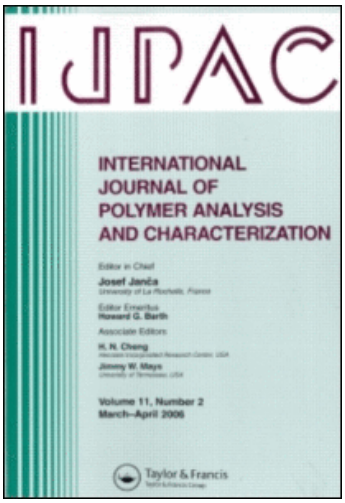

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Mechanism of Fracture of Metallic Coating under Uniaxial Stretching of Polymer Support at Temperatures below Glass Transition

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Abstract: Structure of surface layer of polymer sample with a thin metallic coating after uniaxial drawing of glassy PET is studied. The dependences of the dimensions of fractured fragments on the conditions of deformation are established. Fracture of the coating during tensile drawing of PET is shown to take place in the region of forming neck, and the mechanism of disintegration of fractured fragments into two equal parts is predominant.

Keywords: AFM; Fragmentation; Metallic coating; PET; SEM; Thin films

INTRODUCTION

Polymer films with a thin rigid coating (metals, metal oxides) are widely used as flexible mirrors and sensors and antibacterial, magnetic, electroconducting, and oxygen-insulating materials. However, tensile drawing

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or thermal treatment of such films can lead to the fracture of the coating and can disturb its integrity. Consequently, it is important to have a deeper insight into the character and mechanism of fracture of a rigid coating during plastic deformation of polymer support. The nature of the polymer influences the character of destruction of a film covering a polymer substrate.

The similarities and distinctions in the surface-layer structure of polymer samples with a thin rigid metallic coating during stretching at temperatures above and below Tg have been described in our earlier studies.[1–4] The objective of this work is to study the fracture mechanism of a thin metallic (platinum or gold) coating during uniaxial stretching of amorphous glassy polyethylene terephthalate (PET).

EXPERIMENTAL SECTION

In this study, we investigated commercial films of amorphous unoriented PET with a thickness of 100 μm. The surfaces of the polymer films were decorated with thin platinum or gold layers by the ion-beam coating method using Eiko IB-3 sputtering equipment. The thickness of the deposited layer was controlled by the deposition time and ranged from 2.7 to 27 nm. Then, the test films were stretched at a strain rate of 0.2 mm/min using an Instron-1122 dynamometer. The structure of the films was studied using a Hitachi S-52 scanning electron microscope (SEM) and a Nanoscope-11 la atomic force microscope (AFM) (Digital Instruments, Santa Barbara, USA) in the contact mode. The numerical values of the mean dimensions of the fractured coating fragments were estimated from the corresponding SEM and AFM images using the Femtoscan Online software.

RESULTS AND DISCUSSION

The materials (PET-gold or PET-platinum), consisting of a polymer support and a thin surface layer of metal, were studied. Polymer film and the surface layer of the metal in this material differ in thickness (100 μm for a polymer and 3–30 nm for a metal) and in the ability to be deformed up to a large degree of stretching. Plastic deformation of amorphous glassy PET occurs in a local area of deformation and is accompanied by quick narrowing of the film in the zone of a formed neck. Natural draw ratio of the polymer is about 270% in a zone of a neck, while the ultimate strain at break of bulk metal does not exceed 30–50%. As a result, destruction of metallic coating in separate fragments is observed along with the neck development.

Figure 1 shows typical AFM images illustrating the surface pattern of metal-coated polymer films in the neck region. Apparently, the covering collapses on separate fragments as the asymmetric ribbons oriented perpendicularly to the direction of the stretching. With increase of covering, the width of ribbons increases but their length and degree of coherence with each other decrease. When thickness is low, most fragments are interconnected, thus forming a network, but for large thicknesses of the layer, the fragments are more isolated.

As a result of stretching, there is not just a simple destruction of the covering on separate fragments but also the formation of a relief on the film surface. The layer of polymer adjoining the surface of a metal fragment is deformed to a less degree than the polymer between fragments. The deformation of polymer is accompanied by contraction of the film and by a decrease of its thickness. Heterogeneity of polymer deformation (in the places connected and untied with a metal covering) results in a relief formation on the film surface, which can be observed by AFM. The height of ledges, or depth of hollows, are about 100–200 nm, considerably exceeding the thickness of the metal surface layer (no more than 30 nm). This means that metal covers only the top part of fragments, as shown in Figure 2.

Thus, at a stretching of a metal covering on a flexible polymer substrate the surface of the film gets a relief caused by fragmentation of the covering and heterogeneity of deformation of the polymer.

In Volynskii, et al.,[5] the possible mechanisms responsible for the fracture of a rigid coating on a pliable substrate were theoretically analyzed for rubbery polymers. In the case of uniform deformation of the polymer substrate, the fragmentation of the coating at early stages of deformation (at low tensile strains of the polymer substrate) is primarily determined by surface microdefects, which are known to exist in any real solid and to initiate fracture of the coating at their localization sites. Such defects are randomly distributed in the coating; hence, the induced

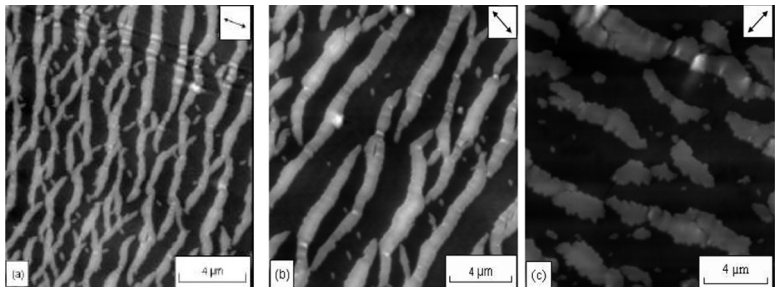

Figure 1. AFM image of the PET film with a gold coating ((a) 3 nm, (b) 5 nm, (c) 30 nm) stretched by 50% at 20°C via neck.

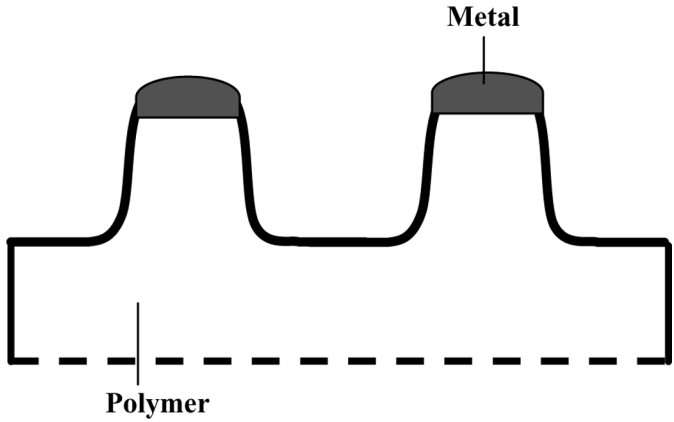

Figure 2. Schematic representation of the surface layer of PET sample with metallic coating after stretching at 20°C via neck.

fracture of the coating is also irregular and random. However, this initial stage of random fracture is followed by a highly intriguing and unique process, where each fractured fragment experiences further breakdown.

The point is that, after this initial stage of random fracture of the coating, the process of substrate stretching still develops and each fractured fragment remains under the action of a tensile stress. The stress distribution in each fractured fragment is highly nonuniform. Evidently, the stress at the ends of each fragment is zero. With increasing distance from the ends, the stress in each fractured fragment increases; precisely at the center of the fragment, it attains the maximum value. Figure 3 shows the schematic representation of stress distribution in the separate fragments of a coating during tensile drawing of the polymer substrate.

As the tensile strain of a rubbery polymer is increased, the stress in the sample also steadily increases. Therefore, the stress in each separate fragment becomes higher and equal to the strength of the coating. This stress level is at first attained precisely at the center of the fragment. As a result, this behavior leads to the fascinating process where the fracture of the coating proceeds via disintegration of each fragment into two equal parts. This mechanism of fracture is active while the soft and compliant substrate is able to transfer a stress exceeding the strength of the coating to fragments of the coating. Once the dimensions of all fragments become so small that the substrate is no longer capable of transferring the breaking stress to them, this disintegration process is terminated. For the above reasons, the dimensions of the fragments finally become more or less equal to each other and the resultant size distribution of the fractured fragments formed on the surface of the polymer substrate is very narrow.

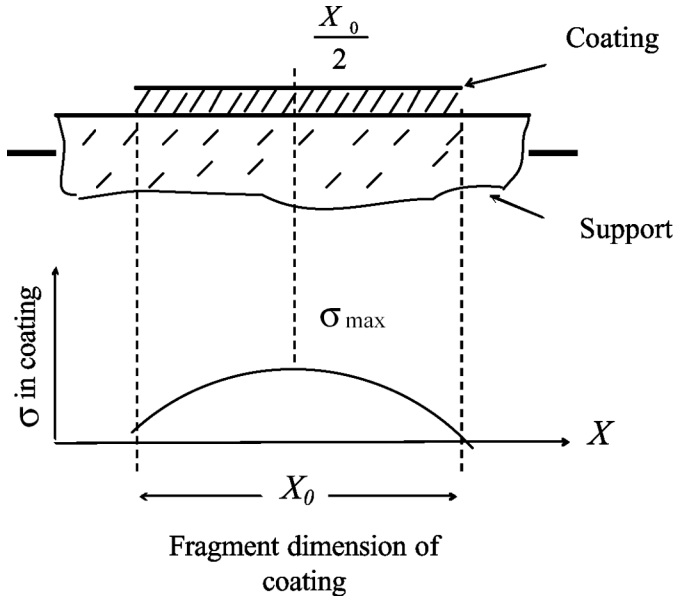

Figure 3. Schematic representation of stress distribution in a fragment of the coating during tensile drawing of the polymer substrate. X_0 is the size of the fragment. Arrows show the direction of stretching.

Hence, one can conclude that fracture of a coating on a rubbery polymer substrate proceeds via both random fracture and disintegration of the fragments into two parts.

The mechanism of coating fragmentation during nonuniform polymer deformation (via necking) at temperatures below Tg has not yet been studied from this standpoint.

Figure l(c) presents an AFM image where fracture (into two parts) of some fragments formed during uniaxial stretching of a glassy PET sample with a gold coating is seen to begin in their central regions. This observation implies that the possibility of coating fracture via disintegration into two parts is not excluded even during deformation of a glassy polymer that is accompanied by neck formation. As is known, the deformation of a glassy polymer is largely controlled by the initial content of defects. Evidently, disintegration of the coating into individual fragments at the first moment of neck formation will also proceed randomly (via the detachment mechanism) at stress concentration sites. However, both the width and the thickness of the sample in the region of the originating neck sharply decrease at the same time; this decrease corresponds to the natural draw ratio of polymer, and the true tensile stress in the region of the forming neck increases. If this stress exceeds

the strength of the coating in the central part, further disintegration of the metal takes place and this process will develop until the cross section of the sample ceases to charge and the tensile stress during further stretching becomes invariable. Let us mention that earlier studies analyzing the mechanism of fracture of a thin rigid coating on a polymer substrate or in similar fiber-filled polymer systems usually consider the average dimensions of the fractured fragments. The analysis of size distribution of these fragments allows one to gain far more complete information concerning fracture processes in the coating during deformation of the polymer substrate. Nevertheless, such analysis has still been described in only a few publications[5] and confirmed mainly the deformation of PET samples with a thin aluminum coating. To unambiguously answer the question about the actual predominant mechanism of the coating fragmentation during tensile drawing of a glassy polymer that deforms via necking, statistical analysis of fragment widths was performed, the corresponding size distribution curves were plotted, and their relative variances were estimated.

As was shown earlier,[5] random fracture of a coating leads to a wide width distribution of the fragments and the relative variance is close to unity. When fracture of fragments proceeds via their disintegration into two equal parts, the corresponding width distribution is narrow and the relative variance is ~ 0.2. In this study, the width distribution of fragments of platinum or gold coatings deposited on a PET substrate is analyzed. Stretching was performed at room temperature, where PET exists in the glassy state.

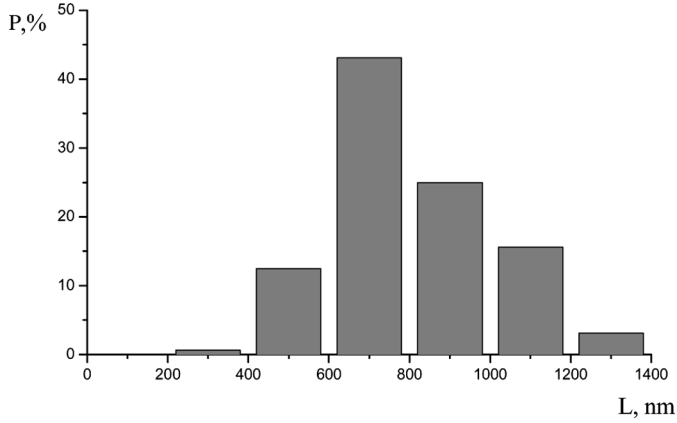

Figure 4. Fragment width distribution curve for PET films with a gold coating of the thickness of 5.4 nm after their stretching at 20°C at a strain rate of 0.2 mm/min. P is probability of fragments with given dimensions.

Figure 4 presents the typical size distribution curve of gold fragments for a PET sample stretched at 20°C. The thickness of the deposited gold layer was 5.4 nm. As can be seen, the width distribution of the fragments is fairly narrow and shows a distinct maximum. The relative probability of this distribution is 0.27 for gold and 0.38 for platinum. This observation implies that, during stretching of glassy PET, fragmentation of a rigid coating primarily proceeds via disintegration of each randomly formed fragment into two equal parts.

Thus, plastic deformation of glassy PET with a rigid metallic coating is accompanied by fracture of the surface layer in the region of the forming neck. Nucleation of initial cracks is random; however, the predominant mechanism is disintegration of fragments into two equal parts and the final width of the fragments is controlled by this mechanism. In conclusion, let us mention that a similar mechanism of coating fragmentation was also proposed for uniaxial stretching of PET at temperatures above its *Tg*. However, the width distribution of fragments formed during tensile drawing of glassy PET is narrower and has a smaller relative variance, indicating more marked influence of the mechanism of fragment disintegration into two equal parts.

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