Synthesis and Characterization of Shape Memory Polymers

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Abstract: Shape memory polymers (SMPs) have gained a lot of importance in essential and basic research to modern and common applications since they have risen as a practical and proficient other option to understood metallic shape-memory composites. Among them, shape memory polymers claim assorted applications, for example, aviation, vehicles, biomedical, apply autonomy, sensors and actuators because of adaptability in union with various kinds of atomic plans by changing their synthesis and characterization methods. In this paper, the blend and portrayal of shape memory polyurethanes, in light of two-advance polymerization, is clarified. The hard portion of SMPU was made out of disiocyanate and a chain extender. Further, the delicate fragment was set up by polyols with various molecular weights. Contingent upon the structure of the integrated polyurethanes, the materials introduced diverse properties. Portrayal was performed by methods for TEM and X-Ray diffractogram (XRD). Moreover, mechanical properties and shape memory impact were additionally controlled by shape recovery test and Dynamic Mechanical Analysis (DMA).

Keywords: Shape memory polymers, X-Ray diffractogram, Dynamic Mechanical Analysis, Shape Memory Effect.

Introduction

Shape memory polymers (SMP's) display the ability of changing their shape in a predefined conduct because of external stimuli like temperature [1]. A twisting actuated brief shape is changed to a preparatory harmony setup characterized by the substance or physical crosslinkings inside the polymer [2]. Till today, shape memory impact in polymers is activated by light, temperature, electrical and magnetic stimuli [3]. Frequently, shape memory technique includes, two unique stages understood as "programming" and "recovery". All through the programming, the material is disfigured more than the
softening temperature, where the conformational entropy of the material is lessened [4]. Hence the material is cooled to temperatures not as much as the segmental changeover under compelled conditions to accomplish the "brief shape" due to the consolidated sub-atomic developments at temperatures lower than progress temperature [5]. Finally, the material recovers its essential changeless "permanent shape" upon the utilization of the outer boost which triggers the shape memory impact (Figure 1). Contingent upon their microstructure and compound nature various classes of SMPs may be found. Among all the current kinds of materials demonstrating a shape-memory impact, shape memory polymers have indicated fitting physico-mechanical properties to be utilized as a part of uses as shifted as stents, microactuators and materials [6]. Across the world broad work has been committed in creating SMP's, slight intrigue has been paid in seeing how the chain microstructure influences the shape-memory execution and mechanical properties of the subsequent material [7]. In this structure, this work manages the blend and portrayal of 4,4’-diphenylmethane diisocyanate (MDI) based SMP's. Progress temperatures have been controlled by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Thermomechanical programming tests were done to assess the shape-memory impact of created materials [8].

Fig:1. Schematic representation of the mechanism of the shape memory effect

2. Materials and Methods

2.1 Materials:
The materials utilized in this work were obtained from sigma-aldrich. The polymers utilized here is Polyethylene glycol (Mw~6,000), which is likewise called as delicate section, Diisocyanates employed are 4,4’-diphenylmethane diisocyanate (MDI), Isophorone diisocyanate (IPDI) which are additionally termed as hard fragments, were refrigerated before utilize, dimethylformamide (DMF) as a dissolvable solvent, Polyethylene glycol (Mw~200), as a crosslinking specialist, 1, 4-butandiol (BDO) as a chain extender, dibutyltin dilaurate as an impetus and CNT as a filler.

2.2 Method of preparation
The procedure for synthesis is as below. The arrangement included a 250 mL round base two-neck carafe, a hot plate oil shower with a temperature regulator and an stirrer placed on top. The flask was expelled with a predictable stream of dry nitrogen and the temperature of the blend was monitored by a thermometer. A deliberate quantity of CNT is included into flask alongside dimethylformamide (DMF) and sonicated for 1hr, after that it is blended with PEG-6000, IPDI and two drops of dibutyltin
dilaurate impetus and allowed to mix for two hrs at 90°C. Following two hours of response PEG-200 and MDI the blend was responded for an extra hour with reliable mixing. The methodology was closed by including BDO, as a chain extender for the concoction response at 60°C for an extra hour. The SMP specimens were placed on glass slabs. At that point the samples were prepared at 60°C for 12h, 80°C for 24h and 100°C for 8h, individually, in a oven [9]. The compound creation of Soft portion, Hard fragment were recorded in table 1.

**Table 1**: Display chemical configurations of SMPs prepared.

| Sample Identity | Soft segment (wt%) | Hard Segment (wt%) | CNT (Wt%) |
|-----------------|--------------------|--------------------|-----------|
| SMP-1           | 49                 | 33                 | 0.1       |
| SMP-2           | 50                 | 34                 | 0.2       |
| SMP-3           | 51                 | 35                 | 0.3       |
| SMP-4           | 52                 | 36                 | 0.4       |
| SMP-5           | 53                 | 37                 | 0.5       |

3. Results and Discussions

3.1 Shape Memory Test

Shape recovery is a more significant property of shape memory polymers, which suggests to the ideal opportunity for a twisted SMP test to recover their unique shape. The recovery times for SMP's are in the scope of around one moment to more than one hundred minutes, any lengthier than those of shape memory polymers [10]. For instance, SMP's with lifted speed and low Tg have unrivaled possibilities for therapeutic applications, for example, sedate conveyance frameworks, stents and smaller scale surgery devices or sutures [11]. In this work, the shape recovery tests were achieved to contemplate the recuperation execution and recovery speed of the SMP's. The examples with a thickness of 0.5 mm, a width of 3 mm and a length of ~70 mm, were utilized for the tests with one example as shown in Figure 2.

![Fig: 2 Shape memory behavior of SMP showing 100% Shape recovery.](image)

3.2 XRD analysis

The distinctive diffraction curves in Figure 3 demonstrate the number of important peaks and the intensity of the peaks. As depicted in Figure 3, the PEG sample series are crystalline peaks around, alike to those detected in the pure PEG polymer with a few swings to high angle due to stress, once the hard segments were added. XRD was used to examine crystalline structures of the polymers. D8 Discover X-ray diffractometer furnished with Cu Kα radiation of a wave length of 1.542 Å was used to inspect the crystalline structures of the SMPUs, with a scanning angle 2θ between 5 to 40°.
KeV and 35 mA. Though increase in IPDI content slowly increases the diffraction intensities for all peaks, 20°, 25° and 28° representing that the crystallinity of the polymers enhances with IPDI content, in concurrence with the examination by Yang et al [12] linear shape IPDI appears to have some benefit over bent-shaped MDI in receiving more crystalline structure when they stacked in polymeric chains.

Fig: 3. Diffraction curves of the PEG based SMP filled with CNT.

3.3 Tensile Test
The pliable bends of the PEG/CNT mixes are portrayed in Figure 4. A diagram of the different mechanical properties of these materials are appeared in Table 2. As a rule, the sturdiness and percent augmentation of the PEG/CNT mixes expanded with expanding CNT creation and a definitive elasticity expanded with expanding CNT [13]. This advancement was foreseen since unadulterated PEG and CNT have the advantage of being intense and solid, separately. The 50/50 PEG/CNT SMP mix had a triple abatement in yield quality and Young's modulus, however at the comparative time, showed a more prominent than overlay increment in toughness. It is entrancing to make a note of that an expansion in rigidity and sturdiness were seen in the 65/35 and 80/20 PEG/CNT SMP mixes at the comparative time.

Fig: 4. Stress/strain tests for PEG/CNT SMP’s at room temperature.
Table 2: Showing the results of tensile test

| Sample | Ultimate Tensile strength (Mpa) | Young’s modulus (Mpa) | Percent elongation to break |
|--------|-------------------------------|-----------------------|---------------------------|
| SMP-3  | 5.181                         | 0.32                  | 692.55                    |
| SMP-4  | 2.158                         | 1.26                  | 315.23                    |
| SMP-5  | 0.229                         | 5.825                 | 0.373                     |

3.4 Dynamic Mechanical Analysis
The capacity modulus of a PEG/CNT SMP measures the put away vitality in the viscoelastic state, speaking to the flexible bit of the material. This information could be utilized to decide the shape recovery under an assortment of stacking conditions. Here, the dynamic mechanical properties were tried on a DMA at 200°C and the capacity moduli of the SMP’s as a component of temperature were acquired. All examples were tried in a three-point twisting mode with an enduring warming rate of 10°C for each min. The examining temperature extended from 20 to 120°C and the wavering recurrence was 1 Hz [14]. Furthermore, the material extend limit and warm properties will be influenced in the meantime. As appeared in Figure. 5, where the capacity modulus is recorded against the temperature, in a temperature of 20°C, the capacity modulus of the PEG/CNT SMP’s expanded remarkably with the expansion of CNTs [15].

Table 3: Showing DMA results.

| Freq. (Hz) | Temp. (°C) | E'(G) Pa | E''(G) Pa | dLum | tanD | Ft Mn | Time (min) |
|------------|------------|----------|-----------|-------|------|------|------------|
| 5          | 32.1641    | 3.73E+09 | 5.65E+08  | -135.416 | 0.151542 | 1892.057 | 0.133333   |
| 2          | 32.1661    | 3.41E+09 | 5.39E+08  | -134.027 | 0.157864 | 1892.057 | 0.283333   |
| 1          | 32.1760    | 3.19E+09 | 5.22E+08  | -131.249 | 0.163712 | 1892.057 | 0.466667   |
| 0.5        | 32.1804    | 2.97E+09 | 4.99E+08  | -129.86  | 0.168215 | 1892.057 | 0.683333   |
| 0.2        | 32.2257    | 2.69E+09 | 4.72E+08  | -129.166 | 0.175571 | 1892.057 | 1.1         |

Fig: 5 Amplitude sweep test at different temperatures: variation of the storage and loss shear moduli with strain amplitude.
4. Conclusion
A progression of shape memory polymers of PEG/CNT with different wt% of filler substance up to 1wt% have been synthesised, and their far reaching properties have been efficiently explored. The arranged SMP materials demonstrated an extensive variety of exchanging temperature 30–80°C, high E’ at room temperature up to 5.0 MPa, high twisting capacity over 10% at a high temperature near the Tg, high recovery rate up to 30 MPa, and quick response time at 20s. It was additionally discovered that a little measure of CNT fillers (0.75 wt%) could essentially expand every one of the three significant mechanical properties (E, σm, and εb) at high temperature near the Tg, recovery rate, and the cyclic mechanical properties. The outcomes have exhibited the properties of SMP material can be additionally enhanced by well controlling the substance structure and microstructure of the framework.

References

[1] Miriam Sáenz-Pérez1, José Manuel Laza, Jorge García-Barrasa, Luis Manuel León and José Luis Vilas “Synthesis and Characterization of Shape Memory Polyurethanes” Mol2Net, 2015, 1(Section C), pages 1-8, Proceedings.
[2] Yen F., Lin L., Hong J. (1999). Hydrogen bond interactions between urethane-urethane and urethane-ester linkages in a liquid crystalline poly (ester-urethane), Macromolecules, 32(3), pp.3068-3079.
[3] Ferrillo R.G.; Achorn P.J., (1996), “Comparison of thermal techniques for glass transition assignment. II. Commercial polymers”, Journal of Applied Polymer Science, 64(1), pp.191-195.
[4] Li S., (1999), “Hydrolytic degradation characteristics of aliphatic polyesters derived from lactic and glycolic acids”, Journal of Biomedical Materials Research Part B: Applied Biomaterials, 48(3), pp.342-353.
[5] Uan-Zo-Li, Julie Tammy. “The effects of structure, humidity and aging on the mechanical properties of polymeric ionomers for fuel cell applications.” MS thesis. Virginia tech, 2001. Print.
[6] Buhler W.J., Gilfrich J.W., Wiley R.C. (1963), “Effect of low temperature phase changes on the mechanical properties of alloys near composition TiNi”, J. Appl.Phys., 34(5), pp.1475-1476.
[7] Chang L.C., ReadT.A., (1951), “Plastic deformation and diffusionless phase changes in etals. The Gold-Cadmium Beta Phase”, Trans. AIME, 189, pp.47-52.
[8] Chaterji S., Kwon IK, Park K. (2007), “Smart polymeric gels: redefining the limits of biomedical devices”, Prog. Polym.Sci., 32(8-9), pp.1083-1122.
[9] Dietz B., Tong T. (2007), “A review: features and benefits of shape memory polymers (SMPs)”, J. Adv. Mater., 39, pp.3-12.
[10] U.S. Mallik, V. Sampath, “Effect of composition and ageing on damping characteristics of Cu-Al-Mn shape memory alloys” Materials Science and Engineering A 478 (2008) 48-55.
[11] V. Sampath and U.S. Mallik, “Influence of minor additions of boron and zirconium on shape memory properties and grain refinement of a Cu-Al-Mn shape memory alloy” ESOMAT 2009, 05028 (2009) DOI:10.1051/esomat/200905028.
[12] Finklemann H., Nishikawa E., Pereira G.G., Werner M. (2001), “A new opto-mechanical effect in solids”, Phys. Rev. Lett., 87(1), pp.15501-15505.
[13] Gall K., Yakacki C. M., Liu Y. P., Shandas R., Willett N., Anseth K. S., (2005), “Thermomechanics of the shape memory effect in polymers for biomedical applications”, J. Biomed.Mater. Res. Part A, 73(A3), pp.339-348.
[14] Mondal S., Hu J. L. (2007), “Shape memory study of thermoplastic segmented polyurethane: influence of hard segment”, Polymer-Plastics Tech. and Engg., 46(10), pp.939-942.
[15] Lendlein A., Jiang H., Junger O., Langer R., (2005), “Light induced shape memory polymers”, Nature, 434(7035), pp.879-881.