Volume 15, Number 4, 2022. pp. 377-381

Jordan Journal of Physics

ARTICLE

Improved Structural Bonding, Morphology and Mechanical Properties of Poly (Methy Methacrylate) (PMMA) Thin Film Induced by Chloroform Solvent Casting

N. Jamsuzazilawati[a], **C. K. Sheng**[a] and **W. M. Z. Yunus**[b]

[a] *Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu Darul Iman, Malaysia.*

[b] *Centre for Tropicalization, National Defence University of Malaysia, Sungai Besi Camp, 57000, Kuala Lumpur, Malaysia.*

Doi: **https://doi.org/10.47011/15.4.6**

Received on: 20/01/2021; *Accepted on: 15/03/2021*

Abstract: The purpose of this study is to investigate the role of chloroform solvent in improving the structural bonding, surface morphology and mechanical strength of poly (methy methacrylate) PMMA thin film *via* casting method. The functional group of this material was determined using the Fourier transform infrared (FTIR) spectroscopy and the surface morphology was examined by scanning electron microscopy (SEM). The mechanical properties were further characterized using the tensile testing machine and the hardness tester. SEM images reveal that the PMMA film surface exhibits a large and smooth homogeneous surface area, indicating the formation of a clear and highly transparent optical film. FTIR spectra demonstrate a slight band shift and enhanced intensity of C–O and C-H bands for the PMMA thin film as compared to the one in powder form. The mechanical strength of the present PMMA thin film was found to be much higher than that of the commercially available plastic and PMMA thin films, in which this finding could convey a significant insight in order to boost the availability and functionality of the current polymer applications.

Keywords: PMMA thin film, IR spectra, Young's modulus, Mechanical stretching, Hardness.

Introduction

The use of polymers has been expanding in various fields today, such as in medicine, industry and microelectronic and nanotechnology applications. Polymers have profound interest in society. Also, they are increasingly used in many industries as a metal replacement in diverse fields of life. They can also be further modified according to modern applications. Polymers have highly stress and strain rate-dependent properties and show substantially different properties when being produced under different conditions [1-5]. Nowadays, different types of solvents used for polymer dissolution are practiced to modify the properties of polymers to meet the desired requirements for specific applications. Polymers have many applications in industry, such as microlithography, membrane science, plastics recycling and drug delivery [3, 7].

Poly (methy methacrylate) (PMMA) belongs to one of the acrylic glasses, which is a versatile optical material. PMMA has been widely used in the fabrication of optical devices, residential windows and commercial aquariums. This is due to its excellent optical properties and flexible processability as compared to ordinary glass. PMMA offers a high and clear light transmittance. It can be easily formed without loss of optical clarity. Also, it is widely utilized in consumer products due to its unique

Corresponding Author: C. K. Sheng **Email**: chankoksheng@umt.edu.my

mechanical properties and performances under various processing conditions. Besides that, PMMA has a good degree of compatibility with human tissue. Hence, it is widely used in medicine for orthopedic surgery to fix the prosthetic components [3-8]. In this study, we have carried out a novel characterization on the physical properties of a PMMA transparent thin film prepared by solvent casting at room temperature. Chloroform was firstly employed as solvent for PMMA powder dissolution and its role in improving thin film formulation is thoroughly elucidated. The structural and morphological properties of PMMA were identified by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), respectively. The mechanical properties were characterized *via* hardness and tensile testing machines.

Materials and Methods

PMMA (Sigma-Aldrich) in the powder form and chloroform (Merck) were used as received without further purification. Chloroform was used as solvent for thin-film preparation and to study the effect on the physical properties of PMMA thin film. Firstly, a desired quantity of PMMA powder was dissolved in the chloroform solution. The solution was vigorously stirred in a volumetric flask to obtain a viscous homogeneous mixture and it was then poured into a petri dish and dried at room temperature for 24 hours in a vacuum chamber [6]. Finally, the solid thin film was peeled off from the petri dish and cut into the desired pieces for further characterization. Fig. 1 shows the image of as-received PMMA powder and the PMMA thin film.

The mechanical properties of tensile strength and Young's modulus were characterized using the M350-5 CT universal testing machine and the samples hardness was measured by AFFRI hardness tester, Series 206 EX. On the other hand, the scanning electron microscope (SEM) model JEOL JSM-6360 LA was used to examine the surface morphology and the Fourier transform infrared (FTIR) Thermo Nicolet Alvatar 380 spectroscopy was used to identify the infrared spectral functional groups of the samples.

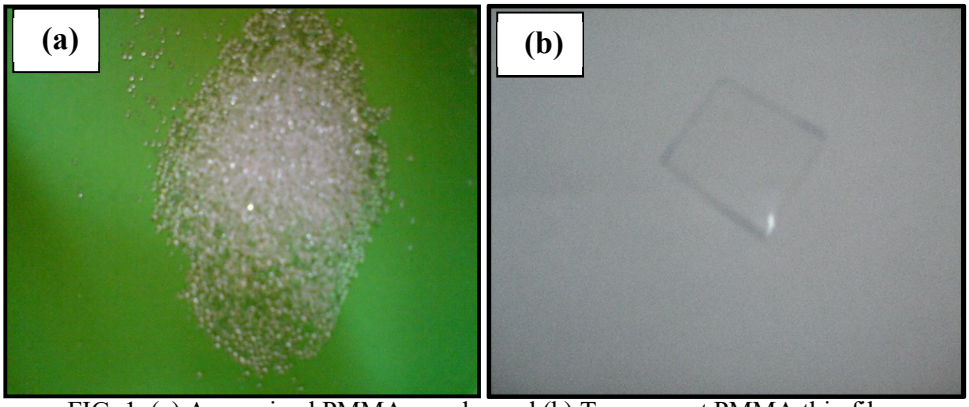

FIG. 1. (a) As-received PMMA powder and (b) Transparent PMMA thin film.

Results and Discussion

A scanning electron microscope (SEM) is capable of producing high-resolution surface morphological images of a studied material. Figs. 2(a), (b) and (c) show the plan-view surface morphology of the PMMA thin film examined by SEM at different magnifications of ×500, ×1000 and ×2000, respectively. From the figures, a smooth, dense and high film uniform surface area is formulated for the present sample, which could signify an optically clear and transparent homopolymer thin-film formulation. Furthermore, there are some small white dots distributed on the sample surface with a size of around 120 nm, which could be responsible for facilitating a high-quality film structure. Chloroform has been reported to serve as a good solvent for most of the polymers/co-polymers and to initiate the dispersion of PMMA nanoparticle residues after solvent evaporation. Furthermore, the homogeneous distribution of the white dots represents the possible presence of quantum dots to improve the structural bonding between the molecules according to Liu et al. [9]. Therefore, it is worth to mention that the present chloroform might play a vital role for nanoparticle dispersion in the polymeric solid film.

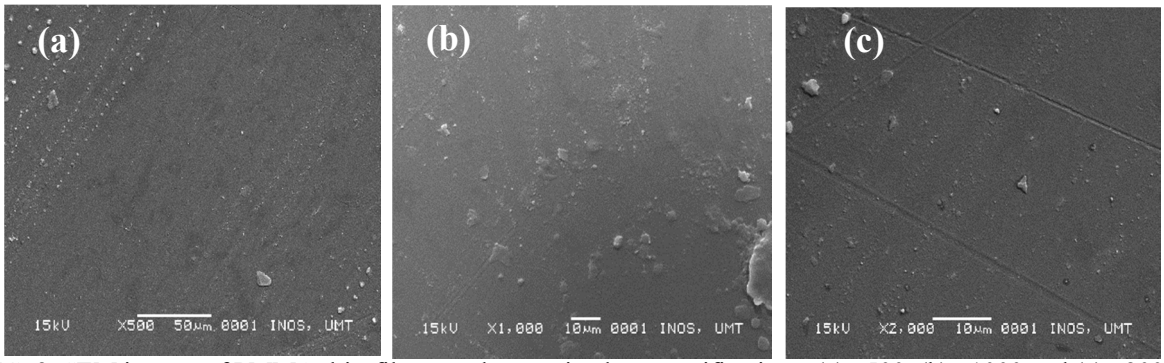

FIG. 2. SEM images of PMMA thin-film sample examined at magnifications: (a) x500, (b) x1000 and (c) x2000.

Almost any organic or inorganic compound that contains covalent bonds would absorb various frequencies of electromagnetic radiation in the infrared region. Hence, the FTIR spectroscopy is a versatile and well-established optical method to study the physical interaction and vibrational mode of the functional group in a material. The IR radiation within the studied energy region corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecules. Fig. 3 shows the FTIR spectra of the as-received PMMA powder and thin film produced by evaporation casting. The characteristic bands of the neat PMMA occurred at positions of 679, 752, 842, 988, 1148, 1192, 1240, 1386, 1435, 1726, 2951 and 3728 cm^{-1}. The small band located at 2951 cm^{-1} can be assigned to C-H stretching mode, while two strong sharp peaks observed at 1726 cm^{-1} and 1148 cm^{-1} correspond to the C=O and C–O stretching vibrations, respectively [10]. Relatively, a small sharp peak observed at 1192 cm^{-1} belongs to $–OCH_3$ stretching vibration. Moreover, the intense sharp bands that appeared at 1435 cm^{-1} and 752 cm^{-1} are attributed to C-H bending in CH_3 and CH_2 groups, respectively. Thereafter, it is interesting to note that all the respective bands shift to higher wavenumber when the PMMA powder is transformed into the thin-film phase. This phenomenon indicates that an interactive-bonding reaction occurs between the molecules in the PMMA thin film, as initiated by the chloroform solvent used in the present study. Furthermore, the intensity of the bands assigned for C–O stretching and C-H bending becomes stronger, which might contribute to the improved tensile properties and hardness of the PMMA thin film as compared to the commercially available polymeric films [10].

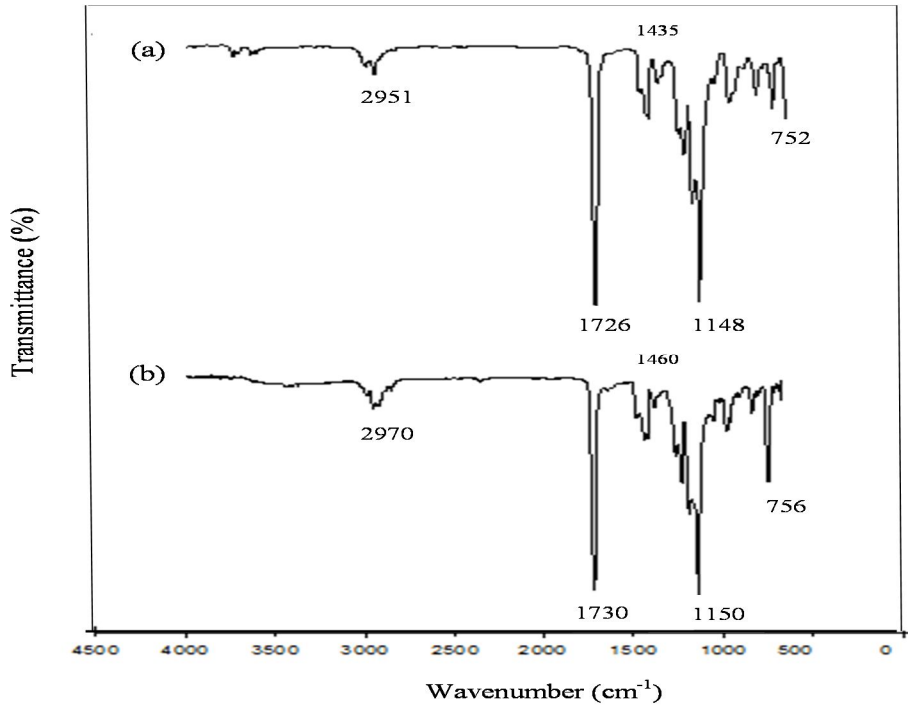

FIG. 3. FTIR spectra for (a) as-received PMMA powder and (b) PMMA thin film.

The tensile test is probably the most widely used tool in order to characterize the mechanical properties of a plastic material. Tensile test measures the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point. Thereby, a stress-strain diagram generated from the tensile test is applied to identify the tensile strength, elongation at break and Young's modulus values. Figs. 4(a) and (b) show respectively the stress-strain curve for the PMMA thin film and a commercial plastic used as the reference sample. The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of materials used in structural applications. The tensile strength of a material is the maximum amount of tensile stress that it can withstand before failure [11-13]. In the present study, the tensile strength of the PMMA thin film is determined to be 57.80 MPa, while the tensile strength of the commercial plastic film is found to be only 2.59 MPa.

The ultimate elongation (fracture strain) of a material is the percentage increase in length that occurs before it breaks under tension. The ultimate elongation of PMMA thin film (3.93 %) is found to be much lower than that of the commercial plastic film (7.93 %), indicating that the PMMA film is less elastic than the commercial plastic film. This result also reveals that the PMMA film could be classified as a rigid plastic film, which exhibits a fracture strain value under 5 % by referring to the study reported by Pharr et al. [14]. The Young's modulus value of the sample is directly obtained from the tensile testing system. The Young's modulus determined for PMMA thin film is 380.76 MPa, which is much higher than that of the available commercial polymer (2.59 MPa). This finding clearly denotes that the PMMA thin film is much harder than the commercial plastic film. The integration of high ultimate tensile strength and low fracture strain would possibly produce materials with high toughness values. This effect could eventually lead to a high Young's modulus that is defined as the ratio of stress to strain in tension. A high Young's modulus value means that the material is rigid, hence more stress is required to produce a given amount of strain [11, 13]. In the present case, PMMA shows highly strain and strain rate-dependent properties and substantially improves the mechanical behaviors as induced by the chloroform solvent. In comparison, the tensile strength values were obtained to be much higher as compared to those prepared by the thermal solvent method [3, 7]. According to Namouchi et al. [7], PMMA is one of the hard materials with significantly lower hardness and Young's modulus that can be more easily deformed when compared to glass.

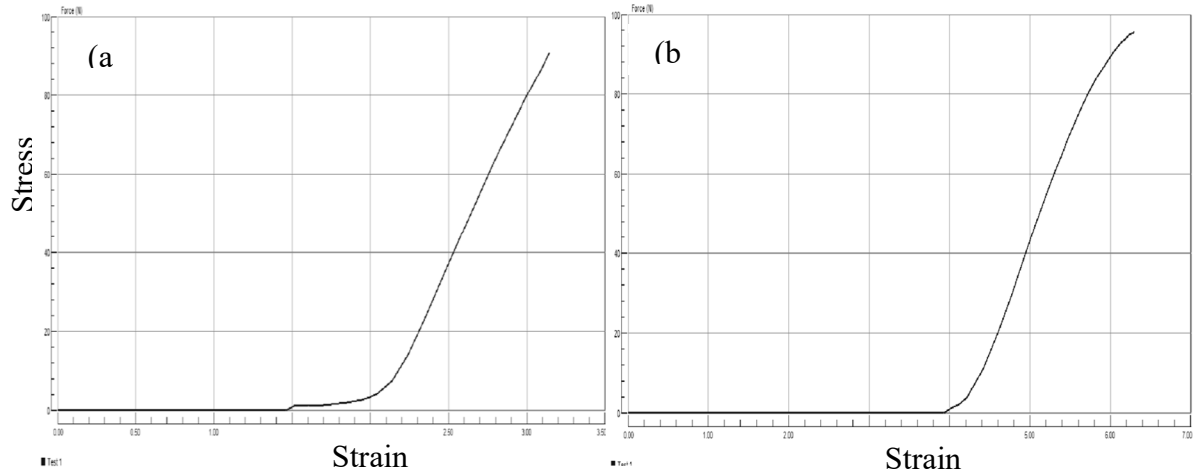

FIG. 4. The stress-strain curve for (a) PMMA thin film and (b) commercial plastic film.

The universal hardness method defines more precisely the hardness of a surface as its general ability to resist plastic deformation by penetration. Recently, Rockwell hardness test has been widely used and proven to be a major advance in the field of hardness testing, which enables the user to perform an accurate hardness test on a variety of sized parts in just a few seconds. In the present study, the Rockwell hardness tester machine was incorporated with a 1/16-inch diameter steel ball (Rockwell B system), with a load of 100 kg for measuring the

hardness of a sample. Under this circumstance, the average hardness value determined for PMMA thin film is 54.30. This result implies that the present film hardness is higher than that of a commercially available plastic film.

Conclusion

The improved structural and mechanical properties of PMMA thin film formulated by chloroform solvent casting was investigated thoroughly by SEM, FTIR, hardness tester and tensile testing machine. A smooth and homogeneous surface is obtained for this sample as observed by SEM. The Young's modulus value determined for PMMA thin film is 380.76 MPa, which is much higher than that of the commercial plastic film. The characteristic bands of PMMA show a slight shift to higher wavenumber and the band intensity assigned to C-O and C-H bonds becomes stronger when the PMMA powder is transformed into the thin film as assisted by chloroform solvent. This effect might contribute to the improvement in tensile properties and hardness of the PMMA film as compared to commercially available plastic and literature-reported PMMA thin films.

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