Materials Science and Engineering A 404 (2005) 208–220

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

The determining role of calcium carbonate on surface deformation during scratching of calcium carbonate-reinforced polyethylene composites

M. Tanniru [a,b], R.D.K. Misra [a,b,*], K. Berbrand [c], D. Murphy [c]

[a] Center for Structural and Functional Materials, University of Louisiana at Lafayette, P.O. Box 44130, Lafayette, LA 70504-3130, USA
[b] Department of Chemical Engineering, University of Louisiana at Lafayette, P.O. Box 44130, Lafayette, LA 70504-3130, USA
[c] Westlake Polymers Corporation, P.O. Box 3608, Sulphur, LA 70664, USA

Received in revised form 18 May 2005; accepted 18 May 2005

Abstract

The scratch-induced surface damage of neat and calcium carbonate-reinforced high density polyethylene is described in terms of characteristics of scratch morphology and scratch deformation parameters. Under identical test conditions, calcium carbonate-reinforced high density polyethylene composites exhibit significantly reduced susceptibility to scratch deformation and stress whitening compared to neat high density polyethylene. The resistance to scratch deformation is discussed in terms of tensile modulus, elastic recovery, and scratch hardness.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Polyethylene composites; Microstructure; Scratch deformation

1. Introduction

Thermoplastic materials are being increasingly considered in automotive, aerospace, electronic, and optical applications where the resistance of the material to surface damage is of particular significance. Thermoplastics such as polypropylene and polyethylene have excellent chemical resistance and have emerged as ideal materials for automobile and consumer products. However, the susceptibility of thermoplastics to surface damage such as scratch is a serious concern [1–5]. Scratch introduces visual damage in materials and may also act as a macroscopic stress raiser reducing the mechanical strength [5–10]. Also, plastically deformed polymeric materials exhibit a whiter appearance called ‘stress whitening’ that is detrimental to optical clarity and aesthetic perception. It is also detrimental to tensile and fatigue loading because it will imply that the energy absorbing mechanisms under stress has been exhausted; therefore, further stress application will lead to early failure. Thus, the increase in the susceptibility of thermoplastic materials to scratch damage is important for maximizing their applications.

Stress whitening is the scattering of visible light after reflection and is a measure of the visibility of scratch. Visible light has a wavelength of 0.6 μm and hence voids in the size range of 0.5–1.0 μm or deformed features that reflect white light efficiently will enhance stress whitening. Polymeric materials experience different extent of deformation depending on the applied load and a number of test methods have been developed to simulate the actual conditions. Under practical conditions, objects of different geometries may be responsible for the scratch. Thus, the understanding of scratch pattern produced by indenters of different geometries is important [11,12]. Briscoe et al. examined the influence of applied normal load, sliding velocity, angle of indenter, and lubrication [1,13]. Scratch deformation processes of diverse nature including fully elastic, elastic–plastic, ironing, wedging, crazing–tearing, grooving, edge-cracking, and chipping were observed depending on the applied normal load, cone angle, and scratch velocity.

The formation of voids and microcrazing are generally believed to be responsible for the origin of stress whitening during scratch damage in polymeric materials. Studies on the mechanism of crazing have shown that the formation of deformation bands initiate crazing and their growth is perpetuated by the extension of existing voids into the

* Corresponding author. Tel.: +1 337 482 6430; fax: +1 337 482 1220.
E-mail address: dmisra@louisiana.edu (R.D.K. Misra).

0921-5093/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2005.05.031

bulk polymer, thereby linking up the stretched fibrils in their path [10,14]. Other micromechanisms such as shear deformation bands, kinking, microcrazing, and ductile ploughing have also been observed. Misra and co-workers studied the micromechanisms of stress whitening in relation to tensile deformation behavior [15,16] and strain rate sensitivity effect [17]. On the basis of these studies, strain–strain rate deformation maps elucidating the deformation processes responsible for stress whitening during scratch damage was developed. The relationship between deformation mechanisms and scratch visibility was examined using the phenomena of light scattering and reflection from scratches [3,18–20]. This approach involved the quantification of polarized light scattered from the scratch by considering the difference in intensities between bright and dark regions to compare the scratch visibility of different materials. The quantification of stress whitening sensitivity method was improved by Wang et al. [10,21,22] with the help of optically scanned images. It was noted that the extent and severity of plastic deformation determined the efficiency of light scattering. Hence, severely deformed fibrils involving tearing/breaking were more visible than smooth and well-defined grooves [10,21,22].

The inherent physical and mechanical characteristics of polymeric materials that influence resistance to scratch deformation are percentage crystallinity, molecular weight, modulus, and yield strength. Previous studies [10,23] have shown that a decrease in crystallinity of about 5% obtained by cooling polypropylene at different cooling rates enhanced stress whitening. The reduction in the susceptibility of high crystallinity polymers to stress whitening was related to their high modulus and yield stress. The desirable mechanical properties required to minimize susceptibility to surface damage and stress whitening can be accomplished by increasing crystallinity, use of short chain polymers, compounding with additives, and more importantly by reinforcement of polymer with micro- and nano-size minerals [24–30]. In general, reinforcement with minerals increases the modulus and yield stress, and influences the mobility of molecular chains. Previous studies on polymer composites containing micrometer size mineral particles have proven that a higher tensile modulus is obtained in comparison to unreinforced polymer [24–30]. Also, reinforcement particles such as clay may provide additional nucleation sites, thereby increasing the number of spherulites and reducing their size, with consequent increase or decrease in crystallinity [30].

A wide range of inorganic mineral reinforcements has been investigated in recent years from the viewpoint of improving scratch resistance. Primary among those are wollastonite [16,17,22,24,31–34], talc [31–34], and clay [29,35]. While significant improvement in scratch resistance was observed with these minerals, they, however, experienced a significant loss in ductility and toughness in relation to their neat counterparts. In contrast to wollastonite, talc, and clay, the reinforcement of high density polyethylene with calcium carbonate enhanced the impact strength, a behavior attributed to particle-induced cavitation [36]. In the study described here, a comprehensive effort is made to establish a link between reinforcement-induced structural changes and mechanical properties to surface damage and associated stress whitening. To accomplish this objective, a microstructural approach has been adopted to make a comparative evaluation of neat high density polyethylene and calcium carbonate-reinforced polyethylene processed under similar conditions, ensuring that the reinforcement-induced structural changes and stress whitening associated with surface damage is a true reflection of the reinforcement.

2. Experimental procedure

2.1. Materials

Standard ASTM tensile bars (ASTM D-638) and Izod impact bars (ASTM D-256) of neat polyethylene and $CaCO_3$-polyethylene composites (5, 10, and 20%) were injection molded and slowly cooled under quiescent conditions. The longitudinal axis of the tensile and impact specimens corresponded to the molding direction. The median size of $CaCO_3$ was ∼1.2 μm. Izod impact samples were notched according to ASTM D-256 with a notch-cutting device. A v-notch with a root radius of 0.1 mm was introduced into the specimen using a v-notch cutter to a depth of 2.5 mm. A notch verification device verified the depth. The nominal melt flow index of neat polyethylene was 20 g/10 min at 230/2.16 (i.e., at 230 °C and 2.16 kg piston force). The number and weight average molecular weights were 14,600 and 55,000, respectively and the polydispersity index was 3.77.

2.2. Structural characterization

2.2.1. Crystallinity and lamellar thickness

The study of degree of crystallinity assumes particular significance because higher crystallinity, in general, increases modulus and yield stress, and reduces toughness. The degree of crystallinity and lamellar thickness was measured by X-ray diffraction. Samples with a thickness of ∼2 mm were used for the X-ray diffraction measurements with the plane of view being parallel to the injection molding direction. The 1D WAXS detector was first calibrated using the known peak positions of polyethylene for the given wavelength (Cu Kα radiation = 0.1542 nm) using Bragg's law:

$$n\lambda = 2d\sin\theta \quad (1)$$

where n is the order of reflection, λ is the wavelength of incident radiation, d the interplanar spacing, and θ is the scattering angle. The degree of crystallinity, χ, of semi-crystalline sample was determined by:

$$\chi = \frac{C - A}{C} \quad (2)$$

where C is the area of the crystalline profile, and A is the area of the amorphous profile. The crystalline long period, D, is

Download English Version:

https://daneshyari.com/en/article/9795952

Download Persian Version:

https://daneshyari.com/article/9795952

Daneshyari.com