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Moisture uptake of a polycarbonate blend exposed to hygrothermal aging

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ABSTRACT

As an extension of an earlier study on aging of a polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) blend, this paper has explored the roles of two competing phenomena, physical aging and moisture diffusion, during hygrothermal aging. Moisture absorption experiments at four different relative humidity conditions were compared with full immersion condition. Uptake curves show two different diffusion behaviour including Fickian moisture absorption and anomalous peak overshoot. The equilibrium moisture uptake in the polymer system, the coefficient of diffusion of moisture and the dual glass transitions were characterized. In general, the uptake behaviour could be explained using free volume expansion and contraction concepts that are associated with diffusion and structural recovery theories, respectively. However, using statistical methods, it was found that the relationship between the effects of aging temperature and relative humidity is both complex and interactive, with either diffusion or relaxation processes dominating depending on the extent of hygrothermal exposure.

1. Introduction

Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) is an amorphous resin blend that has been widely used for moulding thin-walled plastic housings for communication and electronic devices. This blend has been replacing polycarbonate (PC) since it offers more advantageous properties than that of the single polymer system. PC is a tough, high-impact, versatile thermoplastic that can retain mechanical properties over a wide range of service temperatures. Acrylonitrile-Butadiene-Styrene (ABS) is also a common thermoplastic used for its light weight and good shock absorbance. The actual properties of ABS depend greatly on the blend ratio of the three major components. The acrylonitrile component is responsible for chemical resistance and thermal stability; the butadiene component is the cause of toughness and impact strength; and styrene, which usually constitutes the largest portion in ABS, gives rigidity and processability. By combining the strength of PC and the flexibility of ABS, PC/ABS blends have improved stiffness over conventional high-impact PC or ABS alone, and more importantly, are easier to process than PC.

Studies on the moisture absorption and hygrothermal properties of PC (*e.g.*, [1–8]) have spanned over 25 years. It is known that humid environments can significantly alter the mechanical properties of PC including impact strength [6], fracture strain [7], moduli [7], and also thermophysical properties such as glass transition temperature [7] and viscosity [3]. With growing demand for PC/ABS blends in recent years, however, the interest has shifted to physical and mechanical properties of the blends [9–19]. There is, however, limited data on the moisture absorption behaviour of this material, and to the best of our knowledge, the structural changes due to hygrothermal exposure of PC/ABS have yet to be reported widely.

Hygrothermal exposure of a polymer material is commonly associated with a form of hot-wet conditioning. Although there are actually two physical mechanisms at play – moisture absorption and structural recovery/relaxation associated with physical aging – during prolonged hygrothermal exposure, most studies have focused on the former since the effects of structural relaxation are more difficult to delineate during moisture uptake at high temperature.

In general, the sorption of small molecules by polymers during moisture uptake has been of fundamental research interest and polymer–water systems have been of particular interest. Diffusion is a process by which molecules are transported through the surface to cause swelling of the free volume of the material. The most common formulation of the diffusion process is Fick's Law [20]. Fickian diffusion is, however, one of three distinguishable classes of transport behaviour, depending on the contributions of diffusion and relaxation mechanisms [21]. Structural relaxation, which occurs in glassy polymers as a consequence of the rearrangement of molecular chains to reach an equilibrium state, causes the polymer structure to contract. Hence, the diffusion process and structural relaxation are competing mechanisms during long

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term hygrothermal aging and the comparison between the rates of the two processes gives an approximation of the class of transport behaviour. In Case I, resembling Fickian diffusion, the diffusion process is much slower than the relaxation process. In contrast, when relaxation occurs much slower than diffusion, this is known as Case II transport behaviour. Lastly, Case III includes the anomalous and non-Fickian behaviour in which the diffusion and relaxation rates are comparable. A brief description of some anomalous transport behaviours have been described elsewhere [22].

Structural relaxation or recovery, as pointed out above, is an inherent process which occurs when a material in a non-equilibrium state spontaneously evolves towards equilibrium [23]. In glassy polymers, the non-equilibrium state is formed because of very rapid cooling from above the glass transition temperature to below it. This is a spontaneous mechanism in processed polymer parts using most industrial processing methods. The non-equilibrium structure has excess thermodynamic quantities of enthalpy and volume. During the recovery process or *physical aging*, a term first introduced by Struik [24], it is thus possible to characterize the thermodynamic state of the glassy material by measuring changes in volume or enthalpy [25–29]. The phenomenon of physical aging is most commonly studied as a function of aging time and temperature. The process is accompanied by profound changes to material properties due to structural densification, mostly caused by free volume contraction and intermolecular relaxation processes. With progressive physical aging, the free volume of the system gradually contracts and is continually *relaxed* towards an equilibrium state. The closer the aging temperature is to the glass transition temperature of the material, the quicker the *recovery* or relaxation rate. The *physical aging* process therefore causes reversible changes on the material's properties and in this sense is different from other kinds of aging mechanisms such as *chemical aging* which generally results in permanent changes such as material degradation in polymer materials. There is also suggestion in the literature (*e.g.*, see reference [30]) that relatively high aging temperatures used in physical aging experiments may trigger high-activation processes which may not accurately represent the low-activation processes that occur in physical aging.

In our previous work, the aging behaviour of a PC/ABS blend at a temperature near the two component glass transition temperatures was studied [18]. As an extension of that work, our attention is now focused on the effects of hygrothermal conditions on moisture uptake behaviour in the material over a prolonged period. The objective is to explore the effects of the two opposing mechanisms, moisture diffusion and structural relaxation. The temperatures studied are within the range of low-activation processes associated with physical aging. Gravimetric experiments are conducted on the PC/ABS specimens and the effects of two factors of relative humidity and aging temperature on the obtained results are investigated.

2. Experimental

2.1. Material preparation

A commercial grade of 75:25 PC/ABS from SABIC (formerly, GE Plastics), designated as Cycoloy C6600, has been used in this study. It is a widely used PC/ABS ratio with a melt flow rate of 21.5 g/10 min at 260 °C with 2.16 kgf in accordance to the ASTM standard [31]. The weight average molecular weight (M_w) of the blend was found to be 45,000 by Jordi FLP using gel permeation chromatography with RI (GPC–RI) and GPC–FTIR techniques. The size of the molecules in solution was found to be the same and could not be resolved using GPC. Moreover, GPC–FTIR confirmed that they were eluting at the same time.

Sheets of this material were moulded and further cut to size for experimentation purposes. According to ASTM D570-98 Standard [32], test samples were cut in the form of a bar with nominal dimensions of 76.2 mm (3 in.) by 25.4 mm (1 in.) by the thickness of the sheet, 2.84 mm (0.11 in.). In order to measure the dual glass transition temperatures (T_g) of the blend material after moisture uptake, another set of bar shaped samples were cut. In accordance to ASTM D 5023-07 Standard [33], sample dimensions of $64 \times 13 \times 3$ mm were used with a 50-mm span bending clamp to achieve a span-to-depth ratio of 16:1. Cut edges were smoothed so as to be free from cracks and were polished slowly to avoid heating the surfaces.

2.2. Procedure

Samples were conditioned prior to moisture absorption and physical aging to ensure that moisture uptake measurements were taken from the same reference point. First, test specimens were stored inside a dessicator for 48 h before testing in accordance to the ASTM D 618-08 Standard conditioning guidelines [34]. They were then placed into an oven at 135 °C for 10 min which maintained a dry atmosphere to erase any previous thermal history [18]. Specimens were then removed from the oven, weighed to obtain the mass of dry samples, and placed directly into five conditioning environments as described below. During weighing of the specimens they were exposed to room temperature for about 1 min, therefore the cooling rate was the same for all the samples. Preliminary tests showed that the brief exposure did not cause the temperature of the samples to drop below the aging temperatures.

Samples were subjected to 5 different conditions: (i) 65 °C and 50% relative humidity (RH); (ii) 50 °C and 93% RH; (iii) 65 °C and 93% RH; (iv) 50 °C and 50% RH; and lastly (v) stored at room temperature fully immersed in distilled water, to investigate their effects on the coefficient of diffusion and equilibrium moisture content. Hygrothermal aging for conditions (i)–(iv) was conducted inside environmental chambers with the samples standing on one end in grooves machined into an aluminum block such that both surfaces of each sample were equally exposed to their conditioning environment. Samples fully immersed in water were rested on one end inside an enclosed container.

2.2.1. Moisture uptake measurements

The ASTM D570-98 Standard [32] was adopted for the sampling frequency of moisture uptake measurements. Samples are initially weighed prior to conditioning; after 1, 3, 7, and 10 days; and then once every week thereafter until the increase in weight indicated by three consecutive readings average less than 1% of the total increase in weight or 5 mg, whichever is greater. Each condition was replicated with 3 samples for moisture uptake monitoring. An analytical balance capable of reading 0.0001 g was used to record the mass of prepared specimens.

In order to obtain more accurate values of coefficient of diffusion, another set of specimens were conditioned at the same hygrothermal conditions and their moisture uptake was recorded every hour until the samples reached at the half of their equilibrium moisture uptake.

2.2.2. T_g measurements

Determination of T_g was conducted using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). The tests were performed in bending mode of the instrument using a 3-point bending clamp. T_g determination tests were conducted on hygrothermally aged samples at the four hygrothermal conditions after 7 days of moisture uptake. The specimens were heated from 40 °C to 125 °C (a temperature level above $T_{g,PC}$ ($\sim$112 °C), which is higher than