Relationships between Low Temperature Impact Performance and Structures of Rotationally Molded Crosslinked High Density Polyethylene

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Abstract

The low temperature impact performance of rotationally molded specimen is of great importance for the final products. Crosslinked high density polyethylene (XL-HDPE) is a preferred material for large chemical and fuel tank due to its superior environmental stress crack resistance and high impact strength. In the present research the drop weight impact strength (defined as ARM impact strength) of rotationally molded XL-HDPE was carried out at -40 °C and the relationships between impact strength and microstructures were investigated. The results confirmed that the microstructures of XL-HDPE molecules in the innermost surface layer dominated the low temperature impact performance of rotationally molded XL-HDPE articles.

Introduction

Rotational molding is a processing method for manufacturing hollow plastic products. During the process, a pre-weight charge of plastic powder is placed into a mold. Then the mold is subjected to a biaxial rotation under heating so that the rotating plastic powders contact the inner surface of the mold and change into the melt. With a continuous rotation, the plastic melt sticks to the whole inner surface of the mold and then cooled to near room temperature to obtain the final product [1, 2].

Rotational molding has many advantages over other molding processes; e.g. it is suitable for hollow plastic products with complex molding shape, precise surface texture and large or especially large size, and the end products also have no residual stress [3]. Thus, it has reached a wide application and drawn more attentions from researchers to optimize its fabrication process to obtain better product’s performances, especially for impact strength [4-7]. The impact strength of the final products is of great importance in the rotational molding industry. Several products made by rotational molding are used in outdoor applications, for example, boats, tanks, and car body parts. In such applications, impact loading is a distinct possibility and quite often the products will be used at sub-zero temperatures [8]. Therefore, it is important to know the impact performance of the final products over different temperatures. More recently, the rotational molding of high density polyethylene (HDPE) has gained considerable importance, due to its proven advantages in the manufacture of hollow plastic products [9]. HDPE is the preferred polyethylene for chemical containers due to its excellent chemical resistance [10, 11]. However, the poor creep resistance and impact strength of HDPE limit its applications as chemical tanks or fuel tanks. HDPE is frequently chemically crosslinked. Crosslinking prevents molecules from sliding over long times, and greatly increases stress crack resistance and impact strength. Crosslinked high density polyethylene (XL-HDPE) has excellent chemical resistance, environmental stress cracking resistance (ESCR) and impact strength, being a preferred material for chemical tank, fuel tank, boat, etc.

In this work, the impact performance of rotationally molded XL-HDPE fuel tank was investigated. The structures of rotationally molded XL-HDPE were also studied. The paper attempts to describe the structure-properties relationships of the rotationally molded XL-HDPE to address the underlying causes for the observed low temperature ARM impact performance.

Experimental

HDPE DMDA 8007 was purchased from Shenhua Group with a melt flow index of 10 g/10 min and a density of 0.955 g/cm\textsuperscript{3}. The polymer was compounded with a crosslinking agent to prepare the XL-HDPE samples. The XL-HDPE pellets were ground into a fine powder and sieved for use. Rotational molding was carried out using a F01-1000 Rotational molding machine developed by Fangda Corporation in China. Four kilogram of XL-HDPE powder was added into a 500×500×250 mm\textsuperscript{3} rectangular steel box mold and heated.
for 28 min at a set oven temperature of 280 °C. The rotational speeds of the major axis and minor axis were 5 rpm and 8 rpm, respectively. The wall thickness of the mold was 2.5 mm. After heating, the mold was removed from the oven and cooled for 50 min to room temperature using an air fan. The thickness of the rotationally molded box was about 4.5 mm.

ARM impact strength specified by the Association of Rotational Molders International was carried on a SLC-200 drop weight impact test machine. The dart weight was 9 kg and the dart had a hemispherical nose with a diameter of 25.4 mm. The test was carried out on 12.5×12.5 cm² test specimens cut from the flat part of the molded XL-HDPE box. During the ARM test, two test methods were used as illustrated in Figure 1. The first method was consistent with the ARM impact test standard. The specimen was placed in the sample holder such that the dart impacted the surface (defined as outer surface) that was in contact with the mold when molded. The inside surface of the sample was placed downwards. For the second method, the outer surface of the sample was placed downwards and the dart impacted the inner surface.

![Figure 1. Schematic diagram of the ARM impact test.](image)

The inner surface layer (about 0.3 mm thickness) was first removed with 200-mesh sand paper and then polished using 800 and 1500 mesh sand paper in sequence. The final specimen, defined as the polished sample, was impacted from the outer surface to investigate the possible effect of the inner surface layer on the low temperature impact performance.

Compression molded sheets were achieved using a Collin testing platen press type P300 PM (Germany). Pressing was carried out at 210 °C using a pressing time of 10 minutes at a pressure of 100 bars. The sheet was left to cool down to room temperature in the mold at a cooling rate of 10 °C/min. The thickness of the sheets was about 4 mm. ARM impact strength of the sheets was measured to investigate the possible difference of impact performance of different molding methods.

Specimens of different thickness gradient were cut from the rotationally molded sample (as showed in Figure 2). The thickness gradient of the outer surface was defined as 0. About 0.3 mm of specimen was cut from different thickness gradient to perform structural analysis.

![Figure 2. Schematic diagram of sample preparation of different thickness gradient for structural analysis.](image)

The gel content was determined by xylene extraction according to the ASTM D2765 standard. Approximately 0.3 g of sample was placed in a pouch made by 120 mesh stainless steel cloth and extracted in boiling xylene for 12 h to remove the soluble part of PE. After the extraction the samples were dried to a constant mass at 150 °C. The gel content ($X_{gel}$) was calculated according to the following equation:

$$X_{gel} = \frac{m_1}{m_0} \times 100\%$$  \hspace{1cm} (1)

where $m_1$ is the final mass after extraction and $m_0$ is the initial mass of the sample.

The crystallization characteristics were investigated by a Q2000 differential scanning calorimetry (DSC). About 5 mg of the sample were measured under nitrogen atmosphere in a heat-cool method. The sample was heated from -45 to 180 °C, held for 5 min, and then cooled to 0 °C. The heating rate and cooling rate were 10 °C/min. The melting enthalpy, which might be related with the mechanical properties of the sample, was obtained using the first melting curve that contained the thermal history of rotational molding process. The crystallinity ($X_c$) was calculated by using the following equation:

$$X_c = \frac{\Delta H}{\Delta H_{100\%}} \times 100\%$$  \hspace{1cm} (2)

where $\Delta H_u$ is the integrated melting enthalpy of the melting peak between -40 and 150 °C from DSC endothermic curve, $\Delta H_{100\%}$ is the melting enthalpy of polyethylene crystal with 100% crystallinity, which is set as 287.3 J/g in this study [12].
The ultra-thin sections (60~70 nm) of the samples were prepared by ultramicrotomy at -140 °C using a Leica EM UC7 ultramicrotome and stained with RuO₄ aqueous vapor at room temperature. Specimens of the innermost surface layer (within 0.3 mm of the innermost surface) and body part (specimen that innermost surface removed) were cut from the rotationally molded sample using the ultramicrotome. The morphology observation was performed on a JEM-ARM2007 transmission electron microscope (TEM) using an accelerating voltage of 200 kV. The lamella thickness distribution was obtained by measuring the thickness of more than 100 lamellae. The thickness was counted for every 1 nm and the area occupied by the lamella was obtained for each thickness division. A frequency histogram was expressed as an area-based occupation fraction [13].

Results

The low temperature ARM impact test was carried out at -40 °C according to the ARM standard. The ARM impact strength and the impact fracture fragments of the rotationally molded XL-HDPE are shown in Figure 3 and Figure 4. It can be seen that the ARM impact strength impacting from the outer surface is 1 J/mm and the fractured specimen is shattered into several pieces, free from stress-whitening at the impact point (Figure 4a). This indicates that the fracture is attributed to a brittle failure mode. When impacting from the inner surface, the ARM impact strength increases to 11 J/mm with only a punctured central hole where the sample is free from stress-whitening at the impact point (Figure 4b), illustrating that the sample fails in a brittle mode. It can be seen from Figure 4b' that the punched fragment has a trapezoidal shape (where the inner surface is smaller than the outer surface). This indicates that the specimen firstly cracks in the inner surface and then the cracks propagate through the impact direction. The difference of the -40 °C ARM impact strength impacting from outer vs. inner surface is possibly due to its different micro-structures.

For the polished sample, the ARM impact strength increases to 24 J/mm. The innermost surface removed specimen shows an apparent stress-whitening (Figure 4c) indicating that the fracture is attributed to a ductile failure mode. The brittle-ductile transition and the increase of the ARM impact strength before and after removing the inner surface layer indicate that the inner surface predominates the -40 °C impact performance of the rotationally molded XL-HDPE.

Samples of different thickness gradient were cut from the rotationally molded XL-HDPE. The gel content and crystalline characteristics of the different thickness are shown in Figure 5 and Figure 6, respectively. Except for the innermost surface layer, the gel content decreases and the crystallinity increases slightly from the outer to the inner surface layers. The gel content of the inner surface decreases significantly compared with the other thickness gradients, accompanied with significantly higher crystallinity of the inner surface layer. The lower gel content and higher crystallinity of the inner surface account for the lower ARM impact strength and failures in brittle mode of the unpolished sample. In contrast, for the polished sample, the gel content of newly created inner surface layer remains high, leading to higher molecular weight, enhanced molecular chain entanglements, and reduction of the brittle-ductile...
transition temperature [14, 15]. As a consequence, the polished sample changes to a ductile failure in the ARM impact test. This result illustrates that the microstructure of the XL-HDPE molecules in the inner surface, usually exhibiting lower gel content and thus lower degree of crosslinking, dominates the low temperature impact performance.

In fact, for the compression-molded XL-HDPE sheet, the gel content is 79.8 % and the crystallinity is 67.8 %. The -40 °C ARM impact strength of the sheets increases significantly to 35 J/mm. This result further proves that lower degree of crosslinking of the inner surface layer is the cause of lower -40 °C ARM impact strength of rotationally molded XL-HDPE. Moreover, the results also show that, in order to obtain better -40 °C ARM impact strength, the producers and manufactures of the final products of rotationally molded XL-HDPE should adjust their processing conditions to obtain high degree of crosslinking in the inner surface layer.

The lamella crystal morphologies and lamella thickness distributions of body part and innermost surface layer are shown in Figure 7. It can be seen from Figure 7a and Figure 7b that the lamella thickness of the body part is thinner than that of the innermost surface layer. The lamella of the body part shows a narrow distribution; all the lamellae have thicknesses between 8 and 15 nm (the average lamella thickness, \( l_{c,av} = 12.2 \) nm, standard deviation, SD = 1.3 nm). The inner surface layer exhibits a wider lamellar thickness distribution, with thicknesses between 11 and 20 nm (\( l_{c,av} = 15.7 \) nm, SD = 2.3 nm). The thicker lamella of the inner surface layer caused by its lower gel content is responsible for its lower -40 °C ARM impact strength.

![Figure 5. Gel content of different thickness gradient.](image)

![Figure 6. Crystallinity of different thickness gradient.](image)

![Figure 7. TEM images of the body part (a), the innermost surface layer (b) and lamella thickness distribution of the body part (a’), and the innermost surface layer (b’).](image)

**Conclusions**

In the present research work, the relationships between the -40 °C ARM impact strength and microstructures of the rotationally molded XL-HDPE was studied. Samples with lower internal gel content and higher crystallinity failed in brittle mode in the ARM impact test with low impact strength. The inner-surface-removed samples with higher internal gel content and lower crystallinity exhibited ductile failure in the ARM impact test. The results indicate that the microstructures of XL-HDPE molecules in the inner surface layer of the rotationally molded container dictates the low temperature impact performance. This finding and validation of the causes of the observed low impact strength in the -40 °C ARM test has practical utilities for producers of XL-HDPE articles such as oil tanks and sporting boats. In order to obtain better -40 °C ARM impact strength, the producers and manufacturers of the final products of the rotationally molded XL-HDPE should adjust their processing conditions to ensure high degree of crosslinking of the inner surface layer.
References