C/min under nitrogen, N_2 (g) with flow rate of 20mL/min. A temperature range of 0 to 1000°C as used in each of the sample analyzed. Tensile test specimen of PMMA/OMMT composites were prepared by using Haake Minijet injection molding. The tensile test was performed using a load cell of 10kN at a cross-head speed of 60 mm/min and a strain gauge extensometer with a gauge length of 30 mm. This test was conducted with five times repetition to obtain the average reading. The maximum tensile strength and elongation at break of the composite were determined.

III. RESULT AND CHARACTERIZATION

A. Surface modification of MMT

The MMT showed basic absorption of a broad band at 3624 cm^{-1} which is a characteristic of Al-OH stretching mode of MMT structure (Figure 1). The broad band at 3438 cm^{-1}

is due to -OH stretching mode of the interlayer water and 1643 cm^{-1} is attributed to -OH deformation vibrations of the interlayer water of MMT. The broad band near 3400 cm^{-1} that exists in Na^+-MMT spectrum which is ascribed to -OH stretching mode of interlayer water becomes narrow compared with OMMT spectrum due to the changing nature of MMT from organophobic to organophilic [11]. Additionally, the peak at 917 cm^{-1} is ascribed to Al-Al-OH bending vibration of the MMT chain [12]. The most significant difference between Na^+-MMT spectrum with OMMT spectra are located in the range of 2850-2954 cm^{-1} which corresponds to methylene group (CH_2) asymmetric stretching, CH_2 symmetric stretching and CH_2 plane scissoring, respectively. This is proof that there is a presence of alkyl group in the organoclays. The range of 1464-1468 cm^{-1} is also indicative of stretching of aliphatic C-C bonds in a long chain.

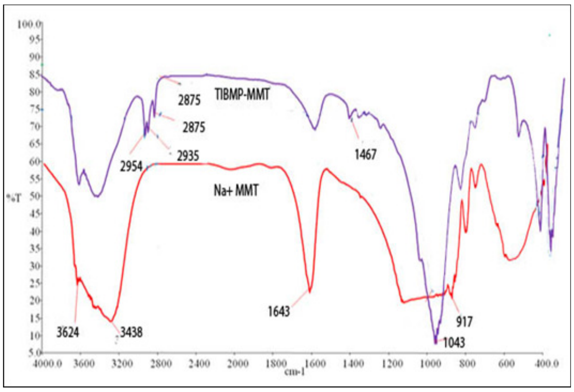

Figure 1. FTIR Spectra of MMT and OMMT (TIBMP-MMT)

Figure 2 shows PXRD diffraction of the OMMT and Na^+-MMT. The diffraction peak at $2\Theta=7.08°$ belongs to the (001) plane of Na^+-MMT with the characteristic peak of 1.25nm. The terms 001 is a set of indices for a plane that intercepts only at z-axis which also corresponds to clay layers. The d001 spacing was calculated from the PXRD peak position using Bragg′s law. The diffraction plane of d001 for OMMT shifted towards the lower angle with the interlayer distance of 1.46nm. The basal spacing of OMMT was larger than the Na^+-MMT since the Na^+ ion had successfully been exchanged with long alkyl chain of TIBMP thus expanding the interlayer distance of MMT.

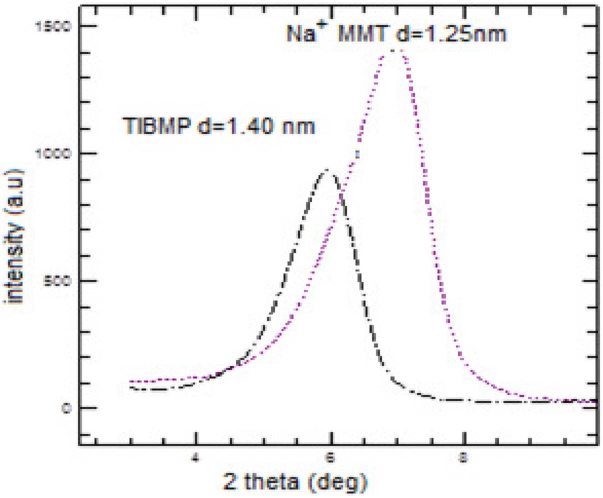

Figure 2. X-Ray Diffractogram of MMT and OMMT (TIBMP-MMT)

As expected, percentage element of carbon increased dramatically indicating the presence of TIBMP in MMT from 0.2 to 11.03 percent. The percentage of Carbon increased corresponds to the presence of the alkyl groups in TIBMP, as supported by the FTIR analysis. By assuming all the carbons content were totally from TIBMP ions, 59.33% percent of ion-exchange had occurred between Na^+ and TIBMP ions.

Figure 3 shows the TGA thermograms of MMT before and after modification. The MMT exhibits two major degradation steps. The first degradation step occurred at the temperature less than 200°C due to the volatilization of both the free water from the water sorbed on the external surfaces of crystals. Na^+-MMT gives the highest amount of weight loss, about 13.5%, in this region due to the higher quantity of water that intercalates within the clay layers and thus, exhibiting highly hydrophilic characteristics compared to OMMT. In the case of organoclays, the quantities of the water loss reduces to 4.55% when treated with TIBMP and thus, altering the clays into having hydrophobic characteristics. The second degradation step, OMMT experiences the main thermal decomposition in which organic substance starts to decompose at the range of 200-500°C with the total weight loss for about 7.33%.

At temperature of 500-800°C the hydroxyl group, which is covalently incorporated in the crystal lattice dehydrated and the final dehydration reactions occurred in the range between 800 and 1000°C. The Na^+-MMT shows stable patterns as the temperature increases while the OMMT continues to lose weight. The TIBMP-MMT gives value of weight loss about 3.20%. OMMT showed good thermal stability because of the lower weight loss obtained at the higher temperature.

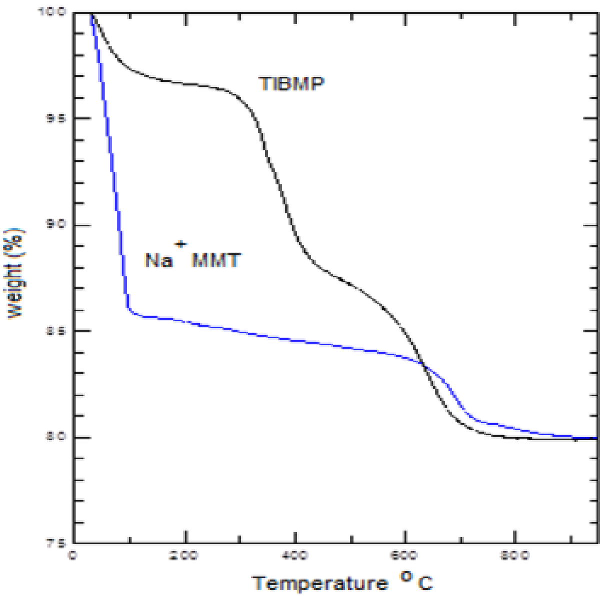

Figure 3. TGA thermograms of MMT and OMMT(TIBMP-MMT)

B. Properties of PMMA composite

Surface morphology of PMMA composites

Figure 4 shows that there were no d_{001} diffraction plane for PMMA/ Na^+-MMT composites for 1 and 2 wt. % of clay loading. It could be that the structure could not be verified since poor distribution of small quantity of Na^+-MMT that was contributed in the PMMA matrix. For 3 to 5 wt. % of clay loading, the PXRD showed the conventional form of composites because there was no insertion of PMMA directly into the interlayer of MMT. The XRD patterns showed that the basal spacing does not significantly change the pristine MMT. Thus, the basal spacing value showed no shifting and possesses the range of 1.30nm.

Figure 5 shows XRD pattern of TIBMP-

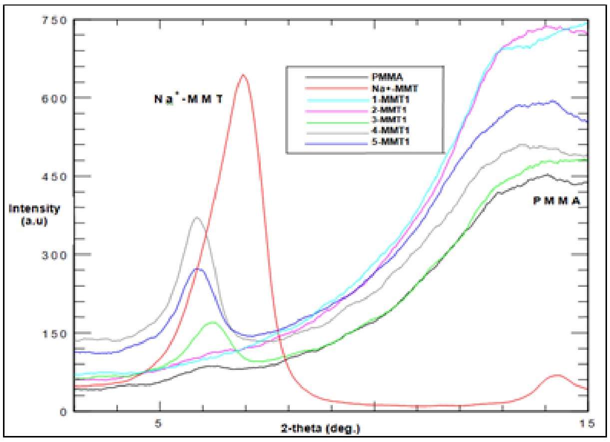

Figure 4. X-Ray Diffractogram of PMMA/Na$^+$-MMT composites

MMT in the PMMA matrix which slightly shifts for 1 to 3 wt% of clay loading. The composite could be classified as intercalated, as it shifts to lower angles due to the insertion of PMMA into the interlayer spacing of MMT. For 4 and 5 wt% of clay loading, the d001 diffraction plane disappeared which suggested that exfoliated composites were obtained. Ying *et al.* (2015) also reported that when the silicate layers are completely and uniformly dispersed in polymer matrix, it suggests an exfoliated structure was obtained [13].

Tensile Properties

Tensile strength was basically about the ability of the composites to withstand with the force that been applied. The ultimate tensile strength of PMMA/Na$^+$-MMT and PMMA/TIBMP-MMT was compared in Figure 6. The ultimate tensile strength continued to increase rapidly to 75.03MPa and about 35.01% of tensile strength obtained. At the 4 and 5 wt% clay loadings; PMMA/TIBMP-MMT expected to be an exfoliated. The composites; PMMA/TIBMP-MMT showed increment; and the highest tensile strength obtained as the increasing clay loading, up to 5 wt% of clay loadings.

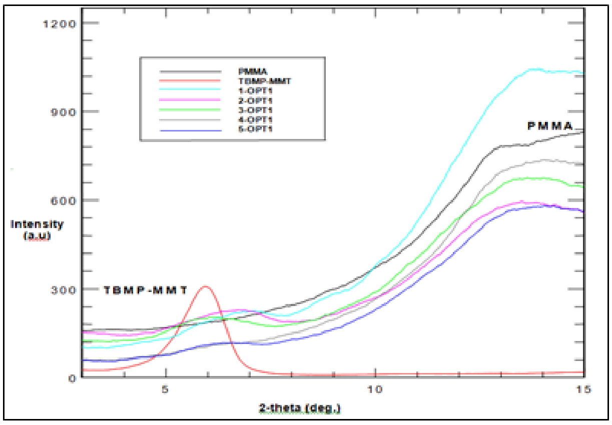

Figure 5. XRD patterns for composites of PMMA and OMMT (TIBMP- MMT)

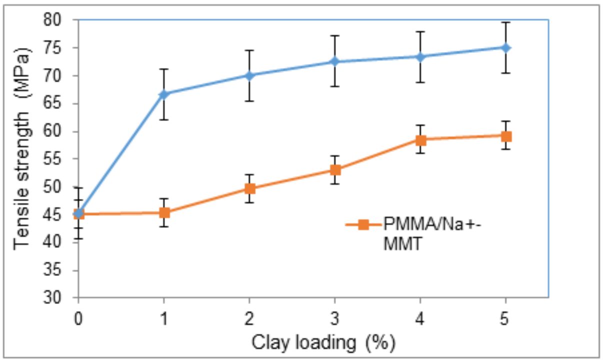

Figure 6. The comparison of the ultimate tensile strength versus clay loading of PMMA/Na$^+$-MMT and PMMA/OMMT (TBMP-MMT) composites

This phenomenon shows that PMMA experiences increment in the value of tensile strength as soon as OMMT was introduced in the PMMA matrix. The tensile strength is also strongly related to the dispersion pattern of clay layers in polymer matrix. So, the dispersion of clay layers in polymer matrix improves as it enhances the tensile properties. The ultimate tensile strength shows maximum values and thus, provides improvement for the ultimate tensile strength. It is probably due to the high surface areas of the OMMT that been exposed to PMMA matrix, which enables the platelets to carry the applied load when dispersed in the PMMA matrix.

The introduction of TBMP-MMT in the PMMA matrix results in a slight increase of elongation at break of composites compared to pristine polymer up to 3wt. % of clay loading, before being reduced with increasing clay loads with about 38.91% obtained. The elongation at break of PMMA/Na^+-MMT composites also shows decrease with increasing clay loading starting from 2wt. % of clay loading (Figure 7). The elongation at break of the composites decreases could be due to the aggregation of organoclay when increasing the clay loading that causes the composites to become more brittle. This is because, PMMA is a thermoplastic material which is naturally soft in a molten state and the introduction of clay platelets in polymer matrix would increase the stiffness thus, increasing the brittleness [14]-[15].

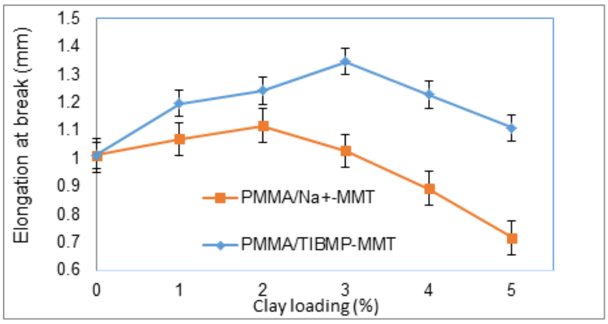

Figure 7. The comparison of elongation at break versus clay loadings of PMMA/Na^+-MMT and PMMA/OMMT (TIBMP-MMT) composites

IV. SUMMARY

The tensile properties of composites is strongly correlated with the dispersion pattern of the clay layers in polymer matrix. The results suggested that optimum dispersion of clay layers will result in the enhancement of composite tensile strength. Surface modification of MMT with TIBMP had significantly improved the clay effectiveness to carry the load applied to the PMMA composite. The increasing of the clay loading also causes the elasticity of each composites to lose its properties, as well as forming the agglomerate structure. Thus, lowering the elongation at break.

V. ACKNOWLEDGMENT

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