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Material Behaviour

Improvement of environmental stress cracking resistance of polycarbonate by silicone coating

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ABSTRACT

To explore the possibility of using surface coating to reduce environmental stress cracking (ESC) of transparent polycarbonate (PC) parts, silicone coated and SiO_2 coated PC were tested in a self-made three-point bending apparatus in the presence of ethanol. The variation of stress with time was recorded, and the surface cracking was observed to evaluate the ESC resistance of samples. Slower stress relaxation rates and fewer surface cracks indicated that silicone coating improved the ESC resistance of PC, but SiO_2 coated PC was found to be no better than that of uncoated PC. Silicone coating reduced the absorption of ethanol in PC, weakening the surface plasticization, thus hindering the formation and development of cracks in PC. Nanoindentation test results showed that the mechanical properties such as hardness and elastic modulus of silicone coating are a better match for PC than SiO_2 coating. This allows the silicone coating to have a favorable effect in providing continuous protection for PC under the combined action of ethanol and stress.

1. Introduction

Polycarbonate (PC) is an important thermoplastic polymer used for various industrial applications due to its favorable balance of stiffness and toughness, good thermal stability and excellent optical properties. The main factor that limits its use (its "Achilles heel" [1]) is environmental stress cracking (ESC) which occurs in the polymer under the combined action of active chemical agents, such as ethanol, and mechanical stress. This phenomenon is more likely to occur in glassy polymers, such as PC, due to their loose structure [2]. Approximately 15% of all failures of plastic components are due to ESC [3], so it is important to develop effective methods that can be used to improve their ESC resistance.

Environmental stress cracking (ESC) of polymers has been studied for more than half a century. Some approaches have been developed to enhance the ESC resistance of polymers, including polymer blending, fiber reinforcement and impact modification. Robeson [4] provided a good review of these methods. Recently, nano-SiO_2 particles were incorporated into PC, yielding positive effects on ESC resistance [5], but the final parts shift from transparent to opaque. In order to maintain transparency, new methods need to be found to improve the ESC resistance of PC. In addition, all the approaches stated above are focused on modifying the bulk properties of polymers, but for most ESC processes, crazing/cracking first appears on the surface of polymer due to the local plasticization effect [6] and then develops into the bulk of polymer. Therefore, protecting the surface of the polymer from the attack of the external environment might be an effective way to improve the ESC resistance of polymer products.

Coating is a widely used surface modification method to enhance the properties of plastic parts. For example, there have been many studies focused on the effects of coatings on the improvement of ultraviolet resistance [7,8], scratch resistance [9,10] and hardness [11,12] of polymers. Recently, polyethyleneimine coating was used to enhance the solvent resistance of microchannels in chips fabricated from PC [13]. Silicone coating is a commonly used transparent anti-scratch coating for PC [14], it has relative low surface energy [15] which benefits by decreasing the tendency of polar solvents to spread out or adhere to the surface of

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samples. Hence, the ESC resistance of PC could probably be improved by silicone coating. To the best of our knowledge, the ESC behavior of coated PC has not been sufficiently studied, so this is the focus of this research.

In this study, injection molded PC samples were coated with transparent silicone, and the ESC resistance in ethanol was evaluated by the three-point bending stress relaxation method. For comparison, the ESC behavior of inorganic transparent SiO_2 coated PC was also evaluated. The mechanical properties of the PC substrate and the coatings were investigated by nanoindentation, and the results were used to compare the ESC resistance of uncoated and coated PC.

2. Experimental

2.1. Materials and sample preparation

The PC grade used was ChiMei110 with a melt mass flow rate of 10 g/10 min (1.20 kg/300 °C) and density of 1.2 g/cm^3. The bending test bars (85 mm × 10 mm × 4 mm) were produced by an HTF80B-W2 injection molding machine (Haitian, China) with a melt temperature of 300 °C, a mold temperature of 70 °C and an injection pressure of 100 MPa. All the samples were heated at 120 °C for 4 h and then cooled slowly to room temperature in order to eliminate residual stress. Before coating, all the PC samples were cleaned with distilled water and 2-propanol and then dried at 80 °C for 1 h.

The silicone coating material was prepared by a sol-gel method, following the procedure described by Zhang [14]. The precursor solution was composed of methyltriethoxysilane (MTES), tetrothoxysilane (TEOS), silica, polycarbonate diol (PCD) and 3-Aminopropyltriethoxysilane (KH550) with a mass ratio of 21:2:2:1:2. The pre-treated PC substrates were dipped into the solution for 2 min and then withdrawn into the open air at a pulling rate of 1 mm/s. The silicone coating on each sample was dried in an oven at 80 °C for 15 min to evaporate the solvent, and then the coating was cured at 120 °C for 2 h.

The SiO_2 coating was prepared with tetraethyl orthosilicate (TEOS). TEOS (Roth ≥ 98%, 29.2 mL) was dissolved first in ethanol (Roth, 99.8%, 5.8 mL). Deionized water (7.2 mL) was added drop wise, and the mixture was stirred for 30 min. Subsequently, hydrochloric acid (Fluka, 37%, 0.03 mL) was added to the solution to catalyze the hydrolysis, followed by further stirring for 60 min. Finally, 10 mL of the resulting solution was diluted with absolute ethanol, yielding a total volume of 80 mL and then stirred at ambient temperature for 24 h. The SiO_2 solution was deposited on the PC surface by the dip-coating method. PC slides were withdrawn into open air at 20 ± 1 °C with a relative humidity of 40–50%. The pulling rate was 1 mm/s. The dip coated films on the PC substrates were dried at 80 °C for 24 h.

2.2. ESC testing

All the samples were tested on a self-made three-point bending test apparatus, which was constructed based on the work of Lutfi [16]. A schematic diagram is illustrated in Fig. 1. The radius of the pressure head is 5.0 ± 0.1 mm. The capacity of sensitivity load sensor is 0–100 N. The maximum flexural strain value, ε_{max}, at the midpoint of the tensile surface of a test specimen, can be determined by equation (1) [16].

$$\varepsilon_{max} = 6\delta T / L^2 \quad (1)$$

where δ is the deflection of the midpoint (measured by the displacement sensor), T is the thickness of the sample, and L is the span length between the two supports shown in Fig. 1. The ESC solvent used this study was ethanol (analytical reagent grade) with a purity of greater than 99.5%.

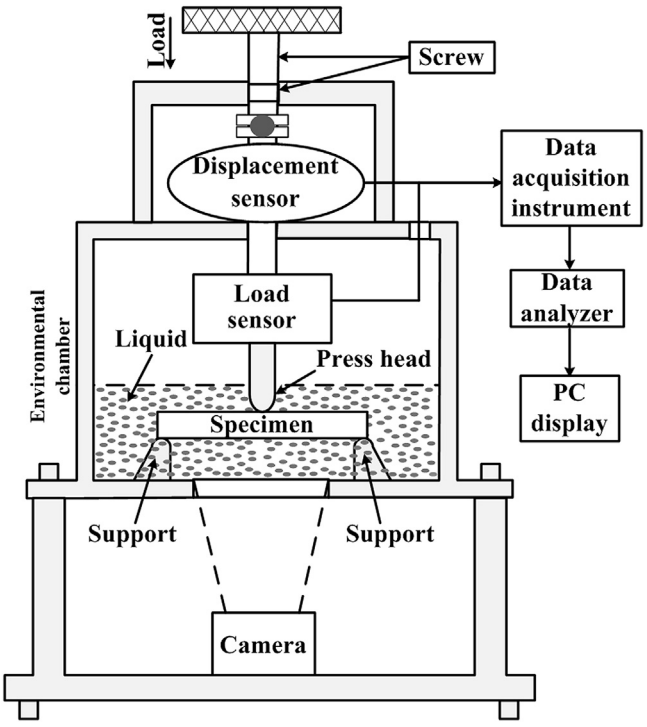

Fig. 1. Schematic diagram of the testing apparatus for ESC.

The sample was loaded to a preset value, and ethanol was slowly poured into the chamber. Timing was started when ethanol first touched the sample. During each test, the variation in stress with time at constant strain was recorded. After 30 min, the sample was unloaded and taken out of the chamber. Surface cracking was observed with a polarized optical microscope (Olympus BX6.1), and micrographs were taken at the center of the cracked surface.

To evaluate the absorption of ethanol into the uncoated and silicone coated PC, rectangular samples with dimensions 40 mm × 10 mm × 4 mm were immersed into ethanol at 20 ± 1 °C. The mass was measured regularly and rapidly, using a balance with an accuracy of ±0.01 mg. Before weighing each sample, excess ethanol was removed from the surface of the sample with absorbent paper.

2.3. Characterization

The variation of hardness and elastic modulus of coated and uncoated PC with contact depth was measured using a nanomechanical test instrument (TI 950, Hysitron Inc., USA). All tests were conducted in indentation mode using a Berkovich three-sided pyramid diamond indenter. For different combinations of coating and substrate, the methods of calculating hardness are different. According to the works of Bhattacharya and Nix [17], for soft coating on a harder substrate (such as the silicone coating on PC used in this study), equation (2) can be used to determine the variation in hardness with contact depth. Similarly, for hard coating on a softer substrate (such as the SiO_2 coating on PC used in this study), the variation in hardness with contact depth can be determined by equation (3). It can be seen from equations (2) and (3)