Exploration of Shape Memory Polymer for Automotive Coating Applications

Ming Wang

Institute of Research for Technology Development of University of Kentucky, College of Chemical and Materials Engineering, 117 F. Paul Anderson Tower, Lexington, KY 40506

Abstract

Shape memory polymer (SMP) is one special kind of polymer which can recover back to permanent shape after being mechanically deformed. As for automotive coating, most of the defects occurs on the clear coat layer, if it can be replaced by shape memory polymer, the defects can be easily removed due to the self-healing ability of shape memory polymer. In this experiment, the self-healing ability of epoxy based shape memory polymer thin film (around 100μm) is examined. Five indents on the thin film shape memory polymer with depths from 4.9μm to 5.5μm are all disappeared after 15 minutes heating at 70°C. The average hardness of the polymer is 165 ± 2MPa and the modulus is 5.76 ± 0.02GPa (assume Possion's ratio 0.4).

Keywords: Epoxy, shape memory polymer, automotive coating,

1. Introduction

Shape memory polymer is one class of the smart materials.[1] Shape memory polymer, typically has two different phases: the permanent phase (frozen phase) and temporary phase (reversible phase). The cause of the recoverability of shape memory polymer is based on the change of properties of the cross lined polymer chains. When the shape memory polymer is deformed by mechanical deformation and fixation of that deformation, the polymer will stay in the deformed phase, which is so called temporary phase. Once the deformed polymer is exposed to an appropriate external stimulus, the polymer recovers back to the permanent phase. Such deforming-recovering cycle can be repeated for several times.[2]

1.1 Thermalset Epoxy Shape Memory Polymer

The shape memory polymer used in this experiment is an epoxy shape memory polymer. This polymer's recover ability can be triggered through thermal stimulus. The recoverability is based in the change in material properties above and below the glass transition temperature, T_g. At temperature above T_g, the polymer is in a rubbery state and the polymer chains have a high number of available configurations. When external mechanical deformation is applied, the spatial change will limit chains' mobility and decrease the entropic energy. To create the shape of permanent phase, the polymer needs to be heated above T_g and an external mechanical load applied. With the load still applied, cool down the temperature to below T_g. Once the temperature is below T_g, the polymer will change from a rubbery state to a glassy state (temporary phase) and the available configurations are significantly decreased. When the temperature is above T_g again, the entropic energy increases and the polymer can recover its original set shape.

The chemical compositions of this epoxy based shape memory polymer are EPON 826, Jeffamine D-230 and NGDE. During the curing process, the EPON 826 chains will cross link with Jeffamine D-230, therefore creating cross-linked points. As the glass transition temperature is closely related to chains mobility and the chains mobility is related to the flexibility. By replacing EPON 826 with NGED, a flexible aliphatic diepoxide with lower epoxy equivalent weight (108) than EPON 826 (approximately equal to 180), the crosslink density and flexibility of the polymer will increase. Therefore, the glass temperature of shape memory polymer will decrease. Based on Tao Xie's previous paper, when the molar ratio of EPON 826 and NGDE is 3:1, the glass transition temperature should be around 70°C.[2]

1.2 How may epoxy polymer be applied to automotive coating

In automotive industries, a coating is applied on the automobile in order to both protect the substrate materials and improve the appearance.[3] Typically, automotive coating contains three layers: primer coat, base color coat and clear coat.[4] Typically, the thickness of clear coat is around 38μm

to 103μm[4] and most of shallow scratches such as the coating defects, swirl marking marring, random deep marring and buffer marks occur in the clear coat. So if the clear coat can be made by shape memory polymer, most of the shallow scratches can be removed due to the good recovery ability of shape memory polymer with external heating.

2. Procedure

2.1 Materials

The diglycidyl ether of bisphenol A (EPON 826) was obtained from Hexion, the poly(propylene glycol)bis(2-aminopropyl) ether curing agent (Jeffamine D-230) was obtained from Huntsman and the neopentyl glycol diglycidyl ether (NGDE) obtained from Aldrich Chemistry.

2.2 Fabrication of Shape Memory Polymer

The solid EPON 826 was heated up to 70°C until all solids turn to liquid. The EPON 826, Jeffamine D-230 and NGDE were added into a clear glass jar with molar ratio 1.5:1:0.5. The mixture was shaken by hand for few seconds until the interface between EPON and other two liquid polymers disappeared.

The glass jar was placed in a vacuum oven at 70°C for 10 minutes. One piece of Teflon (101μm thickness) was cut into a half box bracket shape, as shown in Figure 1, and placed on a clear glass slide as a spacer. The polymer mixture was then poured on to the glass slide. The polymer was then casted into film by a film caster.

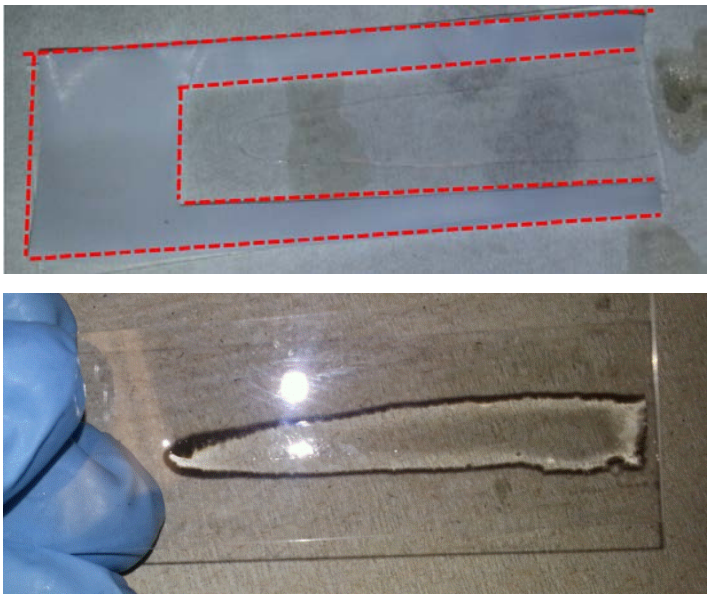


Figure 1: Shape memory polymer fabrication. (a) The polymer casted on glass slide. Note the red dash line indicates the shape of Teflon spacer. (b) Polymer after curing and post-curing.

The casted polymer with glass slide was put into a oven at 100°C and cured for 1.5 hours and then post-cured at 130°C for 1 hour.

2.3 Nano indentation test and thermal self-healing examination

The post-cured sample was marked and fixed on a sample platform of an nano indenter (Agilent Technologies Nano Indenter G200). Five indents were applied on the sample surface around the mark with a 500 mN force. The sample with indents were heated at 60°C for 15 minutes after the depth of each indents was measured (Zygo surface profiler). After the heating, the depth of indents were measured by Zygo surface profiler again to get the change of indents' depth. As there was no change for 60°C heating, the sample was heated at 70°C for 15 minutes and the depth of each indents was measured again.

3. Results and Discussion

3.1 Self-healing examination

The depths of indents after nano indentation were measured as 4.9μm, 5.6μm, 4.9μm, 5.5μm and 5.1μm. Figure 2 shows the sample measuring for one indent. As there were some noise during the indents scanned, the lowest point of each indent scanning image was selected as the bottom of indent.

An example of the Zygo surface maps and optical microscope images are shown in Figure 3. From Figure 3 (a) and (d), the indents are very obvious from both methods. After 15 minutes heating at 60°C, as shown in Figure 3 (b) and (e), the sample indents seems to be narrower but the depths of indents had no change. After 15 minutes heating at 70°C, all three indents are not visible, as shown in Figure 3 (c) and (f). The samples were scanning by Zygo again and there was no indents found on the sample surface. All indents were removed due to the thermal self-healing ability of epoxy shape memory polymer.

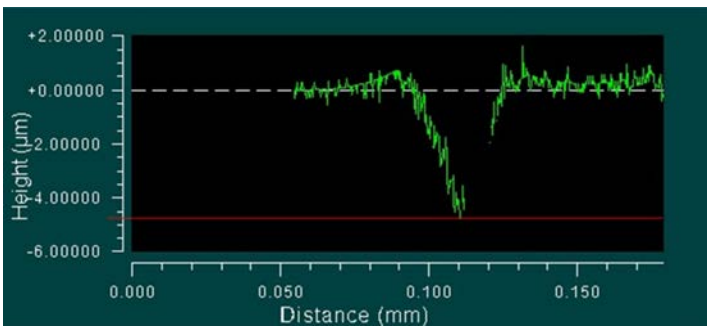


Figure 2: Example of indent depth measurement.

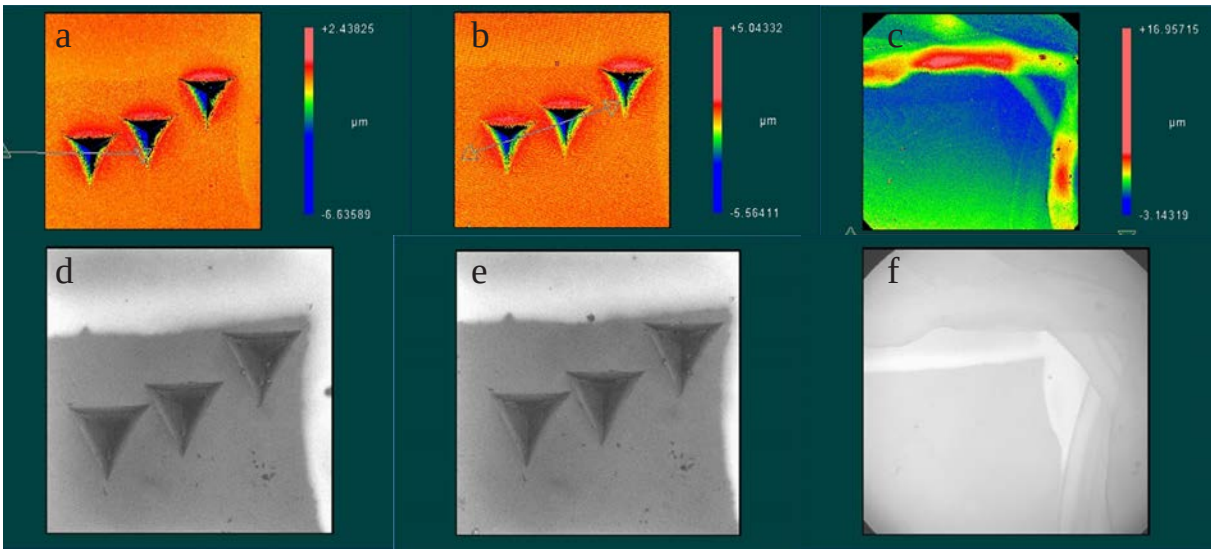


Figure 3: Surface mapping and optical microscope images for indents at room temperature, after 60°C and 70°C heating.

3.2 Nano Indentation data

The nano indentation testing data are shown in Figure 4. The indentation force was set to 50mN and the displacement was set to 10µm. The average hardness at max load obtained was 165±2MPa and the modulus at max load was 5.76±0.02GPa (as the Poisson's ratio of the polymer is unknown, the modulus is obtained by assuming the Possion's ratio as 0.4).

4. Conclusions

The self-healing of the shape memory polymer in thin film shape was examined. The five indents (depths from 4.9µm to 5.5µm) were not visible after 15 minutes heating at 70°C. The glass temperature T_g was measured to be around 70°C, which is consistent with Tao Xie's results.[2] The hardness of the thin film shape memory polymer was 165±2MPa and the modulus was 5.76±0.02GPa (assuming Possion's ratio 0.4).

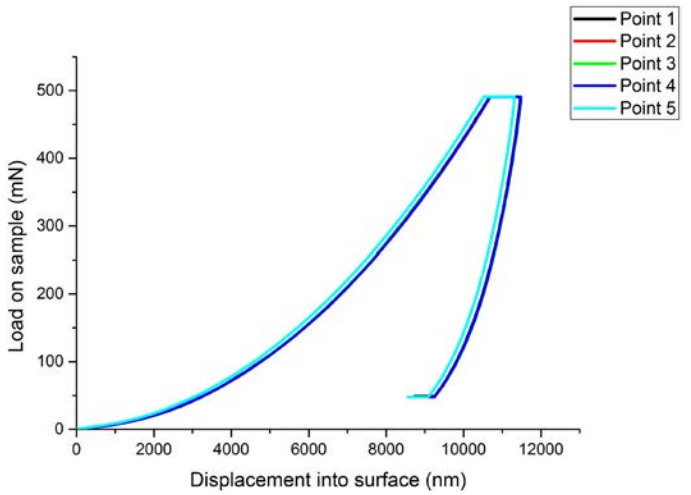


Figure 4: Loading force and displacement plot.

5. Future Work

In the automotive industries, the automobile is coated by the spray method. In the next step, the shape memory polymer should be tested whether it can be coated through spray method both in liquid or powdery shapes. Especially for the powdery shape, although the chemicals used are all liquids, but when the polymers are placed at room temperature for around 2 days after well mixing, the liquid polymer will turn to transparent solid. If the solid polymer can be ground into powder, then the polymer can be tested in spray method. But one issue is that, as the self-healing ability of this polymer is based on the cross link of chemical chains, we would like to know the relation between powder particle size and its self-healing ability and find the smallest possible size while maintaining self-healing ability maximum.

Acknowledgements

This paper is based on the papers of Tao Xie's team. This project is supported by Institute of Research for Technology Development of University of Kentucky and department of material engineering of University of Kentucky. The author would like to thank Professor Yang-Tse Cheng and Professor Douglass S. Kalika for guidance during experimentation.

Reference

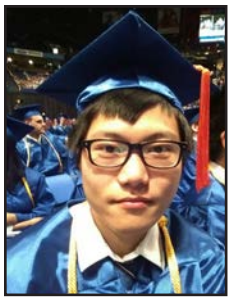
1. Xie, T.; Rodak, D. E.; Rodgers, W. R. Shape Memory Epoxy Polymers. U.S. Patent 8618238 B2, Dec 1, 2013.

2. Xie, T.; Rousseau, I. A. Journal of Materials Chemistry **2010**, 3431-3441.

3. Schmidt, C.; Neuking, K.; Eggeler, G. Advanced Engineering Materials **2008**, 10(10), 922-927.

4. Toda, K.; Salazar, A.; Saito, K. Automotive Painting Technology, Springer Netherlands, 2013.

About the Author



Ming Wang is a transfer student from China to University of Kentucky. He received his B.S. in Materials Science Engineering in University of Kentucky in this May. Before he transferred to University of Kentucky, his major in Qingdao University of Science and Technology (China) was Polymer Science Engineering.

Contact at: wangming1992@hotmail.com