INFLUENCE OF WATER EXPOSURE ON SCRATCH-INDUCED DEFORMATION IN POLYURETHANE ELASTOMERS

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Abstract

The scratch performance of a series of cast polyurethane elastomers (CPU) upon exposure to water is investigated. Four different kinds of CPU were chosen and their scratch performances were compared in dry and water-saturated conditions. The CPU model systems were synthesized containing the same isocyanate and chain extender, 4,4'-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BDO), to form the same type of hard segment, with four different soft segments (polylols): polytetramethylene ether glycol (PT), polycaprolactone (PC), ethylene oxide and propylene oxide based polyether polyol (PET) and adipic anhydride based polyester polyol (PES). Scratch tests were carried out according to the ASTM D7027/ISO 19252 standard. Results indicate the changes in scratch performance are closely correlated with the variations in coefficient of friction, tensile true stress-strain behavior as well as dynamic mechanical behavior of all the CPU model systems upon water exposure. Fundamental structure-property relationships of CPU affected by water content are discussed.

Introduction

Polymeric materials have been widely utilized in various engineering applications due to their low density and low cost compared to ceramic and metal counterparts. However, the susceptibility of polymers to scratch deformation makes them less desirable in many situations, especially upon environmental exposure, such as exposure to water. Numerous research efforts have been made to understand the effects of moisture absorption on the morphology and mechanical properties of epoxy-based polymer matrices [1-3]. And by using the recently developed ASTM D7027/ISO 19252 standardized scratch test [4], some studies have been successfully performed to understand the effects of water exposure on the scratch performance of polymers [5, 6]. Finite element methods (FEM) analyses of scratch process have also been performed to find the quantitative correlation between material and surface properties and the scratch behavior of polymers [7-9]. However, a set of model systems are still needed to carry out a series of systematic studies to understand how the changes in surface and mechanical properties of polymers upon water exposure fundamentally influence their scratch behaviors.

Polyurethane elastomer is one popular elastomer that has been broadly applied in many different applications. It is typically composed of hard segment and soft segment. By changing these chemical constituents, the mechanical properties as well as affinity to water of the system can be varied significantly. Thus, polyurethane elastomer is ideal for the fundamental scratch study in this case.

In the present study, the ASTM/ISO standardized scratch tests were performed on a series of model cast polyurethane elastomers (CPU) in both dry and water-saturated conditions to investigate the effect of water exposure on their scratch performance. Coefficient of friction measurement, quasi-static uniaxial tensile true stress-strain measurement as well as dynamic mechanical analysis (DMA) were conducted to gain fundamental understanding on the observed differences in scratch performance among the model systems upon exposure to water.

Experimental

The CPU model systems were provided by BASF Polyurethane Specialties (China) Co. Ltd. (Shanghai, China). The model systems were synthesized by four different kinds of polylols to form the soft segments, respectively: polytetramethylene ether glycol (PT), polycaprolactone (PC), ethylene oxide and propylene oxide based polyether polyol (PET) and adipic anhydride based polyester polyol (PES). However, all four model systems were synthesized by the same isocyanate and chain extender, 4,4'-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BDO), to form the same type of hard segment. Upon receipt, all the plaques were dried in a vacuum oven, then slowly cooled overnight to room temperature. After drying, the plaques were weighed and immersed in deionized water. The plaques were removed from the deionized water and weighed every week to check the amount of water uptake.

ASTM D7027/ISO 19252 standard scratch machine was used to measure the coefficient of friction (COF) between the model systems and stainless steel. A low
constant normal load was used to carry out the tests at speed of 100 mm/s. Three tests were performed on each model system to obtain an average COF.

Quasi-static uniaxial tensile true stress-strain measurements were carried out by using a custom-built tensile test fixture with Digital Image Correlation (DIC), which was prepared similar to what was described in the literature [10].

A TA Instruments ARES G2 Rheometer was utilized to conduct the dynamic mechanical analysis (DMA). The temperature investigated ranges from -135 °C to 180 °C with a temperature ramp of 3 °C/min.

Based on the ASTM D7027/ISO 19252 standard, scratch tests were performed by applying a linearly increasing normal load of 1-300 N. 100 mm/s scratch speed was utilized for the scratch tests. A 1 mm diameter stainless steel conical scratch tip was used for the tests. Three scratch tests were conducted on each model system for statistical purposes. The onset of cracking/material removal damage was observed and quantified by a Keyence® VK9700 violet laser scanning confocal microscope (VLSCM).

Results and Discussion

All the CPU plaques were placed in deionized water and removed weekly to check the amount of water uptake until saturation. Figure 1 shows the percent weight increase of the CPU model systems upon exposure to water as a function of conditioning time. As can be seen in the figure, all the CPU model systems reached water saturation within 3 weeks, as the percent weight increase remained stable at the end of the test. As expected, the incorporation of different soft segments resulted in varied affinity to water of the model systems, as the water saturation contents of the CPU model systems had great difference with each other.

Figure 2 shows the COF between the CPU model systems and stainless steel surface in dry and water-saturated conditions. Under both conditions, CPU-PET exhibits the highest COF among the four model systems, and CPU-PT shows the lowest COF. However, upon water saturation, only CPU-PC has a decrease in COF, the other systems show an increase. Since all the model systems have a different soft segment, different reactions may occur between the model systems and water. The increase in COF upon water exposure can be due to the water molecules diffuse in the polymer matrix and serve as a plasticizer to weaken the surface mechanical integrity. While, the decrease in COF upon water exposure can result from the formation of water clusters or layer on the surface that act as slip agent to reduce the COF [5].

Figure 3 shows the tensile strength of CPU model systems in dry and water-saturated conditions. As can be seen in the figure, all the model systems display different degrees of deterioration in tensile strength upon exposure to water, which can be due to the plasticization of polymer matrix results from the absorbed water. Among all the model systems, the most apparent drop in tensile strength can be observed in CPU-PT.

The viscoelastic behavior and damping behavior of the water-saturated CPU model systems were studied by DMA and shown in Figure 4. Since the absorbed water improves the mobility of polymer chains, upon water saturation, the glass transitions of all the model systems shift to lower temperatures and result in slightly decrease in damping characteristics around room temperature, where scratch tests were carried out. However, in agreement with the previous investigation on dry model systems, the trend of the damping characteristics around room temperature still remains the same that CPU-PET and CPU-PC exhibit the highest and second highest damping magnitude.

Figure 5 shows the critical normal loads for onset of cracking/material removal damage for all the model systems before and after water saturation. Upon exposure to water, only CPU-PC exhibits a slightly improved scratch resistance, the others deteriorate. These changes in scratch resistances are closely correlated with the variations in coefficient of friction, tensile true stress-strain behavior as well as dynamic mechanical behavior of all the CPU model systems upon water exposure. In the FEM scratch modeling study, it has been shown that the most important material parameter that influences the onset of cracking/material removal damage is the tensile strength [8]. Under both conditions, the trends of the onset of cracking/material removal damage are the same with the trends of tensile strength. Upon water exposure, CPU-PT shows the most significant drop in tensile strength among all the model systems, which can be the reason of the remarkable deterioration in scratch resistance of CPU-PT when exposed to water. Also, another FEM study has found that an increase in COF shifts the stress intensity towards the surface of the sample during scratch process, which leads to an earlier onset of cracking damage [7]. Under both conditions, the trends of the onset of cracking/material removal damage are the same with the trends of COF. The model system shows an increase in COF upon water exposure also exhibits deterioration in scratch resistance. For CPU-PC, it just has negligible degradation in tensile strength in water-saturated condition, but it also shows a drop in COF. This can be the main reason that only CPU-PC exhibits a slightly improved scratch resistance upon exposure to water. In addition, since polymers with higher damping characteristic are likely to have properties to be more strain rate dependent [11, 12], and the trend of the
damping characteristics of CPU model systems around room temperature remains the same under dry and water-saturated conditions, the strain rate dependencies of the model systems are similar in these two conditions. Because the speed at which scratch testing was carried out induced a very high strain rate on the surface, the model systems with higher damping characteristics tend to be more sensitive and easily damaged during scratch.

Summary

In this study, the scratch performance of a series of CPU upon exposure to water has been investigated. The incorporation of different soft segments resulted in varied affinity to water molecule of the model systems, and thus different reactions between water and the model systems. The experimental results indicate that the increase in COF, drop in tensile strength and increase in damping characteristics upon water exposure lead to earlier onset of cracking/material removal damage of CPU during scratch. The present study offers fundamental insights into effective design of scratch resistant CPU.

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References

Figure 1. Weight gain of CPU upon exposure to water.

Figure 2. Coefficient of Friction of CPU in dry and water-saturated conditions.
Figure 3. Tensile strength of CPU in dry and water-saturated conditions.

Figure 4. Variation of storage modulus and tan δ of CPU versus temperature in water-saturated condition.
Figure 5. Onset load of scratch damage of CPU in dry and water-saturated conditions.