Effect of Changing Environments on Microstructure of HDPE Polymer

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ABSTRACT:

The analysis of environmental effects on microstructure of HDPE polymers were done according to their mechanical behavior obtained from tensile, impact and microhardness testing and thermograms obtained from DSC. The samples were conditioned under three different kinds of humidity and temperature environment. With increase in conditioning time, the variations of tensile strength, impact, microhardness were observed to be nonlinear in nature. The high values are possibly due to polymerization such as cross-linking. The low values may be attributed by depolymerization mechanism such as chain scission and bond breakage. The variation of data is due to more physical damage of the polymer because of unequal expansion of the surface. The refrigeration also affects the crystalline regions by changing free volume. Again rearrangement of end groups in the lamella through partial melting and recrystallization are observed due to thermal conditioning and thermal shock.

Keywords: HDPE, Thermal cycling, Humidity cycling, Tensile, Impact, Cross-linking, Degradation.

1. INTRODUCTION

Among the thermoplastic polymers, High Density Polyethylene (HDPE) is an attractive material for scientific and technological studies due to its low cost, good properties and versatility. It is also a material with potential for application in outdoor exposure. For this reason, many studies have been conducted over the years to investigate various aspects of its weathering behavior [1–8]. Environmental parameters acting on a polymer such as temperature, humidity, chemical exposure, radiation, biological agents, and their combinations significantly influence the strength of a polymer through intervening structural changes. The effect of temperature on the stiffness of polymers is probably most important with regard to the design and use of polymers for load bearing
engineering applications. The better mechanical properties of HDPE extend their use into larger shapes, the sheet materials on the interior of appropriately designed vessels, packing in columns, and solid containers to compete with glass and steel.

Humidity affects the performance of the polymer, as the polymer absorbs moisture from air humidity and holds water molecules rather firmly by hydrogen bonding, which causes a slow variation of properties like electrical characteristics, mechanical strength and dimensions [9]. This information will prove to be useful to product design engineers, mold designers, failure analysts and general plastics practitioners in all phases of product design and development [10]. In general, the permeability of plastics depends on crystallinity, molecular orientation, chain stiffness, free volume, cohesive energy density, temperature, and moisture sensitivity [11-13]. The presence of moisture in a polymer often accelerates the creep process, presumably through a plasticization effect. Previous studies on polymer products have indicated that the creep and dynamic loss can be significantly increased for conditions of changing moisture content. This suggests that not only the moisture content, but also the sorption history are important for determining the viscoelastic properties of polymeric fibers [14]. The moisture content of the polyethylene plays an important role in the formation and transport of space charge caused by injected electrons and holes or ionization of impurities, including by-products of cross-linking agents and catalyst residues. Polymer structures, such as straight chain, branch chain, co-monomer and crystallinity, also influence space charge formation and transport in various ways [15].

Thermal energy tends to lead to disorder and thus, strong secondary bonds are necessary to attract polymer molecules in order to produce crystalline arrangements. Semi-crystalline polymers like polyethylene maintain some rigidity beyond glass transition temperature (T_g), though there is still a drop in modulus as the melting temperature is approached.

Measurement of physical properties of materials by analytical techniques is being used to investigate how the polymer is changing during the aging process. Tensile and micro hardness tests measure the bulk property of the material that results from crystallinity, lamella thickness and crystal size [16]. Tensile tests are used to measure the force response when a sample is strained, compressed or sheared at a constant rate. These provide a means to characterize the mechanical properties of a polymer in terms of modulus, strength and elongation to failure which in turn depend on the entanglement between molecules, their orientation and voids within that act as stress raisers initiating cracks and premature failure. Impact tests measure the energy required for a sample to fail under different loading histories [17]. Hardness is an important property as it is easily and rapidly measured based on resistance to penetration by an indentor into the plastic under constant load. Apart from quality assurance tests, hardness tests have been shown to be able to determine changes in morphology and microstructure of polymers [18,19]. Micro hardness measurements have been used to correlate with properties like Young’s modulus and compressive yield stress [20].
On view of the above fact, in the present work, the effect of environmental parameters such as temperature, moisture and thermal conditioning have been studied macroscopically by tensile, impact and micro hardness testing on the HDPE polymers. The objective of this work is to understand the change observed in the microstructure of these polymers due to ageing by correlating them with the changes obtained in their mechanical properties.

2. EXPERIMENTAL

2.1 Sample preparation

Raw materials of HDPE in the form of dried plastic pellets were subjected to high-pressure injection molding machine to obtain the specimens for mechanical tests as per ASTM standard. The samples were exposed to different thermal and humidity cycles in a humidity chamber respectively. Another conditioning was done by subjecting samples in a hot air circulating oven.

2.2 Environmental treatment

2.2.1 By changing temperature at specific humidity

One complete thermal cycle is defined as exposure of sample at 25°C and 95% humidity for 1 hour and at 50°C and 95% humidity for another hour. In each case two samples of the material were exposed, where one is tested directly and other sample is frozen at -20°C and then subjected to testing.

2.2.2 By changing humidity at specific temperature

One complete humidity cycle is defined as exposure of sample at 50°C and 50% humidity for 1 hour and at 50°C and 95% humidity for another hour. In each case two samples of the material were exposed, where one is tested directly and other sample is frozen at -20°C and then subjected to testing.

2.2.3 Thermal conditioning followed by quenching

The samples were then put into hot air circulating oven at the specified temperature of 100°C for 5, 10, 20, 30, 40, 50 and 60 minutes, respectively. When the required time was reached the oven was turned off and the specimens are immediately dipped in water maintained at a temperature less than 5°C. Two specimens of the material are used as the standard specimens without conditioning.

2.3 Mechanical test

2.3.1. Tensile Testing

In the present study, tensile tests were performed on INSTRON 1195 in all the three cases at a fixed crosshead speed of 10mm min⁻¹. Samples were prepared according to ASTM D 638 and tensile strength of standard and conditioned samples was calculated.
2.3.2. Impact Testing

In this test a fast moving hammer strikes a notched specimen (ASTM D 256) and the energy absorbed in breaking a fast moving specimen is measured and impact strength is noted from the calibrated scale in J.

2.3.3. Micro hardness testing

The sample was indented using Durometer following ASTM procedure No. D2240 and the reading is noted from the calibrated scale.

2.4. Thermal analysis by Differential scanning calorimetry (DSC)

Thermal analysis using DSC (Netzsch STA 409C) is done only for samples (2.2.3). Each composition was weighed and put into aluminum pans and are heated from 20°C to 200°C at heating rate of 20°C min⁻¹. Data were collected continuously and then analyzed by the DSC analysis programme. Melting temperature was detected as the peak temperature of the main endotherm from the DSC graph.

3. RESULTS AND DISCUSSION:

With increase in number of thermal cycles at a specific humidity, the variations of mechanical properties were studied. Both the unfrozen & frozen specimens when exposed to less number of thermal cycles show an increase in tensile strength [Fig.1(a) & Fig.1(b)]. This may be due to increase in inter-chain interaction that attributes cross-linking of the carbon chain. When the number of thermal cycles increases, the elongation increases while the tensile strength and modulus diminish. Impact strength of the polymer samples shows a down trend initially because voiding may occur during crystallization and also domination of thermomechanical stress due to thermal cycling, but in the later case the difference of the data obtained. The reason is increase in free volume due to refrigeration that affects the impact strength [Fig.1(c) & Fig. 1(d)]. The microhardness variation [Fig.1(e) & Fig.1(f)] suggest that the aging process initially leads to a closer packing of the material resulting in harder and denser products but prolonged aging shows decrease in microhardness that lead to a brittle, mechanically weaker material [21]. The polymer specimens lose weight in first cycle as the desorption dominates when compared to the absorption of the moisture, but as the number of cycles increases, the gradual increase in the amount of moisture absorbed is observed [Fig.1(g) & Fig.1(h)].
FIG 1(a). Effect of thermal cycling on Tensile strength of HDPE

FIG 1(b). Effect of thermal cycling cum refrigeration on Tensile strength of HDPE
FIG 1(c). Effect of thermal cycling on Impact strength of HDPE

FIG 1(d). Effect of thermal cycling cum refrigeration on Impact strength of HDPE
FIG 1(e). Effect of thermal cycling on Microhardness of HDPE

FIG 1(f). Effect of thermal cycling cum refrigeration on Microhardness of HDPE
FIG 1(g). Amount of moisture absorbed by HDPE Impact specimens

FIG 1(h). Amount of moisture absorbed by HDPE tensile specimens
With increase in number of humidity cycles at a specified temperature, the mechanical properties such as tensile, impact and microhardness data shows a greater variation with respect to refrigeration samples [Fig. 2(a) – Fig. 2(f)]. This is due to the fact that the moisture is absorbed only on the surface of the specimen, which is not penetrated into the core of the specimen, thus leading to the unequal expansion of the polymer and damaging the sample physically [22]. In order to explain the data more clearly this needs further investigation. It is observed that after the first humidity cycling the specimens lose in weight of samples but on prolonged exposure the amount of moisture induced in the sample increases [Fig. 2(g) & Fig. 2(h)].
FIG 2(c). Effect of humidity cycling on Impact strength of HDPE

FIG 2(d). Effect of humidity cycling cum refrigeration on Impact strength of HDPE
FIG 2(e). Effect of humidity cycling on Microhardness of HDPE

FIG 2(f). Effect of humidity cycling cum refrigeration on Microhardness HDPE
FIG 2(g). Amount of moisture absorbed by HDPE impact specimen

FIG 2(h). Amount of moisture absorbed by HDPE tensile specimens

The effect of thermal conditions on tensile, impact, microhardness and melting temperature was obtained. In initial cycles, tensile strength increases because of increase
in $T_g$ value due to chain stiffness [Fig. 3(a)]. So the polymer becomes brittle since the ductility is lost due to heavier crosslinking [23]. Both the microhardness and melting temperature curves [Fig. 3(c) & Fig. 3(d)] show increasing trend at higher conditioning, indicating crystallinity as well as Young’s modulus increase [24]. As the conditioning time increases the depolymerization phenomena dominates, which leads to bond breakages, chain scission and thus reducing the tensile strength of polymer. The impact data shows a decrease in impact strength [Fig. 3(b)] since the crystallinity becomes sensitive to thermal shock, which produces a discontinuous change in free volume.

FIG 3(a). Effect of thermal conditioning on Tensile strength of HDPE

FIG 3(b). Effect of thermal conditioning on Impact strength of HDPE
4. CONCLUSIONS
With the increase in the thermal and humidity cycling, the variations of tensile strength, impact strength and microhardness are observed to be inconsistent. The recurrence of the high and low values of these quantities is due to changes in the organization of the system and morphological changes in the material. The high values indicate an increase in the polymer’s crystallinity and/or the occurrence of cross-linking that includes entanglement of chains. The low values are due to depolymerization, which includes either/both thermal degradation and moisture degradation that were attributed to chain breaking. The refrigeration also affects the free volume of the polymer thus leading to mechanical stress in the polymer. Slow cooling from melt or annealing just below melting point produces thicker lamellae. Where long molecules emerge from the lamellae they may crystallize in one or more adjacent lamellae thereby forming tie molecule. In rapid cooling, some side branches may become incorporated as crystal defects in the crystalline regions. Thermal condition data show a different behavior than the other two cycles. The variation in the microhardness is attributed to the changes in surface because of configurational rearrangement of end groups and by rapid changes induced by the thermal shock at the surface. Near the melting point, the regular good lamellar stacking is destroyed through partial melting and recrystallization, yielding a larger proportion of new thin lamellae which contribute to the drastic hardness depression observed. At late stages of aging voiding may occur during crystallization process resulting brittleness.

REFERENCES

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