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Physical, Thermal, and Mechanical Characterization of PMMA Foils Fabricated by Solution Casting

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Abstract: The physical, thermal, structural, and mechanical properties of poly(methyl methacrylate) PMMA foils cast from solutions of toluene were investigated by differential scanning calorimetry, optical microscope, Fourier infrared spectroscopy, and dynamical mechanical analysis. The PMMA foils were prepared from a different ratio of PMMA powder with toluene solvent by the solution cast method. The surface features, glass transition temperature, and C-H bonds of foils were investigated and compared with commercial PMMA foil. The mechanical characterization of foils was examined by using static and dynamic loads in axial and transverse modes. The tensile behaviors of the commercial and as-prepared foils were investigated by using a strain rate of 0.01/s. The dynamical behavior of the foils was tested in tensile mode using 0.1 N of stress with a frequency of 1 Hz for the determination of storage, loss modulus, and damping values of the tan delta. A significant shape memory was observed in all of the prepared PMMA foils. The solution cast method allows for tuning the glass transition temperature of polymer foil that could easily integrate with the NiTi alloy phase transition temperature to fabricate a suitable composite structure. Integrating both structures will open the flexibility in bistable actuators in composite structures as a function of thermal cycles.

Keywords: PMMA; toluene; glass transition; modulus; as-cast; glass substrate

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1. Introduction

Poly-methyl methacrylate (PMMA) is an amorphous thermoplastic polymer with moderate mechanical properties at room temperature. At a strain rate of 10^{-3} s^{-1}, the tensile strength (UTS) has a value of 70 MPa, elastic modulus (E) of 3.3 GPa, and low density as compared to metallic materials of 1.19 g cm^{-3}. Importantly, PMMA is biocompatible, making it highly desirable for use in not only electronics, microelectromechanical systems (MEMS), and micro-optics but also biomedical and microfluidic devices [1–3]. PMMA has many advantages over other transparent polymers (e.g., polystyrene, PC, etc.), such as high resistance to UV light and weathering and excellent light transmission. PMMA is produced from the monomer methyl methacrylate. It is a colorless polymer available in the form of powders, pellets, granules, and sheet forms. Thin polymer films are usually obtained by solution casting for many applications, such as paints, varnishes, and adhesives. The properties of a polymer film obtained from a solution can differ from the original bulk polymer, which may have some consequences on the behavior of the final film. PMMA foils are produced by the casting method followed by polymerization and molding steps. Polymeric materials depend strongly on the rheological behavior of surfaces during casting processing, and the mechanical behavior of the samples depends upon the final products. However, rare attention has been focused on the physical, structural, and mechanical properties of PMMA foils prepared by the solution casting method. The samples prepared from various solid-to-liquid ratios (S/L ratios) with solvent toluene by solution casting method could be different in thermal, and mechanical properties.

PMMA is commonly known as acrylic glass or plexiglass polymer that could be used as the main component of positive resists for UV photolithography [4,5]. PMMA is considered an imprintable material for hot-embossing soft lithography because of its transparency in the visible spectrum [6]. It is widely used in optical applications, especially as a matrix for nonlinear optical composite materials [7,8]. PMMA polymer considers one of the individual components of composite structure because of its shape memory effect and is biocompatible in nature. Various techniques have been implemented to combine polymer into the substrate, such as spin coating and injection molding methods [9–11]. The interfacial adhesion of polymer onto the substrate is a crucial factor for the application of the composites in aggressive environments [12]. PMMA is commonly used in denture material with poor antimicrobial effects [13]. PMMA composite plays a significant role in modern optical devices due to its transparency and high hardness nature [14]. Various surface treatment methods such as UV irradiation have been used to increase the adhesion of PMMA polymer [15]. Prior to use as one of the components in composite materials, it is essential to study the individual component behavior of PMMA polymer prepared by the as-cast method. There are extensive studies that have been carried out in the literature about PMMA samples cast from various solvents. The influence of various solvents was studied on the morphology of PMMA foils towards the mechanical properties [16]. The study also focused on the effect of solvents on the structural behavior of the relaxation temperature of as-cast PMMA foils [17], as the effect of solvents influences acid–base interaction between the basic sites of PMMA and the acid character of the solvent. The effect of ultrasonic fields on the dilution of PMMA in the solvents has been studied for PMMA films obtained by the drop-casting method. The ultrasonic vibration decreases the amount of residual solvent in the film to one-twelfth of the value, which occurs by spontaneous evaporation [18]. Other studies focused on the effect of dimethyl formamide and tetrahydrofuran (THF) on the miscibility in the liquid phase between PMMA and polyvinyl chloride at different relative concentrations [12] and the effect of solvents on the morphology of films prepared by either laser evaporation [16] or drop-casting [19].

However, it is very rare that information is reported in the literature about the thermal, structural behavior, and mechanical properties of PMMA obtained by solvent evaporation from solution casting methods. Although various types of solvents for casting PMMA foils have been discussed before [20,21], various ratios of S/L (solid/liquid) of a specific solvent, such as the most common one, Toluene, to PMMA powder are rarely discussed. The novelty of this work is to tune the glass transition temperature of prepared PMMA foils by varying the concentration of solutions. The tune glass temperature will integrate with NiTi alloy for the formation of the composite. The composite could be able to deflect the behavior of sensors and actuators as the function of heating and cooling cycles with the combined effect of polymer–alloy behavior. The aim of the present work is to investigate the thermal, surface features, structural, and mechanical properties of samples obtained by casting PMMA prepared from solution cast method curing in dry, ambient air at room temperature. PMMA as-cast foils were prepared from various ratios of PMMA powders-to-toluene (solid-to-liquid) ratios and investigated experimentally. The as-cast PMMA foils were characterized by various S/L ratios by thermal, microstructural, structural, and mechanical properties. Different experimental techniques are used, such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and Fourier-transformed infrared spectroscopy (FTIR), which allowed the examination of thermal (i.e., glass transition temperature), thermomechanical (i.e., storage modulus, loss modulus, tan delta), and structural properties of the samples (i.e., bonding type and occurrence), respectively. Simultaneously, the surface features were observed with an optical microscope with the following shape memory behavior of commercial and as-cast PMMA polymer foils.

2. Materials and Methods

2.1. Materials

Conventional PMMA powder was obtained from Sigma Aldrich and had a molecular weight of 102,000 $gmol^{-1}$. The solvent of toluene was purchased from Sigma Aldrich. Clean glass substrate discs were used for as-cast foils. The reference commercial 0.25 mm thin foil of PMMA was purchased from Konig film (Germany).

2.2. Methods of Fabrication of Cast Foils and Characterization

2.2.1. Sample Preparation Using the Casting Method

The PMMA powder was first dissolved in the three different S/L ratios of toluene. The solubility of the solvent with the solution was calculated from the solution parameters by considering their mutual molecular interactions. The molecular interaction was based on the dispersion bonds, the polar bonds, and the hydrogen bonds. The closer the value was selected for the solution, the smoother the resulting solution. Then the solution was placed on the stirrer using a magnetic stirrer for miscibility for the formation of a clear solution. The solution was stirred for 24 h at 2 rpm for the concentrated solution. After the PMMA powder was completely dissolved, a clear solution was obtained. The solution was poured into the glass plate and allowed to dry for 24 h at ambient temperature. The cast film was dried at room temperature for 4 days to remove residual solvent. After the solution was dry enough, the sample peeled out of the substrate. Figure 1 shows the schematic diagram for the sample preparation by solution cast method.

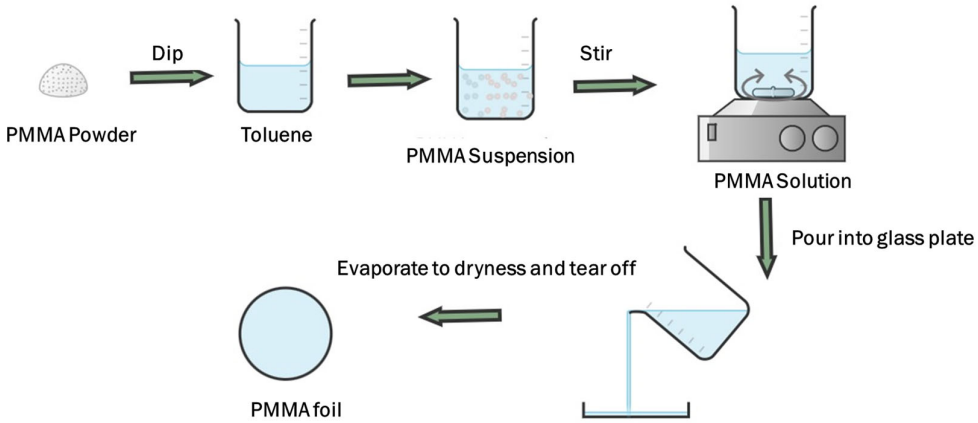


Figure 1. Schematic diagram of PMMA polymer foils by casting method.

The PMMA foils from different S/L ratios using the solution casting method.

2.2.2. Characterization Techniques

PMMA foils prepared by various S/L ratios were characterized by physical, thermal, and mechanical characterization. The quality and uniform thickness of the foils was observed with Keyence Optical Microscope VHX-7000N. Thermal characterization for analyzing glass transition temperature (T_g) by differential scanning calorimetry (DSC) analysis was carried out with DSC 25 (TA Instruments Trios v5.1.1.46572, New Castle, DE, USA). The sample was cooled to 0 °C, then heated up to 150 °C for cast foils. However, for PMMA powder and commercial foils, the temperature was swept between 0 and 130 °C and 0 to 270 °C. The analysis was performed at the rate of 5 °C/min with a flow of N_2 gas in the chamber with a flow of 60 mL/min.

2.2.3. Fourier-Transform Infrared Spectroscopy (FTIR-ATR)

The chemical structure and bonding of molecules were examined by the FTIR method. Infrared vibrational spectra of PMMA foils and PMMA powder and the spectra of toluene were measured using a Thermo Scientific Nicolet iS50 Fourier transform infrared spectrom-

eter with the attenuated total reflection (ATR) accessory. The spectra were collected with 60 scans at 4 cm^{-1} resolution. The analysis was carried out for the PMMA powder, toluene solvent, commercial PMMA foil, and prepared cast foils from various S/L ratios.

2.2.4. Mechanical Characterization

PMMA foils of 100 mm in length and about 3 mm wide were chosen for the tensile test using a thermomechanical tester (Walter + Bay) with a strain-controlled mode at room temperature. The sample stretching in the tester was controlled by engineering strain. The span length was kept fixed at 80 mm. Thermomechanical analyzer (TMA) test was performed on the PMMA foils in flat punch bending mode using the constant load of 50 mN. The sample was tested in thermal cycles from room temperature to −100 °C. Tensile experiments that failed in the clamping position are excluded from the data. The sample configure followed the standard from the in-house built Mitter machine [22].

Dynamical mechanical characterization was performed on the commercial PMMA foil and prepared foils in tensile mode. Thermodynamic analysis was conducted using DMA analysis (DMA 850 tester from TA Instruments). The fixed frequency was 1 Hz, and the temperature range was from 30 to 160 °C. The loss and storage modulus and tan(delta)—internal friction was evaluated in the temperature range. In this instrument, a force was applied to a sample in sinusoidal form, and the amplitude and phase of the resultant displacement were measured [23–25]. By measuring both the amplitude of the deformation at the peak of the sine wave and the lag between the stress and strain sine waves, quantities such as the modulus, viscosity, and damping can be calculated in the viscoelastic material such as PMMA. The stored energy as storage modulus, dissipation energy as loss modulus, and damping behavior of PMMA foils were measured as the function of temperature.

The shape memory effect (SME) was characterized by combining deformation, heating, cooling, and heating cycles for PMMA commercial and cast foils. The SME behavior of the foils was carried out by manual heating and cooling cycles.

3. Results

3.1. Surface Features of PMMA Powder, Foils, and As-Cast Foils

The surface features of PMMA powder and foils were prepared by the solution casting method and investigated with the microscope shown in Figure 2a–d. The PMMA powder shows a hollow structure. The commercial foil of PMMA shows transparent surface film without any inhomogeneities. However, in the sample prepared from 18 mL, the solution shows undissolved powder particles on the surface of the film. This indicates that complete solubility of powder within the solution was not achieved, and, as a consequence, there was some remaining undissolved powder left behind in the solution. The foils generated from the 24 mL solution showed a smoother, transparent surface without any inhomogeneities.

The uniformity of the surface features is investigated by examining the surface area in a three-dimensional image profile. The photographic image of the foils with corresponding 3D images was examined. The images are shown in Figure 3a–d.

The surface thickness and uniformity are well-marked from the 3D image profile. The PMMA foils prepared from 18 mL solution showed uneven surface thickness, which confirmed the height of the image profile, whereas the foil prepared from 24 mL solution shows uniform surface thickness with the confirmed image of the surface depth profile.

3.2. Thermal Characterization of PMMA Powder, Commercial Foil, and Prepared As-Cast Foils

The glass transition temperatures (T_g) for the PMMA powder, commercial foil, and other two solution casting foils were investigated. Figure 4a–d represents the glass transition temperature, and corresponding values are presented in Table 1.

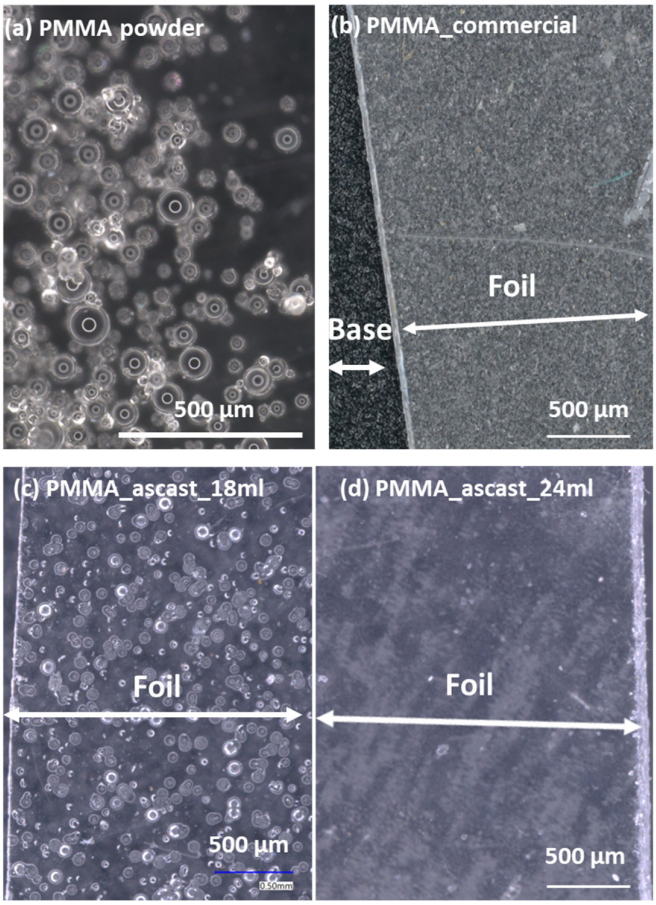


Figure 2. (**a**) Surface image of PMMA powder and (**b**) Commercial PMMA foil (**c**,**d**) prepared PMMA foils from 18 and 24 mL concentrations.

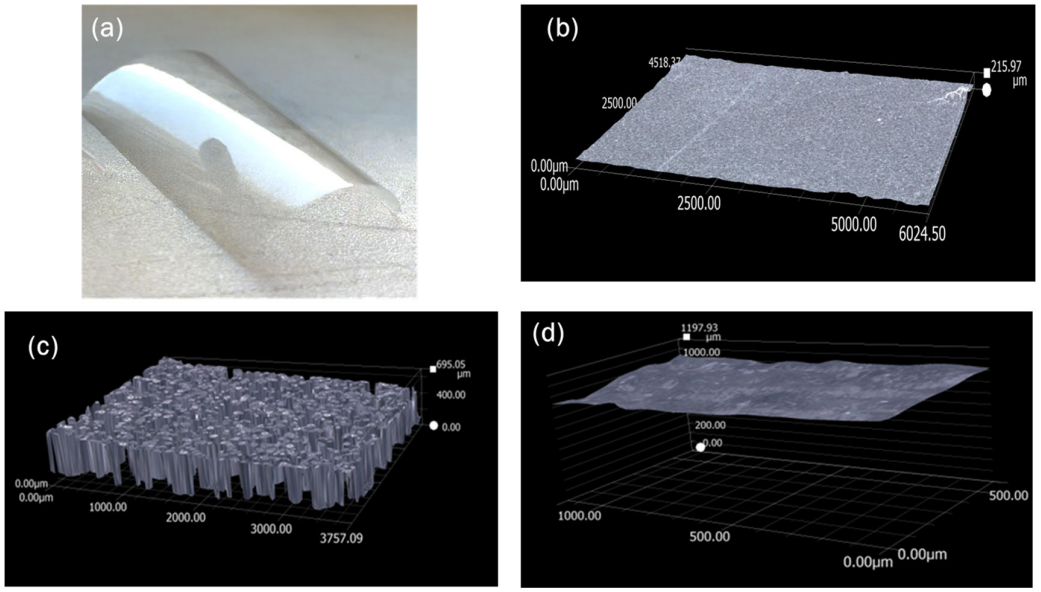


Figure 3. (**a**) Photographic image of solution cast PMMA foils (possibly air voids in sample). (**b**–**d**) 3D image of commercial foil (purchased from Konig film) and as-prepared foils.

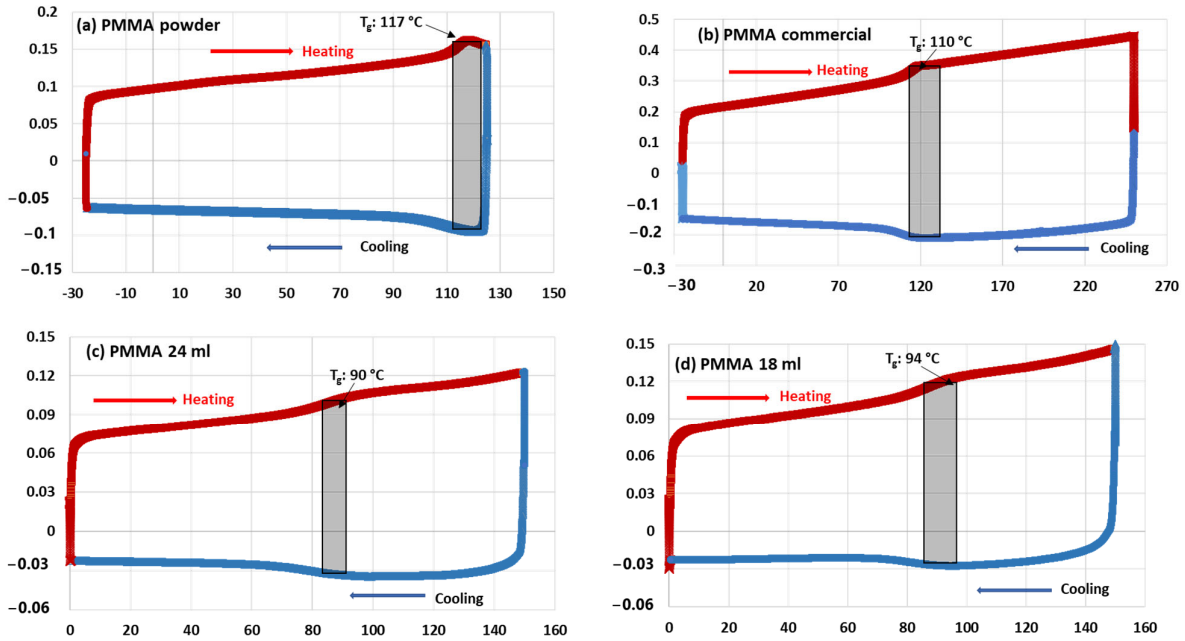


Figure 4. DSC curves of (**a**) PMMA powder, (**b**) commercial foil, and (**c**,**d**) as-cast samples from S/L (1/24, 1/18).

Table 1. As prepared sample thickness with follow-up glass transition temperature.

Sample	PMMA/Toluene Ratio (g/mL)	Thickness (mm)	Glass Transition Temperature (T_g)
PMMA powder	-	Powder	117 °C
Commercial sample	unknown	0.25	110 °C
Sample 1	1:18	0.21	94 °C
Sample 2	1:24	0.37	90 °C

The glass transition temperature of PMMA powder is 117 °C, which may correspond to the volume of various sizes of powder. However, the values of Tg are lower in commercial foil, and the value decreases significantly in solution-cast samples. However, PMMA foils obtained from an S/L ratio of 18 and 24 mL show very similar values of Tg that arise from the combined reaction of solvent with solute. This may correspond to the solvent toluene remaining in the polymer foil that arises from different states of entanglement. The lower value arises from the weaker interaction of toluene and PMMA during the heating cycle.

Based on the application of composite in sensors and actuators it is crucial to integrate both shape memory effects of NiTi alloy with PMMA foil. As the transformation temperatures of NiTi can be adjusted between room temperature and 100 °C, a very interesting composite can be designed. The glass transition temperature of polymer foil is desired to be at a lower temperature than the austenite finish temperature of NiTi alloy. At a temperature above 100 °C, NiTi alloy will be in the austenite phase; however, the polymer will be above glass transition temperature with a viscous stage (zero storage modulus). In this stage, the polymer will adhere to the engraving valley of the NiTi surface. However, during the cooling stage, the alloy will soften while the polymer will stiffen. That will create a lag force with a reverse one-way effect in the composite structure. In this aspect, a polymer with lower Tg is more suitable for application as a composite in various sectors for actuators with a two-way shape memory effect

3.3. Structural Characterization of PMMA Foils

Figure 5 shows the infrared spectra of PMMA powder, two produced PMMA foils of thicknesses of 18 and 24 um, commercial PMMA, and toluene. IR spectra of produced

PMMA foils of different thicknesses are qualitatively the same in the whole range. They differ only in intensities. This difference is not caused by different thicknesses (the penetration length of the evanescent wave during ATR is max 2 um) but rather by slightly different pressures applied to the sample during the measurement and thus a differently close fit to the diamond prism used in the ATR accessory. The spectra of the produced PMMA differ from the spectra of the commercial PMMA and PMMA powder in the absorption of around 735 nm. Commercial PMMA and PMMA powder show only one peak in this region, whereas custom PMMA shows two peaks. In this spectral region, there also occurs the most intensive absorption pattern of toluene that is caused by the bending of an aromatic ring. This suggests that toluene did not evaporate completely during the preparation of PMMA foils and is still present in very low concentrations. Other toluene peaks cannot be observed in PMMA spectra because of their low concentration.

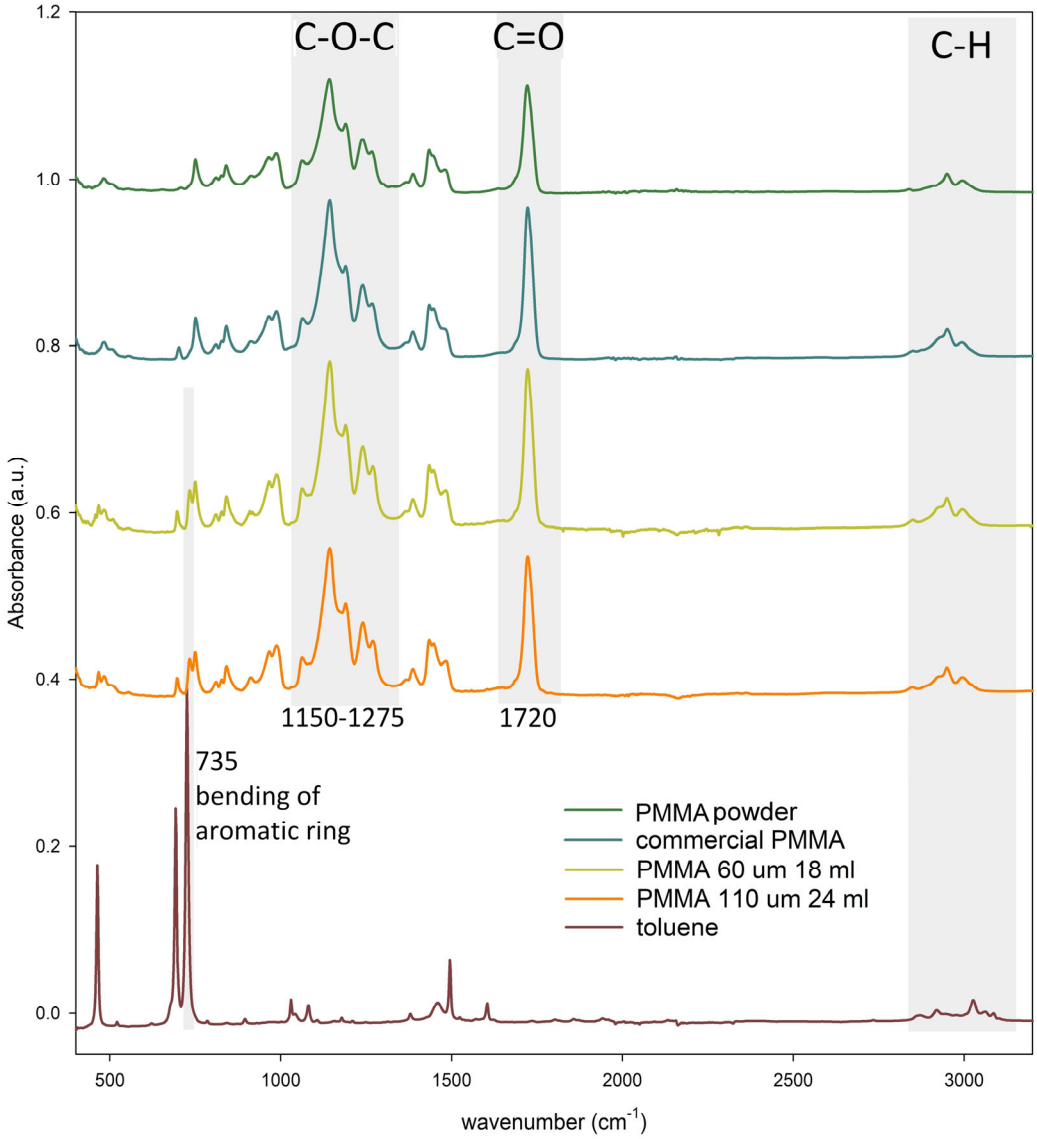


Figure 5. FTIR spectra for PMMA powder, commercial, and as-cast foils.

3.4. Dynamical Mechanical Characterization of Commercial PMMA Foil and Cast Foils

Figure 6a–c represents dynamic studies of the commercial and prepared foils. The study measures storage and loss modulus as the function of temperature. Tan delta is defined as the ratio between loss modulus/storage modulus.

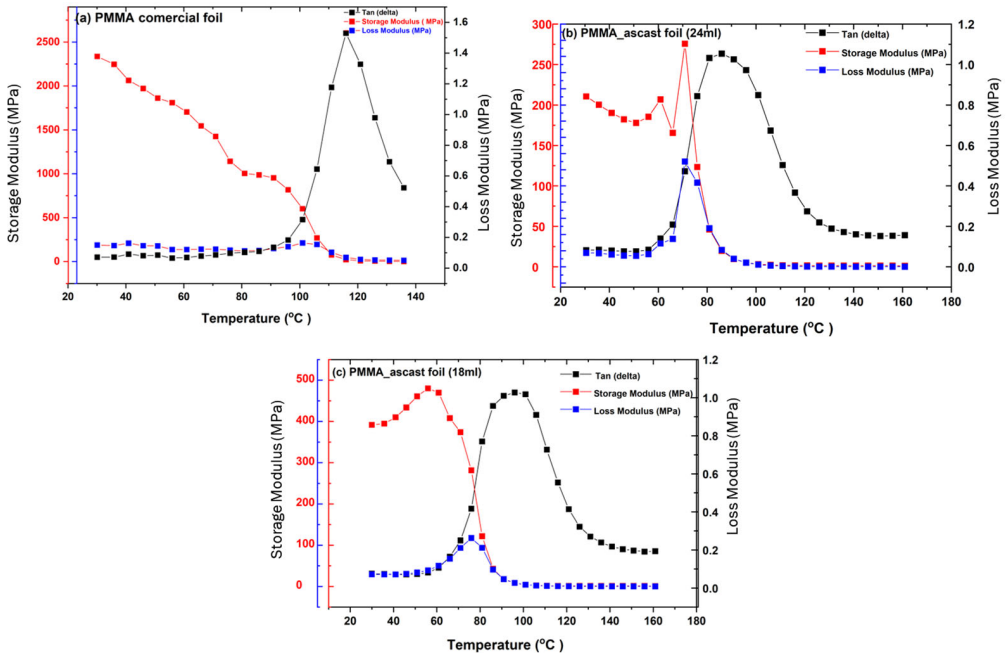


Figure 6. DMA behavior of (**a**) commercial foil and (**b**,**c**) as cast foils from 1/24 and 1/18 (S/L) ratio.

Storage modulus decreases as temperature increases. This behavior of storage modulus with temperature can be explained based on the mobility of molecular segments. At lower temperature ranges, the oscillations of molecules are small due to their low kinetic energy. When the temperature is increased, the kinetic energy of molecules increases, which increases the mobility of molecular segments or oscillations of molecules about the mean position, resulting in an increase in the free volume between molecular segments and thereby reducing the storage modulus. Mechanical loss factor (tan delta) decreases beyond T_g. T_g is also known as the alpha transition temperature. T_g is a large transition because the material moves from a hard glassy state to a soft rubbery state. At higher temperatures, there is an increase in elongation at the break because of more strain caused by the increased motion of the chain segment. The value of the storage and loss modulus decreases to zero value above the glass transition temperature of the polymer. This value does not correspond to zero. Rather, the polymer loses stiffness, and as a result, the machine could not detect the presence of polymer, and a limit has been reached.

3.5. Tensile Test of PMMA Foils

Tensile tests of PMMA commercial foils were carried out in normal and parallel directions. Two tests of the commercial sample were considered for each direction, as presented in Figure 7 (norm_dir 1,2 and parall_dir 3,4). Samples prepared from the bulk sample in a parallel direction display a tensile strain above 15%. However, the samples prepared from the normal direction show a noticeably lower strain in the range of 5–10%. Finally, the samples prepared by the solution cast method either from S/L ratio 18 or 24 mL show a very fragile nature in the tensile test with a strain up to 1–2% at rupture. This signifies that the commercial PMMA samples show better responses in the tensile test. The as-prepared (fabricated) sample shows a weak response in the tensile test. However, the bending deformation of the samples is evaluated in the following section. The shape recovery is examined by functioning the sample under thermal cycles.

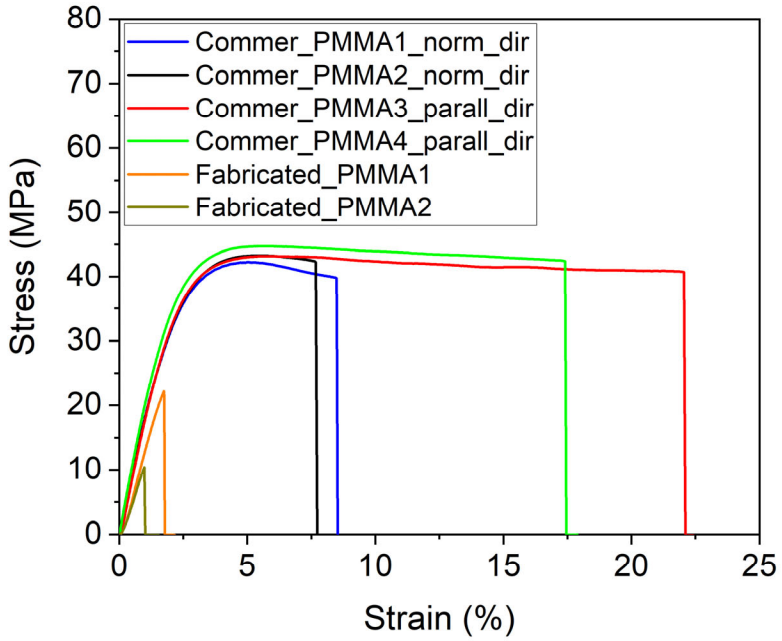


Figure 7. Tensile strength of PMMA commercial foil in both normal and parallel directions and prepared foils (1 and 2 from 1/24 and 1/18 mL). (Three samples are tested for the analysis.) However, two-sample test results are presented.

3.6. Shape Memory Effect of Commercial PMMA Foil and Cast Foils

Figure 8a–c represents the shape memory effect of PMMA commercial foil and prepared foil from two different solutions (S/L ratio of 1/18 and 1/24 mL). The PMMA foils are deformed at 25 °C with a follow-up deformed shape restored at cooling of the sample at −5 °C. The sample holds a deformed shape. The recovery to the original step is followed by heating to 25 °C with subsequent heating to 50 °C in sequence steps, showing partial recovery of the sample. The commercial sample and prepared sample show a shape recovery effect without full recovery to the original position.

PMMA shape fixed ratio and shape recovery are the two significant parameters that represent the shape memory effect of PMMA. Therefore, we studied the shape memory properties of PMMA in bending mode [26]. The shape recovery of PMMA was recorded by a camera and a program that was used to measure the angles of the bending polymer. The sample was in a temporary shape after cooling down. The fixed angle θ_F (the angle between the horizontal line and the free side of the sample) was measured. Thus, we could calculate the shape fixed ratio Rf according to Equation (1). Then the temporary shape was heated up again at 50 °C, and the recovery of the permanent shape was achieved. The sample shows recovery angle θ_R. Using θ_R, we could obtain the shape recovery R_r from Equation (2). These two significant indexes determine the shape memory effect in PMMA polymer in bending. The value of the fixed ratio represents the percentage of bending deformation for the temporary shape, and the value of the recovery ratio represents the maximum percentage of recovery from the deformed shape to the permanent shape. The equations are presented below.

$$R_f = \frac{\theta_F}{180} \times 100\% \quad (1)$$

$$R_r = \frac{\theta_F - \theta_R}{\theta_F} \times 100 \quad (2)$$

where R_f represents the percentage of shape fixity ratio, and R_r represents the shape recovery ratio with respective shape fix angle θ_F and shape recovery angle θ_R, respectively.

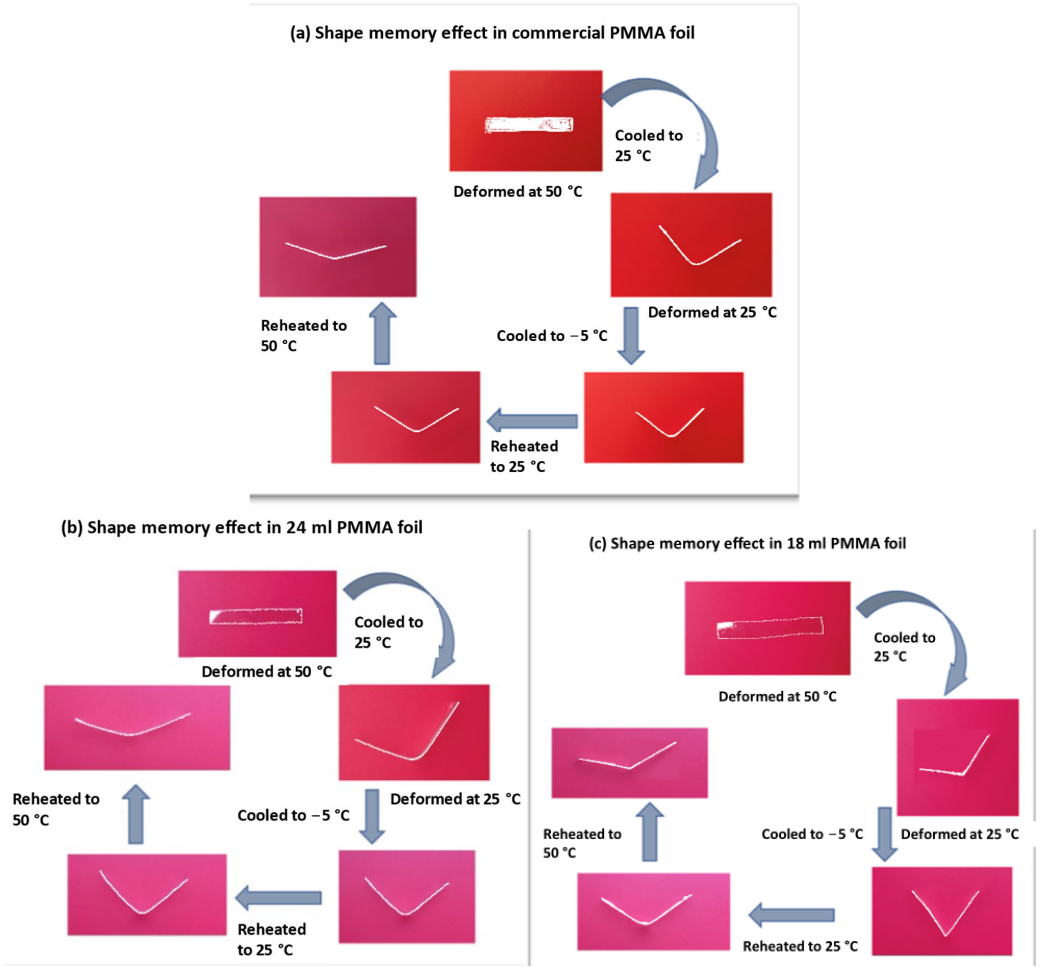


Figure 8. (**a**–**c**) Shape memory effect of PMMA commercial foil and prepared as-cast foils from 24 and 18 mL.

4. Discussion

The shape recovery (%) was calculated using Equation (2) from the shape memory effect from Figure 9 for the commercial and prepared samples. It has been observed that the commercial samples could recover more than 75% when samples were heated at 50 °C from the temporary bending shape to the recovery shape. However, the as-prepared samples show a recovery of more than 65–70%. The recovery was tested for samples as a function of the number of cycles. The result is presented in Figure 8. Both commercial and prepared samples from the solution casting method effectively show better shape recovery from the bending deformation.

The future perspective of the work is to integrate either commercial or prepared PMMA foils with a shape memory alloy of NiTi, as the shape setting of NiTi flat samples is effectively modified towards the application of sensors and actuators, combining the polymer with bending deformation for the formation of composite [27,28]. The adhesion of NiTi alloy with polymer will improve in various ways, beginning from mechanical to chemical bonding [26]. Shape memory alloy with polymer as a composite constitutes as both an actuator and active component. It could mimic the low stiffness and large deformation characteristics of biological tissues using a composite comprising SMA ribbons and a low-hardness polymer matrix. The bending and dynamic behavior of advanced composite plates use a simple shear deformation on plate model [29]. Finite elemental analysis was carried out in static bending and buckling analysis of plates. The buckling effect was studied with deflection and distribution of pores within the composite [30]. They showed that when the SMA is electrically actuated, small strains within the SMA could

achieve an order-of-magnitude larger strain within the composite for application in the sensor [31,32].

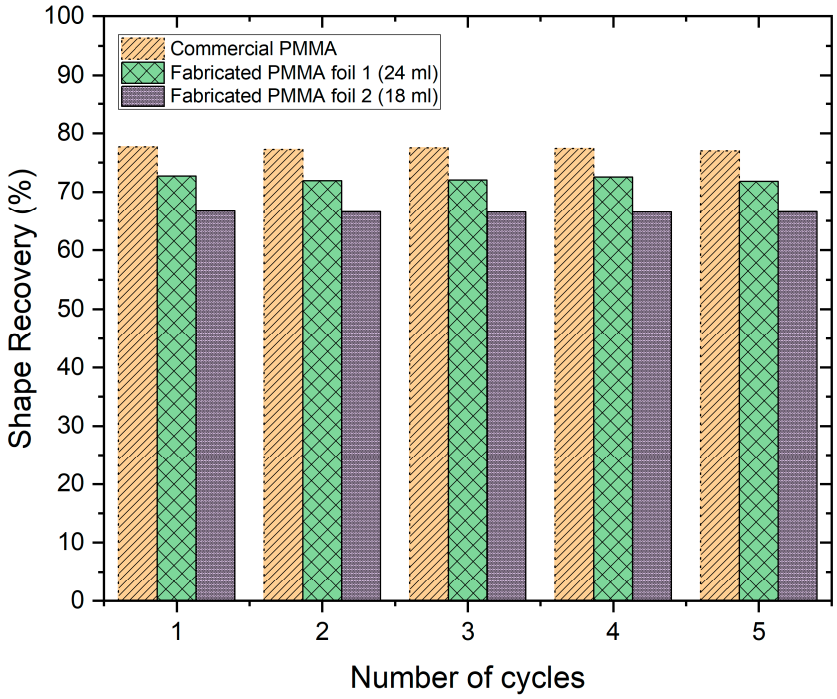


Figure 9. Shape recovery (%) for commercial PMMA, fabricated 1 and 2 as the function of number cycles.

The results obtained by the PMMA foils show that glass transition temperature could easily be tuned by varying the concentration of the solvent. The transformation temperature of NiTi alloy and PMMA foil could easily integrate for the formation of the composite structure. The shape memory behavior of PMMA foil is achieved as a function of bending stiffness and heating cycles. This could lead to more compatible components in composite structures with NiTi foil. These composite structures could reflect the behaviors of bending and recovering in control of heating and cooling cycles. This structure will have application in the actuators field.

5. Conclusions

In this work, the effect of two different concentrations of solution of toluene as the ratio of (S/L) was used in the preparation of solution-casting PMMA foils. Characterization techniques such as DSC for the detection of the glass transition in the PMMA samples, microscopy to observe the surface images, a DMA test to measure mechanical properties, and FTIR spectroscopy for detecting structural changes were employed in combination. Both the thermal and mechanical properties of the as-prepared PMMA foils are strongly influenced by the solvents used for the preparation due to their polarity and capability of forming H bonds with the polymer. The reference sample of commercial PMMA was tested to compare the properties of as-prepared PMMA foils. In particular, the samples prepared with toluene as solvents show a glass transition temperature of 16–20 °C below the bulk commercial PMMA sample. Similarly, the prepared sample shows lower storage and loss modulus in comparison to bulk samples. The spectroscopic analysis provided a comprehensive analysis of structural changes in commercial and as-prepared PMMA samples with the response from the solute powder and solvents toluene. The polymer network structure arises from different hydrogen bonding with chain rigidity in the samples. The polymer chain distortion caused the weakening of the samples prepared from the toluene solution. This behavior is reflected in the tensile test of PMMA samples, as it shows a weaker response in comparison to bulk samples. However, a significant shape

memory effect is observed for the solution-cast PMMA films that matches quite well with the commercial sample. The solution cast method allows for tuning the glass transition temperature of polymer foil that could easily integrate with the NiTi alloy phase transition temperature for the fabrication of a suitable composite structure. Integrating both structures will open the flexibility in bistable actuators in composite structures as a function of thermal cycles.

Author Contributions: Conceptualization, S.S. and D.V.; methodology, B.S. and O.T.; formal analysis, B.S.; investigation, O.T. and M.S.; resources, O.T.; data curation, S.S.; writing—original draft preparation, S.S.; writing—review and editing, S.S.; supervision, S.S.; project administration, S.S.; funding acquisition, I.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data will be available at the request of readers.

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