TAILORING PROPERTIES OF SHAPE MEMORY POLYMERS USING CELLULOSE NANOCRYSTALS

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1 ABSTRACT

Shape memory polymers (SMP) are a type of smart materials that can recover their original/permanent shape after being deformed under specific conditions. The recovery process happens when a given triggering mechanism; such as heat, UV light, and moisture, is applied to the deformed shape. These materials are attractive for a broad range of applications, including micro-aerial vehicles and biomedical devices, due to their tailorability and ease of manufacturing. Important properties of consideration during the use of shape memory polymers are their activation temperature and mechanical / thermo-mechanical properties. These properties can be affected from environmental conditions, such as humidity. Additionally, they can also be tailored using additives. Consequently, it is crucial to document these effects prior to use SMP in different applications. The present work investigates moisture regulation and addition of Cellulose Nanocrystalls (CNC) as potential methods of tailorability for Shape Memory Polyurethane based polymers (SMPU).
Effects of moisture were investigated with reference to polymer absorption of water. A plasticizing effect was observed with respect to immersion time of the polymer in water. This result was found to translate into a significant decrease of the polymer's activation temperature. Effects of moisture also showed a decrease in the elastic moduli and significant decrease in the shape recovery properties. Additionally, effects of CNC as filler for SMPU were investigated. Percentages of 0, 1 and 4 wt.% of CNC were added to SMPU via melt-extrusion. The investigation shows that moisture has an impact on the activation temperature, mechanical, and shape recovery characteristics of the polymer, whereas addition of CNC improved flexural properties and shape recovery properties of the polymer. In combination these two mechanisms can shape SMPU's properties for future field applications.

2 INTRODUCTION

Shape memory materials are a type of smart materials that are able to recover their original/permanent shape after a stimulus is applied[1]. Change in temperature, UV-light exposure, pH, magnetic field and electric field are some of the typical stimuli that can be applied to obtain a shape recovery response[2]. Thermo-responsive shape memory materials are easy to program into a desired shape and can be tested in controlled laboratory conditions. A typical thermal-responsive shape memory cycle consists of a programming and a response phase. A programming procedure takes place by 1) raising the temperature above the transition temperature of the material, 2) application of a strain and 3) cooling of the material while holding the applied strain. The response phase, also called activation of the Shape Memory Effect (SME), occurs when the material is subjected to a temperature above its transition temperature to recover the original/permanent shape [2].

Among shape memory materials, Shape Memory Polymers (SMP) have shown to have promising applications in the engineering and biomedical field such as optical systems, coatings, self assembly mechanisms, tissue engineering, biosensors, and the like [3]-[6]. Thermoplastic SMP are preferred over thermosets because of their ease of manufacturing [7], ability to recycle, lower cost, and tailorability of their mechanical properties by particle addition. Thermoplastic Shape Memory Polymers Polyurethanes (SMPU), developed by Hayashi have

become commercially available in a variety of transition temperatures and have good recovery properties, making them optimal for real life applications[8]. However, many of the studied applications have been conducted in well controlled laboratory environments and have not considered real field conditions, such as uncontrolled humidity. SMPU have shown to be dramatically affected by absorbed ambient moisture, this is due to a plasticization effect of water on polyurethanes, which causes to decrease the activation temperature and their mechanical properties[9]-[11]. This plasticization effect limits the possible real life applicability of SMPU. Possible methods to counteract humidity effects on SMPU are addition of particle fillers to improve their mechanical and shape recovery characteristics.

Natural fibers and biomass products are naturally abundant in nature and could potentially be used as reinforcing materials for composite materials engineering. Cellulose nanocrystals (CNCs) are biomass fillers with high aspect ratios (diameters of ~5 to 50 nm and lengths of 100 to 200nm) and mechanical properties, making them appealing to be use as reinforcing agents for common polymeric matrices [12]-[15]. CNCs have been reported to counteract plasticization effects in polymers [12], and maintain the recovery behavior of shape memory polymers while increasing their mechanical properties [16]-[18]. The present study looks upon the humidity effect on commercially available MM4520 SMP and addition of CNCs on the polymeric matrix via melt extrusion for future field applications.

3 MATERIALS, SAMPLE PREPARATION AND METHODS

3.1 Materials

Shape memory polyurethane thermoplastic was used for the present study. The polymer MM4520 was purchased from SMP Technologies and has a proposed glass transition temperature of 45°C. Cellulose Nanocrystal (CNC) filler particles were supplied by Alberta Innovated Technology Futures (AITF), Edmonton, AB, Canada. Prior to sample preparation, SMPU and CNC were dried for 12 hours to avoid bubble formation within the extruded ribbons.

3.2 Sample preparation and methods

SMPU ribbons and SMPU/CNC ribbon nanocomposites were prepared using a melt extruder HAAKE™ MiniLab Rheomex CTW5. This extruder is composed of a conical twin screw extruder with screw lengths of 109.5 mm and conical diameters of 5 and 14 mm. Tests ribbons were manufactured using a die with dimensions of 4 mm by 0.5 mm. Material was fed to keep a constant shear rate of 70N-cm. Extrusion parameters were set to 195 °C and 50rpm. Extruded material was pulled at a constant velocity using a Dynisco™ LME take-up system.

SMPU/CNC nanocomposites were prepared by mixing 0, 2 and 4 wt.% of CNC to SMPU pellets and melt extruding them immediately after. To analyze the effect of moisture on SMPU, ribbons were submerged in distilled water (assuming 100% of moisture) for different periods of time. All samples were vacuum oven dried at 50°C for 12 hours prior to testing or water immersing.

4 Characterization

Characterization and testing was performed in two sections: 1) on dried SMPU, and moisture affected SMPU and 2) on dried SMPU/nanocomposites.

4.1 Thermogravimetric Analysis (TGA)

TGA analyses were conducted using a Q50 Thermogravimetry analyzer from TA instruments. Samples weighting 10-15 mg were heated from 25°C to 400°C with a heating rate of 10 °C/min.

4.2 Differential Scanning Calorimetry (DSC) analysis

DSC analyses were performed on samples weighting 2-5 mg using a DSC Q1000 (TA instruments). Samples were tested within a temperature range of -40°C to 260°C at a heating rate of 20°C/min.

4.3 Mechanical testing

Mechanical testing was carried out using an Electroforce® 3200 Series by TA instruments ™. The device was accommodated with appropriate test jigs to perform tensile and bending tests.

4.3.1 Tensile tests

A gage length of 5 mm was used, having sample gripping-lengths of 10 mm at each side. The specimens were stretched using a rate 0.02mm/s to 100% in strain.

4.3.2 Flexural Tests

"Plastics determination of flexural properties" code (ISO178:2010) [19] was considered to determine a suitable flexural testing procedure. The three point bending supports used in the testing procedure had dimensions of 2.5 mm in radius for the loading edge and fixation points. The specimen's span length to thickness ratio was set at 40 due to machine limitations and to avoid shear stress influence during testing [20]. Therefore sample testing dimensions were set to 20 mm in span length for specimens with cross section of 4x0.5mm. The testing speed selected at which the vertical force was lowered was 0.01mm/s for all specimen testing.

4.4 Shape recovery testing

4.4.1 Shape programming

Shape programming was done using Electroforce® 3200 Series by TA instruments ™ accommodated with a forced convection oven. Shape programming procedure was carried out by: 1) raising the temperature above 50°C (Tg + 5°C) for 3 minutes, 2) stretching the sample to 100% strain at a rate of 0.2mm/s and 3) cooling the sample to 15°C to prevent immediate room temperature activation.

4.4.2 Shape activation

Shape recovery was done using a controlled triggering temperature of 70°C (Tg +25). Additionally a load of ~0.2N was applied at the free end to enforce plane movement. Samples were placed inside a Lindberg/Blue M™ vacuum oven, and the motion of the sample was recorded immediately during a time period of 5 minutes.

5 HUMIDITY STUDY

5.1 Moisture absorption

Field applications require the study of shape memory polymers under different moisture affected conditions. The behavior of MM4520 was studied under the assumption of 100% environment humidity by immersing the SMP samples in distilled water for different periods of time. Figure 1 shows the decrease in weight percentage from immersed water samples after 48 and 112 hours. From Figure 1, water absorption of the polymer can be seen to increase dramatically just within the 48 hour period. The vertical dotted line at approximately 240°C shows the temperature limit at which weight percentage loss by the samples stabilizes before the degradation temperature (Td). Degradation temperature of approximately 300°C is not altered as the polymer absorb different amounts of moisture.

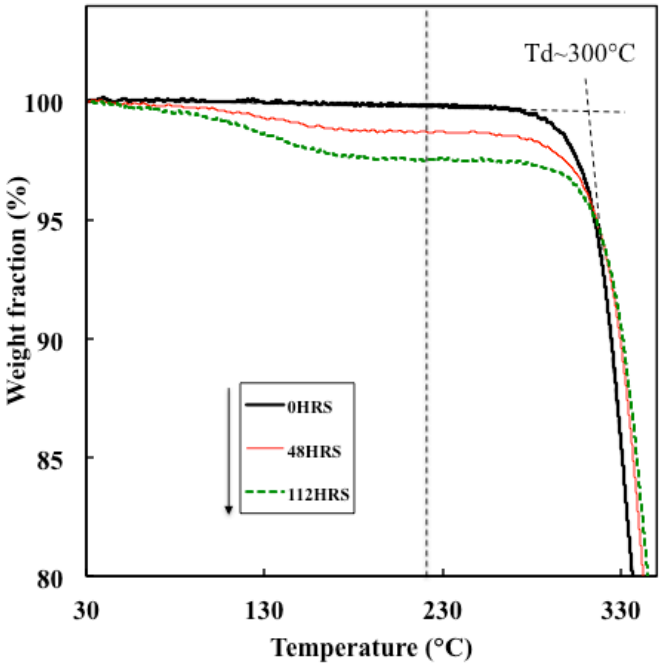


Figure 1. TGA curves of MM4520 under different periods of water immersion.

Although in Figure1 the degradation temperatures do not change by water immersion, studies have revealed that water absorption can produce bounded water and free water in polyurethane based shape memory polymers [21]. Studies have also shown that moisture adsorption by the polymers can cause hydrogen bonding with urethane and ether groups which alters many of the polymer's characteristics [9]. While free water does not affect the behavior of the polymer, bounded water has shown to affect shape recovery percentage, fixity and glass transition temperature of the polymer by means of plasticization of the polymer [10].

5.2 Plasticization

5.2.1 Glass transition temperature alteration

A plasticization effect due to bonded water has been shown to occur in thermoplastic-based polyurethane shape memory polymers [10]. A plasticization effect lowers the glass transition temperature of the polymer, therefore decreasing the activation temperature of a shape memory polymer [22]. Figure 2 shows experimental data of glass transition temperature (Tg) with respect to dried Tg MM4520 (~44.5°C). Glass transition temperatures were obtained from DSC experimental data. Figure 2 shows that Tg of MM4520 lowers drastically within the first 5 hours of water immersion and stabilizes after 50 hours of immersion, suggesting that a plasticizing effect is present in MM4520 shape memory polymer. Glass transition temperature is the most important parameter for shape memory polymers activation, shape recovery and shape fixity, as it is the transition temperature at which the temporary shape is stored. Prediction of glass transition with respect to hours of immersion in 100% moisture, can allow for a future fine-tuning mechanism for glass transition temperature. For a material exposed to field environmental conditions, prediction of the glass transition temperature can allow for a correction of temperature activation with respect to polymer moisture exposure, this can guarantee a predicted on-field performance of the polymer.

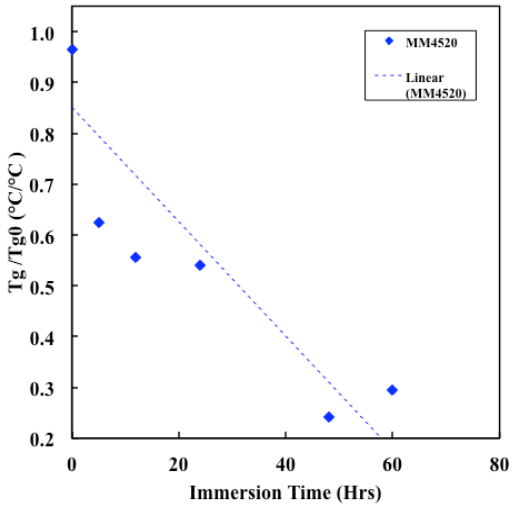


Figure 2. TGA curves of MM4520 under different periods of water immersion.

5.2.2 Mechanical properties alteration

The ISO 527-1, "Determination of tensile properties", [19], was used to calculate elastic moduli of dry and water immersed SMP ribbons. Figure 3 outlines the results of the elastic modulus with respect to immersion time in water of ribbons. A clear decrease in moduli is seen in Figure 3, which stabilizes after 20 hours of immersion time in water.

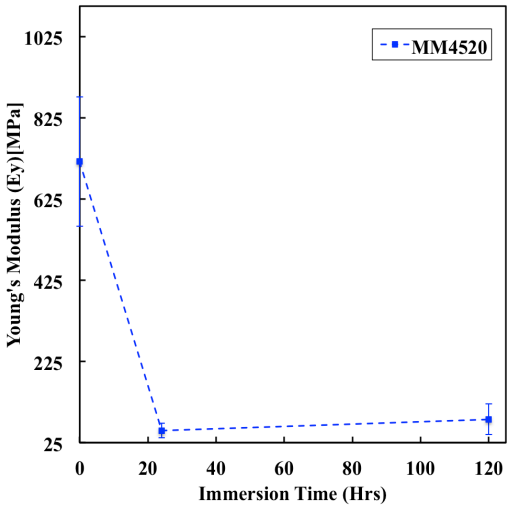


Figure 3. TGA curves of MM4520 under different periods of water immersion.

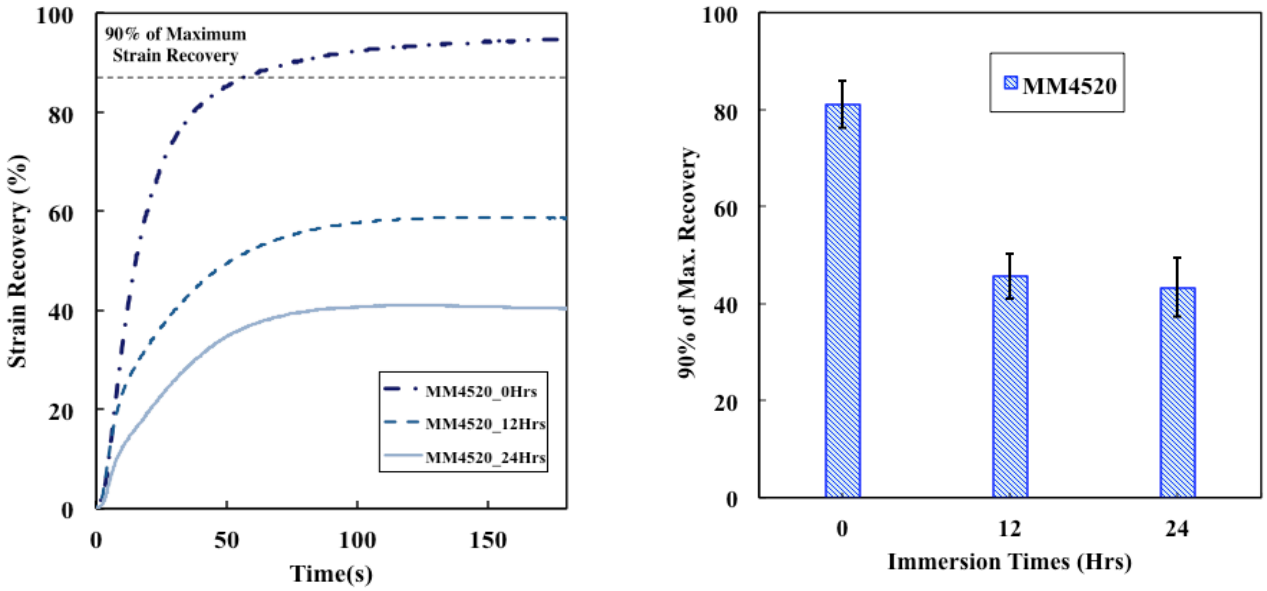
5.2.3 Shape recovery alteration

Shape recovery percentage, R_r, was obtained from images after the sample was activated at T+25°C. Using Equation1 (Eq.1), recovery percentage was calculated, where the measured recovered strain is (ε_r) and the prescribed strain is (ε_p), in our case 100% (Eq.1). Figure 4.a shows the recovery percentage curves with respect to time evolution for 0, 12 and 24 hours of immersed water samples. The total recovery strain was determined at

90% of the maximum recovery strain plateau observed in Figure 4.a as a dotted line. A decrease in the recovery percentage can be seen as immersion time in water increases.

$$\mathbf{R_r} = (\varepsilon_p - \varepsilon_r)/\varepsilon_p \qquad \text{Eq. 1}$$

Figure 4.b shows the decrease of maximum recovery percentage with respect to immersion time in water and one standard deviation at each side. Decrease in the glass transition temperature causes the polymer to be subjected to a greater temperature gradient from its glass transition temperature, producing a relaxation of the polymeric chains before they are able to recover their shape completely.



(a) (b)

Figure 4. (a) Sample representation curves of strain recovery% evolving with time for 0, 12,24hours of water-immersed samples. (b) Decrease of recovery rate with respect to immersion time in water

6 COMPOSITE TAILORING

6.1 Mechanical properties

6.1.1 Tensile properties

Figure 5 shows the Elastic moduli of dried SMP MM4520/CNC nanocomposite at different CNC weight percentage contents. Elastic moduli was calculated with respect to ISO 527-1 "Determination of tensile properties" [19]. An experimental average for the young's modulus of ~720MPa was obtained for polymer MM4520. A one-way ANOVA was conducted to evaluate whether addition of CNC has a significant effect on the elastic modulus of SMPU MM4520. A p-value= 0.3732>0.05, showed that the addition of CNC 2 and 4 wt.% did not have a significant effect on the elastic modulus.

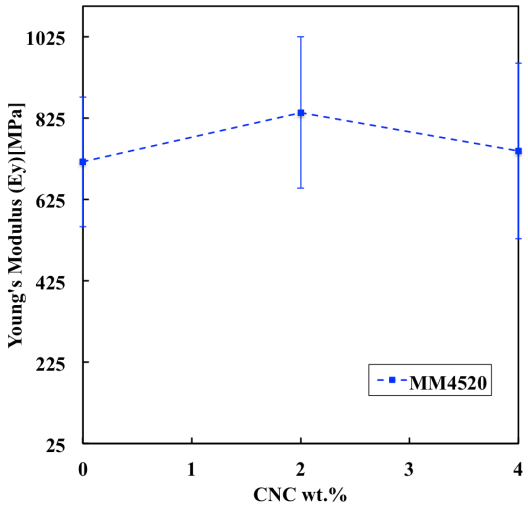


Figure 5. Elastic Modulus with respect to CNC wt.% added

6.1.2 Bending properties

Although elastic modulus was not statistically affected by CNC, a bending tests showed that the flexural moduli of SMP/CNC nanocomposite changed with different CNC weight percentage content. Flexural Moduli was determined using ISO178: 2001, [19]. A one-way ANOVA resulted in a p-value= 2.0630e-05>0.05, showing that the addition of CNC did have a statistically significant effect on the flexural modulus. Increase in flexural modulus reaches its peak with the addition of 2 wt.% CNC. Figure 6 shows the increase of flexural moduli from pure SMP with average moduli of 1185.2 MPa to 2281 MPa, this transforms into an average increase of 92% in flexural modulus.

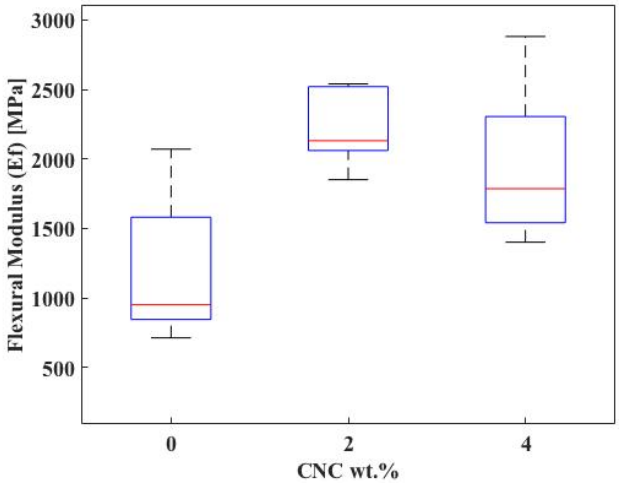


Figure 6. SMP MM4520 Flexural Modulus with respect to CNC wt.%

6.1.3 Shape recovery properties

Shape recovery properties were also analyzed for the extreme cases 0 and 4wt.% CNC. Figure 7.a shows two representative curves of strain recovery percentage with respect to time for pure MM4520 and 4wt.% of CNC in MM4520. Although recovery percentage, taken at 90% on the maximum recovery (As seen by the

dotted line of Figure 7.a), decreased with CNC addition from ~81% to 73% (Figure 7.b), a significant increase was shown in the rate of recovery with the addition of CNC.

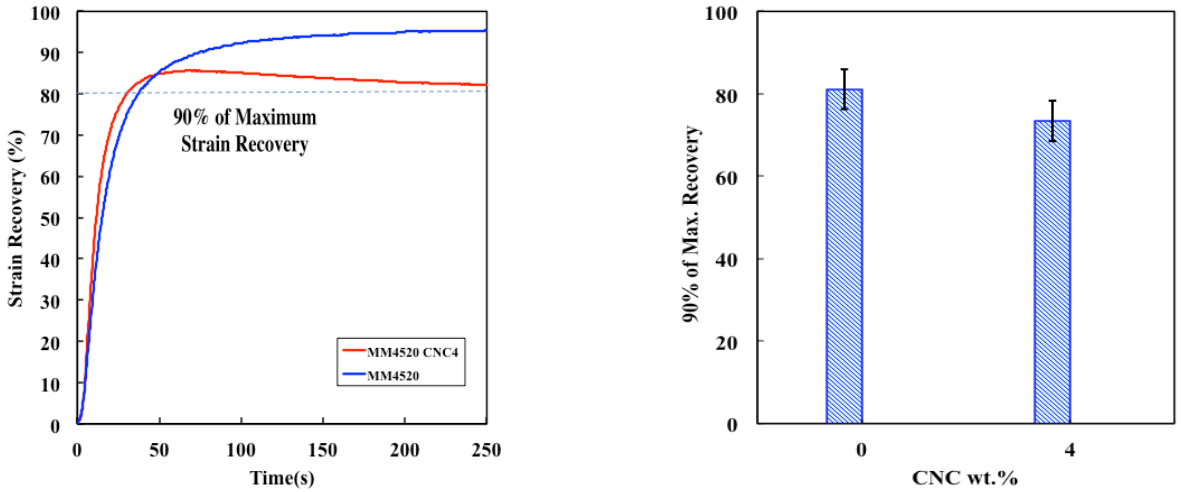


Figure 7. Effect of CNC on the shape recovery properties of SMP MM4520

Figure 8 shows the recovery rate of samples with 0 and 4 wt.% of CNC for SMP MM4520. A one-way ANOVA was conducted and a p-value=0.0213<0.05 was obtained from the analysis. This showed that addition of CNC is significant in the alteration of the recovery rate by 11.2%.

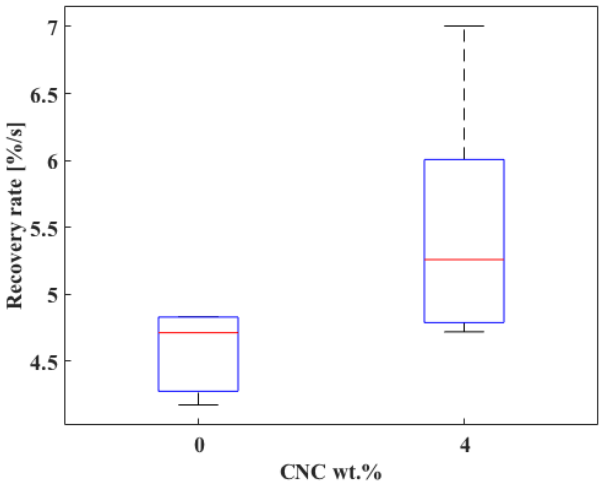


Figure 8. Effect of CNC on the shape recovery rate %/s with addition of CNC wt.%

7 CONCLUSIONS

In this study, a commercially available SMPU (MM4520 SMP)was investigated to determine the influence of moisture (water immersion) on its mechanical and shape memory effect properties. It was found that humidity produces a plasticization effect in MM4520 SMP causing the decrease of its glass transition temperature, mechanical properties, and shape recovery capabilities. Glass transition temperature of the polymer found to decrease to 10% of its original value until stabilizing after 48 hours of immersion in water. Its elastic modulus decreased to 90% of its average elastic modulus, stabilizing after approximately 24 hours.

CNC was added at of 2 and 4 wt.%. Tensile, flexural and shape recovery characteristics were studied with respect to the addition of CNC particles to MM4520 SMPU. The study found no statistically significant effect of the CNC particles on the elastic modulus of the material; however, a significant improvement of the flexural modulus and shape recovery characteristics was found. Flexural modulus increased by ~90% and the recovery rate ratio increased by ~10%. These effects can be beneficial to counteract undesirable humidity effects of MM4520.

Future work will focus on the effect of CNC with respect to effects of immersion in water. Possible effects on the glass transition temperature, mechanical properties and water absorption should be studied. Future work on the effects of CNC on moisture effects of SMP is needed to validate CNC as possible SMP filler in which material tailoring could contribute to eventual field applications of shape memory polymers.

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