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Effect of Solvent on Mechanical and Physical Properties Of PMMA/Sic Composite Films

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ABSTRACT

The selection of solvent in solution casting is crucial as it may affect the morphology and properties of the resulting composite films. In this study, the effect of solvent on the properties of poly(methyl methacrylate)/silicon carbide (PMMA/SiC) composite films was investigated. By using acetone, the solution casting was carried out at various solvent-to-solid (S/S) ratio, from 4:1 to 10:1 at room temperature. It was found that the increasing S/S ratio enhanced the tensile strength and modulus of elasticity of pristine PMMA films but deteriorated its elongation at break, up to 8:1 ratio. The crystallinity of the PMMA films was found to increase with S/S ratio, as confirmed by the higher peak intensity in X-Ray Diffraction (XRD) patterns and the SEM micrographs. In the second part of the study, by using S/S ratio of 8:1, the nano sized SiC (0.25 wt%) was added as a filler into PMMA and toluene with different ratio was added as a secondary solvent. The addition of SiC has increased the tensile strength and modulus of elasticity of PMMA/SiC but decreased its elongation at break. However, the presence of toluene reduced the tensile strength of the PMMA/SiC composite films and resulting in rougher tensile fracture surfaces as shown in SEM micrographs. The toluene with nonpolar nature had affected the distribution of SiC in PMMA. It can be concluded that the properties of the PMMA composites films can be tailored according to the needs of applications.

Keywords: *Time-frequency analysis, Failure diagnosis, Diagnostics in rotating machinery, Vibration analysis*

1. INTRODUCTION

Solution casting is a simple processing method to prepare nanocomposites without using elevated temperature and expensive equipment. It can be conducted at room temperature with the aids of petri dish or glass substrates. Firstly, a solvent is needed to dissolve the polymer. Then, the mixture is usually agitated to speed up the dissolution process. Meanwhile, the nanofillers can be added into the polymer solution. Finally, the mixture is poured into the petri dish and evaporation is allowed to take place. The dried nanocomposites can be removed easily from the petri dish easily when it is dried completely.

Therefore, the selection of solvent is crucial in determining the success of the process. In a polymer solution, solvent with polymer-solvent interaction that is higher than polymer-polymer attraction forces, allows diffusion of solvent molecules and chain segment is extended. It causes more free volume of the polymer matrix and induces swelling. Generally, solvent with the ability to promote greater chain extension is preferred [1].

Many researchers reported the effect solvent on the fabrication of poly (methyl methacrylate) (PMMA) and its composites. The solvents used previously include acetonitrile [2], chloroform [3], toluene [4], tetrahydrofuran [5] and N,N-dimethylformamide [6]. Boulerba and Zoukel [3] discovered that by using chloroform, an apolar solvent, it favours the interaction of PMMA and silica. Therefore, strongest H-bond interaction between the PMMA and silica can be obtained, as compared to acetone and acetonitrile. As a result, chloroform serves as an effective solvent in the synthesis of silica nanoparticles filled PMMA. Recently, authors reported the tensile properties of PMMA films can be enhanced with the presence of SiC nano whiskers together with silane treatment [7].

It is worth mentioning that the evaporation of solvent during the drying process may cause harmful effect to the surrounding and operators. Therefore, acetone was chosen as solvent in this study to fabricate the silicon carbide nanoparticles filled PMMA. In order to prepare the PMMA/SiC composite film with optimum strength, a suitable solvent to solid ratio must be identified through the pristine PMMA fabrication. In addition, toluene was also added to the acetone as secondary solvent with the aim to enhance the properties of PMMA/SiC composite films.

2. MATERIALS AND METHODOLOGY

Poly(methyl methacrylate) was obtained from LG Chemical Ltd. In Seoul, South Korea, in the form the form of pellets with specific gravity of 1.18 g/cc. Silicon carbide nanoparticles were purchased from Nanostructured and Amorphous Material Inc., Texas, USA. Acetone and toluene were supplied by HmbG Chemicals, Hamburg, Germany.

2.1. Preparation of PMMA Films at Different S/S Ratios

Pristine PMMA thin films were prepared by using simple solution casting method. Acetone was used as a non-toxic solvent to dissolve PMMA pellets. The ratio of acetone to PMMA, which was known as solvent to solid ratio (S/S) was fixed at 4:1, 6:1, 8:1 and 10:1, respectively. For S/S ratio of 4:1, 20 ml acetone was added into 5 g of PMMA pellets, and the mixture was stirred for three hours. Then the mixture was poured into a 15 cm diameter petri dish. A perforated aluminum foil was used to cover the petri dish to avoid contamination. After 24 hours of drying in room condition, the thin film was detached from the petri dish. Similar procedure was repeated to prepare pristine PMMA thin films with different S/S ratios.

2.2. Preparation of PMMA/SiC Films By Using Optimum S/S Ratio

In the second stage of study, an optimum S/S ratio was selected based on the tensile strength of pristine PMMA. The S/S ratio that yielded the highest tensile strength was used to prepare silicon carbide filled PMMA (PMMA/SiC) composites. PMMA was dissolved in acetone by using the optimum S/S ratio and a fixed amount of 0.25 wt% silicon carbide from weight of PMMA was added into the mixture. Then it was subjected to magnetic stirring for three hours. After that, the mixture was casted into petri dish and covered with perforated aluminium foil. It was left to dry for 24 hours under room temperature.

2.3. Preparation of PMMA/0.25SiC Composite Films Using Different Binary Solvent Ratio

The use of binary solvent ratio was investigated in the third stage of the study. By using the optimum S/S ratio, part of the acetone was replaced by toluene. The ratio of acetone to toluene was fixed at 5:0, 4:1, 3:2, 2:3, and 1:4, respectively. PMMA was first dissolved in acetone and toluene solvents at the ratio of 8:1 with constant stirring for 3 hours using a magnetic stirrer. Simultaneously, 0.25 wt% SiC powder was added to the mixture slowly. After that, the mixture was poured into petri dish and allowed for 24 hours drying in room temperature. Table 1 shows the formulation of PMMA and PMMA/0.25SiC composite films.

2.4. Tensile Test

A Universal Testing Machine, Instron 5569 was used to conduct the tensile test by following ASTM D882 standard. 1 mm/min cross head speed was used in the study. The thin films were cut into 25 mm x 100 mm prior to testing. Five samples were tested for each formulation and the values of tensile strength, Young's modulus and elongation at break were recorded. An average value was calculated for each of them.

2.5. Morphological Study

The Scanning Electron Microscope (SEM) JEOL JSM-6010LV was used to characterise the tensile fracture of the thin films. A thin layer of platinum was coated on all the fracture surfaces to prevent charging during the morphology observation.

2.6. Hardness Test

Shore A Durometer test was used to determine the hardness of PMMA/0.25SiC composite films. The test was carried out in accordance with ASTM D2240 A at a minimum thickness of 6 mm. For more accurate results, multiple measurements were performed at 3 different locations on the thin film sample and the average hardness value were calculated.

2.7. X-Ray Diffraction (XRD)

Bruker D2 Phaser was used to analyse the crystalline states under normal atmospheric conditions. To conduct this test, an X-ray beam was pointed to a sample, and the intensity of the scattered radiation was measured with respect to the direction of the beam's output. After the beam has been separated, the scatter, or known as a diffraction pattern, reveals the crystalline structure of the PMMA/SiC composite films. The scan range (2θ) for each sample was set ranging from 10° to 80° and PDF card number used was cubic SiC (ICDD 01-073-1708).

3. RESULTS AND DISCUSSION

3.1. Tensile Testing

Figure 1(a) shows the tensile strength of PMMA thin films prepared with different S/S ratios. It can be seen that the tensile strength of PMMA increased with the increasing S/S ratios up to 8:1. Further increase of S/S ratio beyond 8:1 to 10:1 resulted in reduction of the PMMA's tensile strength. It is known that acetone is a good solvent for PMMA [8] as it is capable to dissolve PMMA completely. When PMMA was added into acetone, the PMMA-acetone interaction is higher than the PMMA-PMMA attraction forces. Therefore, the acetone molecules can diffuse into the PMMA and the PMMA chain segments are extended and fully dissolved in acetone.

Table 1 The formulation of the samples and its acronym

Sample acronym	PMMA (wt%)	SiC (wt%)	Solvent to solid ratio	Acetone (vol%)	Toluene (vol%)
PMMA_4A	100	-	4:1	100	-
PMMA_6A	100	-	6:1	100	-
PMMA_8A	100	-	8:1	100	-
PMMA_10A	100	-	10:1	100	-
PMMA/0.25SiC_5A	99.75	0.25	8:1	100	0
PMMA/0.25SiC_4A	99.75	0.25	8:1	80	20
PMMA/0.25SiC_3A	99.75	0.25	8:1	60	40
PMMA/0.25SiC_2A	99.75	0.25	8:1	40	60
PMMA/0.25SiC_1A	99.75	0.25	8:1	20	80

In this study, as the S/S ratios increased, the amount of acetone increased accordingly, the PMMA chains were able to move freely and interact with one another more efficiently. Moreover, a higher volume of acetone would take longer evaporation time before it was dried completely. It provided longer time for free PMMA chains to align themselves in a more uniform manner. It is believed that the improved chain alignment can lead to better crystallinity and further increase the tensile strength of the PMMA. However, it is worth to note that excessive solvent at S/S of 10:1 may lead to solvent retention and compromise the tensile strength.

Next, the elongation at break of the PMMA thin films is showed in Figure 1(b). It was found that the changing S/S ratio from 4:1 to 8:1 did not affect the elongation at break of the composite films as the reading was recorded at 6 %. Further increase of S/S ratio to 10:1 had caused a drastic increase in elongation at break to 9.5 %. The high volume of solvent during the processing may retain in the composite films which increase the ductility of the composite films.

In Figure 1(c), the modulus of elasticity for PMMA increased with the increasing S/S ratio up to 8:1. Similarly, the ample volume of acetone allowed the dissolution of PMMA chains and longer evaporation time of acetone encouraged more organised polymer chains arrangement. As a result, the stiffness of PMMA increased with the increasing S/S ratio up to 8:1. Nonetheless, the retention of solvent at S/S of 10:1 could offer a justification for the decreasing of stiffness of the composite films.

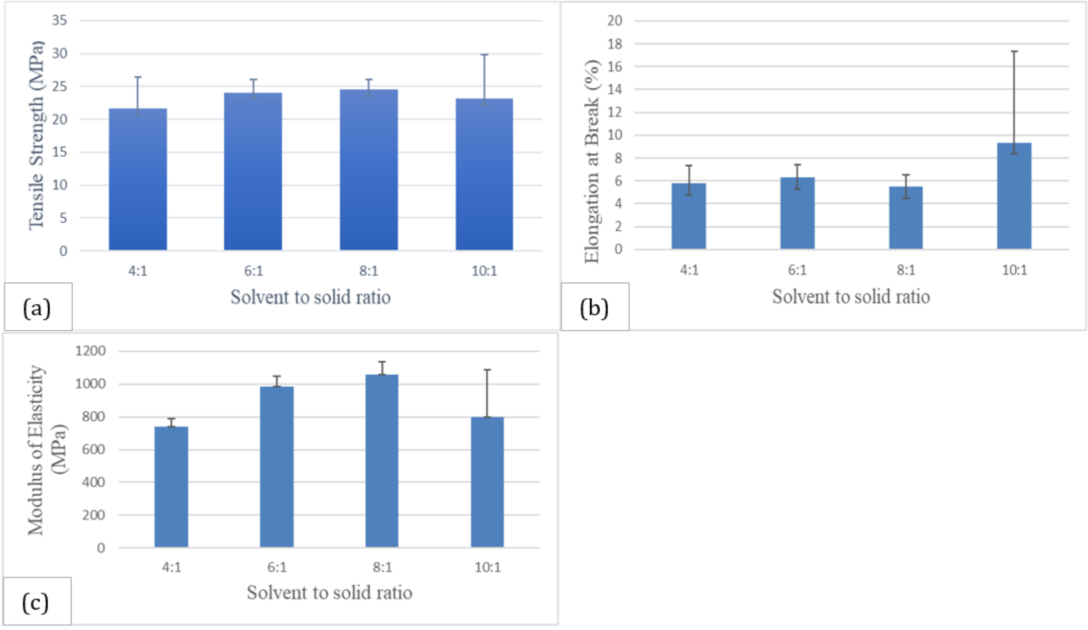

Figure 1. Tensile properties of pristine PMMA films at various S/S ratios.

Based on the results obtained at Stage 1, the ideal solvent to solid ratio was found to be 8:1. Therefore, the effect of binary solvent mixing ratio on the tensile strength of PMMA/0.25SiC was carried out at S/S of 8:1 and depicted in Figure 2. It can be observed that the increasing toluene to acetone ratio decreased the composites' tensile strength. By using 100% acetone (5:0) as solvent, the PMMA/0.25SiC obtained a tensile strength of 26 MPa. However, the tensile strengths of the composites were found to reduce with the addition of toluene as secondary solvent. This is due to the difference of boiling point between toluene and acetone, in which the boiling point of toluene and acetone were 110 °C and 56 °C , respectively. Since the drying process took place at room temperature, toluene with higher boiling point might retained in the composite films for a longer time. As a result, it led to a compromised tensile strength of the films. This can be supported by the study conducted by Eriksson and coworkers [8] in which they discovered that the solvent retention of PMMA/silica films, for acetone and toluene, were about 1.3 wt% and 4.2 wt%, respectively, even after 1 week evaporation at room temperature.

Figure 2(b) shows the elongation at break of PMMA/0.25SiC as a function of different binary solvent mixing ratio. The elongation at break of the composite films prepared in 100% acetone was slightly higher than those prepared in binary solvent. The elongation at break of the composites prepared were about 6.2 % while the other composites films prepared in binary solvent did not elongate more than 6 %. Solvents are known to have the ability to interact with polymer chains, thereby weakening the intermolecular forces that are holding the polymer chains together. The strong interaction of acetone with PMMA chains cause plasticization, where the intermolecular forces are weakened, allowing the polymer chains to move more freely [9]. This increases their capacity to deform without breaking. As a direct consequence of this, the composite films become more flexible and breaks with a greater degree of elongation. On the other hand, the binary solvent systems seem like do not achieve the same degree of plasticization and showed reduced elongation.

The effect of solvent binary ratio on the modulus elasticity of PMMA/0.25SiC is depicted in Figure 2(c). It is found that the tensile modulus of PMMA/0.25SiC in 100% acetone was lower than that of the composite films prepared in binary solvents. This is due to the difference in solubility and swelling behaviour of PMMA in these solvents. When PMMA is dissolved in acetone, it swells more than the counterpart in toluene, which leads to a reduction in the modulus of elasticity. The swelling behaviour of PMMA in a solvent depends on the solubility parameter, which measures the solvent's ability to dissolve the polymer. Acetone has a higher solubility parameter than toluene, meaning it is a better solvent for PMMA and causes it to swell more. The swelling of PMMA in acetone reduces the modulus of elasticity because the polymer chains are more mobile and can move more easily under stress. This results in a lower resistance to deformation and a lower modulus of elasticity. Therefore, PMMA/0.25SiC dissolved in acetone has a lower modulus of elasticity and lower stiffness than PMMA/0.25SiC dissolved in mixture of acetone and toluene. The selection of suitable solvent may affect the mechanical properties of PMMA composites as a results of their polarity and the formation of H bonds with PMMA [10] .

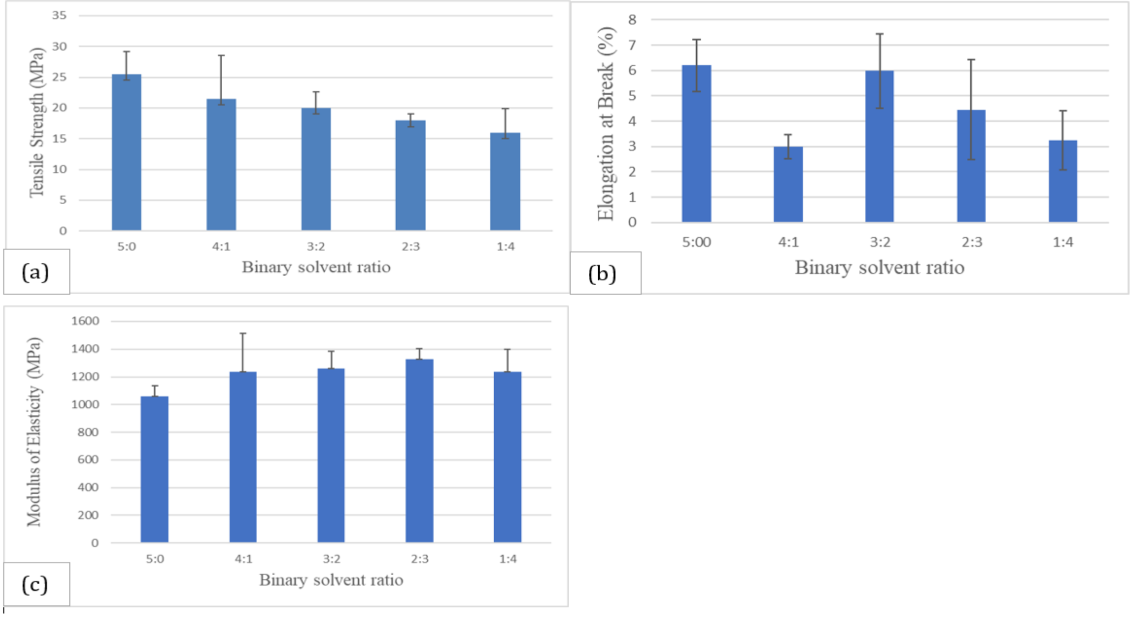

Figure 2. Tensile properties of PMMA/SiC composite films.

3.2. Scanning Electron Microscopy (SEM)

Figure 3 displays the SEM images of the pristine PMMA at x5000 of magnification. Figure 3(a) shows the PMMA_4A, for S/S ratio of 4:1, its fracture surface was rougher than the PMMA_8A shown in Figure 3(b). It is important to note that PMMA is an amorphous material with a brittle texture [10]. As the S/S ratio increased, the fracture surface became smoother. The higher volume ratio of solvent provides more time for the PMMA chains have more time to recrystallize.

Figure 4 displays the SEM images of fracture surfaces of PMMA/0.25SiC_4A and PMMA/0.25SiC_1A. At fixed volume of solvent, the toluene content was higher than acetone in PMMA/0.25SiC_1A. Though both acetone and toluene were good solvent for PMMA, the nonpolar toluene had led to the formation of uneven fracture surface, while the polar acetone caused a smoother fracture surface.

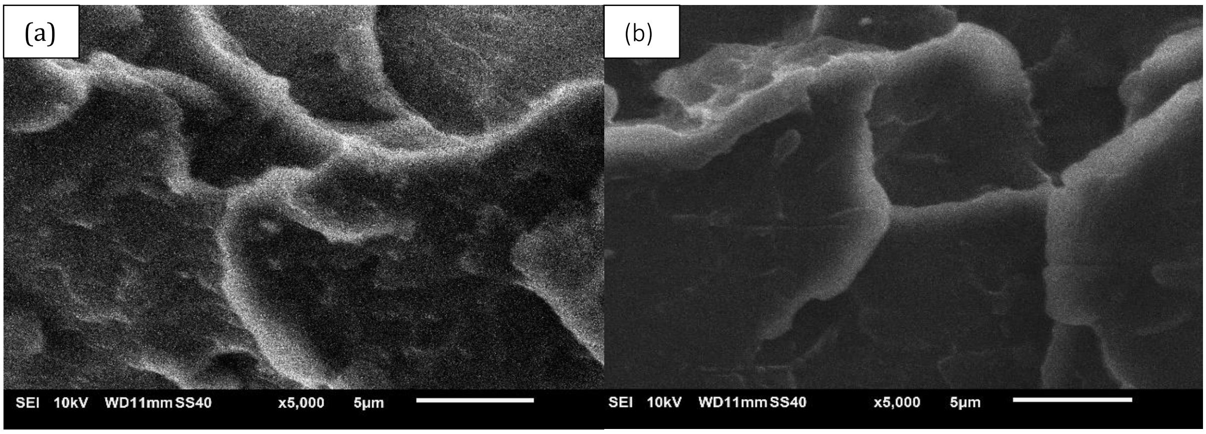

Figure 3. SEM images of PMMA films (a) PMMA_4A (b) PMMA_8A.

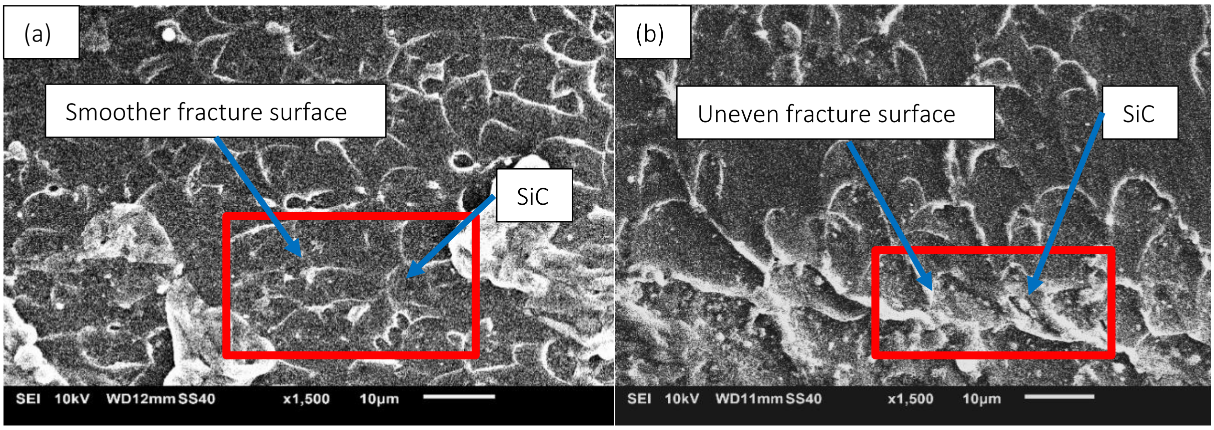

Figure 4. SEM images of binary solvent (a) PMMA/0.25SiC_4A (b) PMMA/0.25SiC_1A.

3.3. X-Ray Diffraction (XRD)

Figure 6(a) demonstrates the XRD patterns of pristine PMMA thin films at different S/S ratio, in the 2θ scan range from 0°to 80°. The intensity of peak for PMMA_8A was higher than that of PMMA_4A. These results confirmed that PMMA_8A had higher crystallinity than PMMA_4A. The higher acetone volume in PMMA_8A led to a slower evaporation rate compared to PMMA_4A. The reduced rate of solvent evaporation for PMMA_8A gave the polymer chains more time to move and diffuse within the solution, leading to more ordered arrangement and a higher degree of crystallinity.

The d-spacing of PMMA/0.25SiC in binary solvent mixtures were illustrated in Figure 6(b). It can be seen that, the d-spacing of PMMA/0.25SiC_5A and PMMA/0.25SiC_4A were very similar, which were 43.67 and 43.69 nm, respectively. However, as the toluene content increased in PMMA/0.25SiC_1A, the d-spacing was decreased to 43.42 nm. The d-spacing represents the distance between adjacent crystal planes or molecular chains within the material. When the SiC particles are well dispersed, the interfacial interactions and stress transfer can cause the polymer chains to slightly separate leading to an increase of d-spacing in composite material. In another word, the reduced d-spacing may indicated the poorer dispersion of SiC in higher toluene solvent mixture.

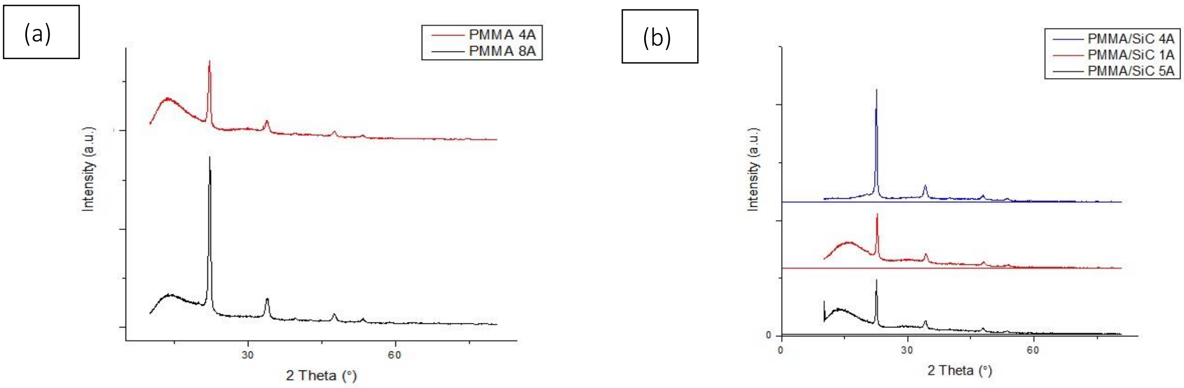

Figure 6. XRD pattern of (a) PMMA films and (b) PMMA/0.25SiC in binary solvent.

3.4. Hardness Testing

Figure 7(a) shows the results of hardness test that were performed on the pristine PMMA films surface using Durometer Shore Hardness ASTM D2240. The hardness of pristine PMMA films was found to increase with S/S ratio. At S/S ratio of 4:1, the hardness value was about 5N It is believed that higher S/S ratio allowed longer evaporation time, led to better PMMA chains realignment, leading to higher crystallinity of PMMA. This was proven with the finding of XRD in Figure 6(a), where the higher crystallinity of PMMA was detected in PMMA_8A as compared to PMMA_4A.

By using S/S ratio of 8:1, the PMMA/0.25SiC films were prepared in the presence of toluene. Figure 7 shows the hardness test results of the PMMA/0.25SiC films in different binary solvent ratio. The presence of SiC in pristine PMMA had increased the hardness of the films. The SiC particles act as a reinforcing phase within the PMMA matrix. Previously, the hardness of PMMA filled with ZrO_2 nanoparticles, TiO_2 nanoparticles, and E-glass fibre were reported to increase with addition of fillers [11]. At fixed solvent volume, the hardness of pure acetone was about 6 N. However, the higher toluene content managed to increase the hardness of PMMA/0.25SiC accordingly. The hardness of the composite films was recorded as 6.8 N at 4:1 binary solvent ratio and showed an increment of 13 % as compare to 5:0 binary solvent ratio. Since acetone can cause significant swelling of PMMA, the addition of toluene may help control the swelling and prevent excessive plasticization of the polymer. In addition, the poorer dispersion of SiC in toluene, as evidenced in XRD patterns, may resists the surface indention and resulting in higher surface hardness of PMMA/0.25SiC.

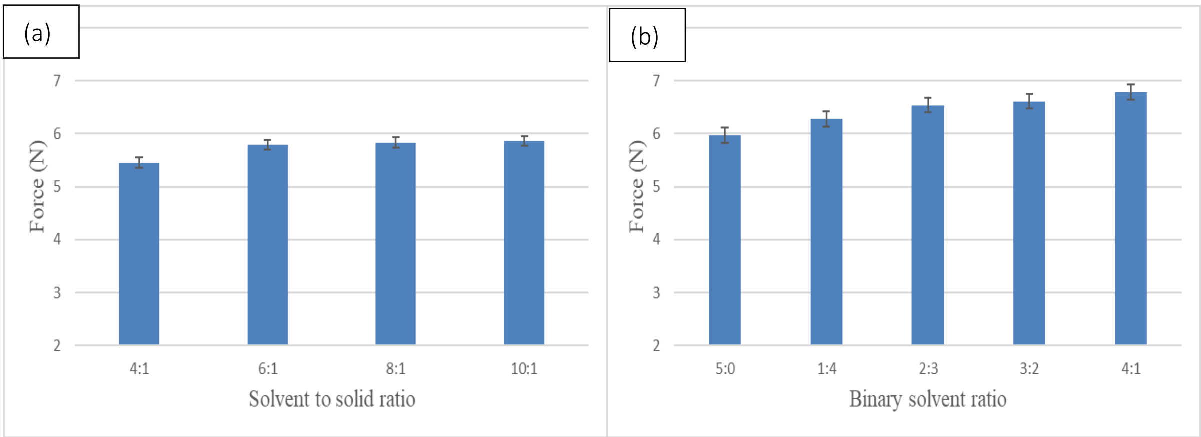

Figure 7. Hardness testing results of (a) PMMA films and (b) binary solvent of PMMA/0.25SiC.

4. CONCLUSION

In conclusion, the pristine PMMA and PMMA/0.25SiC composite films were prepared successfully in acetone solution and mixture of acetone/toluene, respectively. The tensile strength and modulus of elasticity of PMMA increased with the increasing S/S ratio. This was due to the better PMMA chains realignment in higher solvent volume and higher degree of crystallinity was established. It was confirmed by the SEM micrographs, higher peak intensity in XRD and improved hardness values. Meanwhile, the tensile strength of PMMA/0.25SiC composite films has decreased with the presence of toluene as secondary solvent. The higher boiling point of toluene had resulted more solvent retention and therefore compromised the tensile strength. The morphological studies showed that higher toluene content has led to rougher fracture surfaces and poorer SiC dispersion as evidenced by the lower d-spacing. However, the higher nonpolar toluene content had increased the hardness of PMMA/0.25SiC composite films.

The findings of this study showed that mechanical and physical properties of the amorphous polymer is strongly dependable on the solvent to solid ratio and the types of solvent used.

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