Improving the Flexural Properties of Abs/Muscovite Composites by Introducing Modified Muscovite

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Abstract. This paper reports the effect of unmodified and modified muscovite on the flexural properties of acrylonitrile–butadiene–styrene (ABS) composites. The composites were prepared by using melt compounding in an internal mixer. The morphologies of the composites were examined using field emission scanning electron microscopy (FESEM) whereas the structural characteristics of unmodified and modified muscovite were investigated by X-ray diffraction (XRD). The XRD results indicated that by modifying muscovite via two-stage ion exchange treatment, the basal spacing of muscovite was enlarged. The incorporation of treated muscovite (TM) in ABS matrix improved the flexural strength and modulus by 9% and 28%, respectively, compared to neat ABS strength of composites. The FESEM results showed that the fracture surface of ABS/TM composite indicated better interfacial adhesion between the filler and the matrix.

1. Introduction

The surge of layered silicates, mainly clay minerals incorporated with organic polymers, has recently attracted a great attention by researchers and industrial sectors mainly in the filling industry. The innovation of polymer-layered silicate was inspired by the Toyota research group in the early 1990s[1]. They found that the addition of organoclay in minimal quantity showed a substantial improvement in various performances of polymer material[2, 3]. Among all the layered silicates used, those of smectite class, particularly montmorillonite (MMT), have been widely investigated due to the swelling behavior and intercalation properties. However, another important silicate group, mica, especially muscovite, has been studied to a lesser degree.

Muscovite, KSi₃Al₃O₁₀(OH)₂, is a type of 2:1 phyllosilicate. Muscovite has the highest layer charge density and homogeneous charge distribution, which makes this material ideal for reinforcement[3]. The extraordinary properties acquired by muscovite such as high aspect ratio, good dielectric properties, and high thermal stability make muscovite a potential alternative for MMT. However, the fabrication of muscovite with polymer matrices is very challenging due to the intrinsic incompatibility between
hydrophilic clay and hydrophobic polymer matrix. Therefore, surface modification is required to render muscovite layers more compatible with polymer chains. Acrylonitrile–butadiene–styrene (ABS) is an engineering thermoplastic that has been widely used in automotive hardware, pipe fitting, luggage, and appliance housing because of its outstanding hard and tough characteristics. In recent years, growing attention has been focused on ABS/layered silicate composite materials, commonly montmorillonite (MMT)\(^{[4–6]}\), sepiolite\(^{[7]}\), and bentonite\(^{[8]}\) as the reinforcement filler. To the best of our knowledge, the properties of ABS/muscovite composites at various muscovite loadings have not been reported previously. Therefore, this article aims to report on a new approach for the preparation of ABS/muscovite by melt mixing. The effect of untreated and treated muscovite on the flexural and morphological properties of ABS composites was investigated.

2. Experimental study

2.1 Materials

ABS pallets (Toyolac 700) from Toray Plastics (Malaysia) Sdn. Bhd. were used as the matrix. The inorganic filler, muscovite, was supplied by Lingshou County Xinfa Mineral Industry Co. Ltd. Figure 1 shows the particle size distribution of muscovite, showing that the mass median diameter (d50) was 21 µm. Lithium nitrate (LiNO\(_3\)) and cetyltrimethylammonium bromide (CTAB) were supplied by Merck.

![Figure 1. Cumulative particle size distribution of muscovite sample](image)

2.2 Preparation of treated muscovite

The treated muscovite (TM), known as organomuscovite, was obtained with a two-stage ion exchange treatment. First stage: Muscovite (5 g) was mechanically mixed with LiNO\(_3\) (85 g) with a ratio of 1:17 of muscovite/LiNO\(_3\). The mixture was heated in a furnace at 300 °C for 12 hr. Then, it was soaked in 200 ml of deionized water for 2 hr. The solution was vacuum filtered and the filtrate was dried in a vacuum oven at 110 °C for 12 hr. The product is known as Li-muscovite.

Second stage: Li-muscovite was added with an organic surfactant, CTAB, according to our previously reported paper\(^{[9]}\). After conducting the two-stage ion exchange treatment, it was found that the CTAB-
modified muscovite produced an intercalated structure with the basal spacing of 2.79 nm. A similar organomodified-muscovite was used in this study.

2.3 Preparation of composite

Nanocomposite with three different filler loadings was prepared by melt mixing using an internal mixer (Polydrive Thermo Haake R600) at the temperature of 190 °C and rotor speed of 60 rpm. Both clays and polymers were dried for 12 hr at 80 °C prior to their use. The sequences of material addition were: ABS (3 min), followed by various clay loading concentrations, namely 1, 3, and 5% by weight of ABS with a total mixing time of 8 min. The compounded materials were then subjected to compression molding (using a Kao Tich GoTech compression machine) into a 3 mm thick sheet, with the temperature set at 200 °C. The preheating time was set at 6 min, followed by hot compression for 3 min, and then cold-compressed for another 3 min. The detailed compositions of the compounds are listed in Table 1.

Table 1. Formulation of composite samples (wt%)

| Sample code | ABS (wt%) | Untreated muscovite (UM) (wt%) | Treated muscovite (TM) (wt%) |
|-------------|-----------|-------------------------------|-----------------------------|
| Neat ABS    | 100       | 0                             | 0                           |
| ABS/UM 1    | 99        | 1                             | 0                           |
| ABS/UM 3    | 97        | 3                             | 0                           |
| ABS/UM 5    | 95        | 5                             | 0                           |
| ABS/TM 1    | 99        | 0                             | 1                           |
| ABS/TM 3    | 97        | 0                             | 3                           |
| ABS/TM 5    | 95        | 0                             | 5                           |

2.4 Characterization

X-ray diffraction (XRD) analysis was recorded on a Bruker D8 Advance diffractometer with a Cu target of k = 1.5405 Å at a generator voltage of 35 kV and a generator current of 30 mA. The diffraction patterns in the 2θ range from 1° to 10° were collected using a step size of 0.05 and scan speed of 3°/s. The interlayer distance of organoclay in the composites was calculated using Bragg’s equation of 2dsinθ = nλ. A flexural test was carried out in the three-point bending test using Lloyd tensile machine (Model 5533) according to ASTM D-790 at a strain rate of 5 mm/min. The specimen dimensions were 3 mm in thickness and 12 mm in width. The distance between the supports was 75 mm. Five samples were tested for each composition and their average values were reported. The observation of flexural fracture morphology of ABS and its nanocomposites was carried out using a scanning electron microscope (SEM) model ZEISS Supra 35 VP. The samples were mounted on aluminum stubs, sputter coated with a thin layer of gold prior to testing in order to avoid electrostatic charging, and observed at a magnification of 300 and 5000k×.

3. Results and discussion

3.1 X-Ray Diffraction

XRD is the best approach to study the changes in basal spacing and intercalation properties of clay in polymer matrix. Figure 2 displays the XRD patterns of muscovite, Li-Muscovite, and TM in the 2θ range of 1° to 10°. Muscovite showed a d(002) peak at 2θ = 8.87°, corresponding to an interlayer spacing of 0.99 nm. After the treatment with alkaline salt, Li-Muscovite exhibited a basal reflection peak at 2θ = 7.30°, corresponding to an interlayer spacing of 1.21 nm. After the two-stage ion exchange
treatment, the d(002) plane diffraction peak of TM shifted to 3.17°, corresponding to a d-spacing of 2.79 nm. This observation indicated that modifying pristine muscovite with CTAB increased the interlayer spacing, which led to a shift in the diffraction peak towards a lower angle. A shift to lower angles suggests an increase in the interlayer spacing of nanoclay, which shows that the structure has intercalated.

![Figure 2. XRD diffraction patterns of a) muscovite, b) Li-Muscovite, and c) TM](image)

### 3.2 Flexural testing

The results of the flexural strength and modulus of ABS/UM and ABS/TM composites following filler loading are illustrated in Figure 3. Regardless of the ion exchange treatment, the flexural strength of both untreated and treated muscovite-filled ABS showed a linearly increasing trend over neat ABS. Moreover, the flexural strength values of ABS/TM were higher than those of ABS/UM. The same observation was reported in the work conducted by E. Suryani [10]. When the clay loading was 5 wt%, the flexural strength increased from 78 MPa (control) to 85 MPa, corresponding to an improvement of 9%. The increment in flexural strength may also be due to the presence of silicate layer, which may improve the interfacial adhesion between the filler and the matrix.

Moreover, the addition of TM improved the dispersion and compatibility of hydrophilic clay and hydrophobic ABS, which facilitates effective stress transfer from matrix to clay. Therefore, it can be said that the incorporation of TM improved the compatibility with ABS matrix, which enables it to resist stress propagation when bending stress is applied to the samples. On the other hand, the flexural modulus of both ABS/UM and ABS/TM composites was observed to increase continuously with filler loading. Each system containing TM showed higher modulus increase than the ABS/muscovite system and neat ABS. As shown in Figure 3, the increase in flexural modulus from 2,687 MPa (control) to 3,435 MPa was achieved at 5 wt% loading of TM, corresponding to about 28% increment. This observation highlights the fact that the incorporation of organoclay, TM, into ABS can improve the mechanical properties of ABS composite.
3.3 Morphological analysis

The fracture surface of neat ABS and ABS composites containing 5 wt% of filler is presented in Figure 4. From Figure 4 (a), it can be seen that neat ABS exhibited smooth fracture surface. Compared to ABS/UM composite, the micrograph revealed a slight increase of surface roughness after muscovite was embedded in ABS matrix. This probably suggests the inhomogeneity of filler dispersion, with some of the filler was found detached from the ABS matrix. Obviously, the occurrence of more voids and cavities are clearer, which creates sites for crack initiation and leads to localized stress concentration. The existence of gap signifies the weak and poor interfacial adhesion between the filler and the matrix, thus caused a detrimental effect on flexural properties.

On the other hand, the micrograph of ABS/TM as shown in Figure 4 (c) revealed a more homogenous dispersion of filler with reduced aggregation of the particles within matrix. In this case, TM has tight contact with the matrix, which improves compatibility, leading to good interfacial adhesion. Therefore, the improved interaction was subsequently validated with the results of flexural findings.
4. Conclusion

The flexural strength of ABS/UM and ABS/TM composites prepared by melt intercalation was investigated. Following the modification, intercalated muscovite was produced as viewed by XRD. The flexural strength of composites showed an increment of 9% in flexural strength and 28% in flexural modulus corresponding to neat ABS, which suggests that the flexural properties of composites could be enhanced by the addition of organoclay. In relation to this, it was found that ABS/TM nanocomposites displayed higher values of strength and modulus compared to ABS/muscovite composites. The improvement was contributed by the homogeneous dispersion of TM, which was provided by the two-step ion exchange treatment as indicated by FESEM.

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