Multiple Cracking of Rigid Platinum Film Covering Polymer Substrate

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ABSTRACT: Multiple cracking of a thin platinum film deposited on polyethylene terephtalate, isoprene rubber, and natural rubber substrates under tensile deformation was studied by light and scanning electron microscopy. The cover fractures on several fragments elongated in the direction perpendicular to the loading direction. The width of the fractured platinum fragments depends on the thickness of the deposited layer and applied tensile stress. A semiempirical equation describing the average width of the cover fragments was obtained. Appearance of a wavy pattern on an originally smooth surface of composites with rubberlike polymer substrate was observed. The mechanism of the appearance of the surface wave is a mechanical buckling instability of the cover under compressive force. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1267–1275, 1999

Key words: coating; cracking; polymer

INTRODUCTION

Tensile loading of homogeneous materials usually leads to its fracture by separation of a sample on two parts. In composite materials made of different components, multiple cracking of the more brittle component on several fragments is often observed. Multiple cracking of glass or carbon fibers is typical for fiber-reinforced composites with epoxy matrices.[1] Similar behavior was observed in multilayer bisphenol-A polycarbonate/poly(styrene-*co*-acrylonitrile) (PC/SAN) composites consisting of alternating layers of comparatively brittle SAN and ductile polycarbonate.[2]

Tensile deformation of a two-layer composite, a polyimide covered with a thin (only tens of nanometers in thickness) copper or chromium film, was studied.[3] Elongation resulted in multiple cracking of the cover and appearance of a two-dimensional irregular network of cracks. Regular cracking of a metal layer on long and comparatively narrow bands, oriented perpendicularly to the elongation direction, was observed in polyethylene terephtalate (PET) covered by platinum.[4,5]

The goal of the present work was to study multiple cracking of a thin (≈10 nm) platinum cover deposited on PET and natural rubber.

EXPERIMENTAL

Commercial films of amorphous unoriented PET, synthetic isoprene rubber (SR), and natural rubber (NR) were used as a polymer substrate. The PET film was 100-μm thick. The NR was crosslinked at 150°C by 4 weight parts of dicumyl

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peroxide per 100 weight parts of raw rubber. The SR was crosslinked at 150°C by 1.5 weight parts of dicumyl peroxide per 100 weight parts of the rubber. The NR and SR layers were 500-μm thick. Samples, dumbbell in shape, were cut from the polymer layer. The gauge of samples was 6 $\times$ 22 mm.

The method of ion deposition was used to cover specimens with a thin ($\approx$10-nm thick) platinum layer. Then the specimen was elongated with the universal testing machine (Instron model 1122). Rubber samples were elongated in special hand-operated clamps. After elongation, cracked metal surface was covered by the second platinum layer and studied with a Hitachi S-520 scanning electron microscope (SEM).

The dynamic elasticity modulus of PET was studied with a Rheometrics solids analyzer at 31-Hz frequency and 2°C/min heating rate.

The thickness of the platinum layer was changed by variation of time of metal deposition. Control measurements of the cover thickness were made by depositing a platinum layer on a glass plate. After that, the cover was scratched, and the depth of the scratch in the platinum layer was measured by a nanoscope atomic-force microscope (Digital Instruments, Santa Barbara, CA) in contact force regime. The probe–sample interaction force was maintained constant and equal to 10^{-9} N. The cover thickness was proportional to time of metal deposition. The coefficient of proportionality was found, thus determining the thickness of the platinum layer as a function of deposition time.

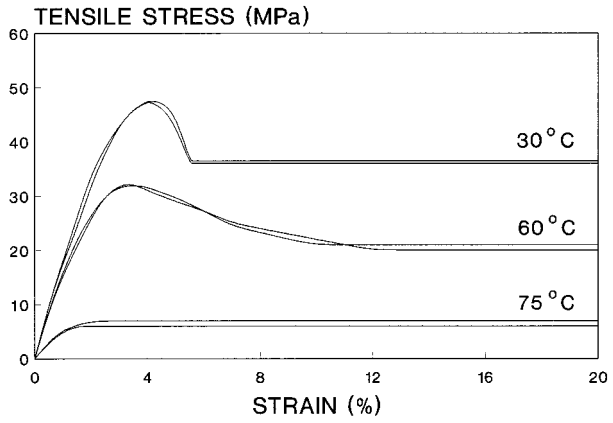

Figure 1 Stress–strain curves for pure PET and Pt/PET composites at 30, 60, and 75°C.

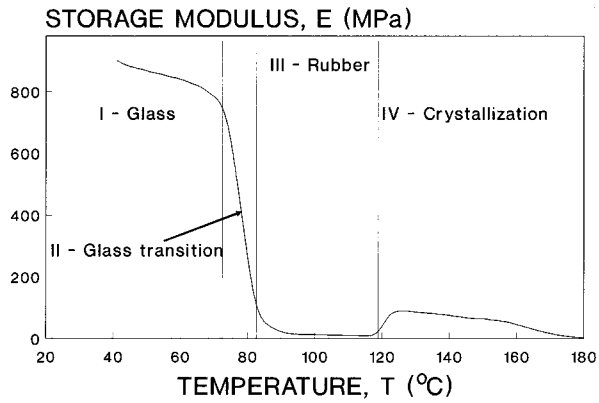

Figure 2 Elasticity storage modulus E' of PET plotted against elongation temperature T.

RESULTS

Mechanical Properties

Figure 1 shows the stress–strain curves for pure PET and Pt/PET composites at different elongation temperatures. Curves for pure and covered PET practically coincide due to an approximate 10,000-fold lower thickness of the cover in comparison to that of the PET substrate. The difference is within data scattering for different pure PET specimens. In the glass-state region, the stress has a maximum related to necking of PET. The yield stress reduces with increased temperature. In the glass transition (T_g) region (75–80°C), the maximum stress is not observed and the polymer deforms uniformly. At temperatures higher than T_g, the yield stress of PET is too low, and reliable stress–strain curves were not obtained. To characterize mechanical properties of PET at temperatures higher than T_g, dynamic storage modulus was measured.

Figure 2 shows dynamic storage modulus of PET plotted against test temperature T. Four different regions can be distinguished in the curve. In the glass state region (I), storage modulus E' slowly reduces with increased temperature. In the second, glass transition, region E' abruptly drops. In the third region, PET is in rubberlike state, and E' slowly reduces with an increase in temperature. In the forth region, PET crystallizes, and a significant increase in elasticity modulus E' is observed.

Figure 3 shows the stress–strain curve for an isoprene rubber at room temperature. Tensile stress monotonically increases with strain.

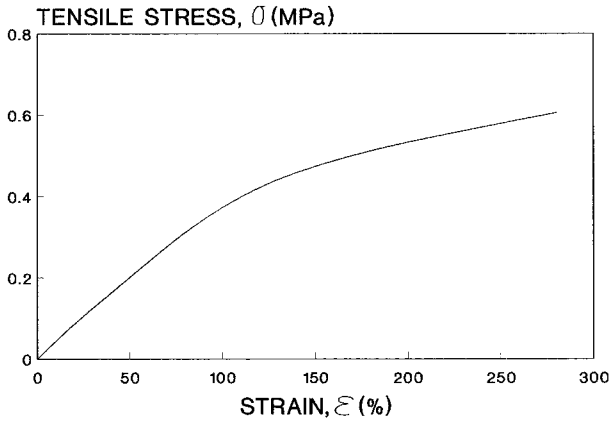

Figure 3 Stress–strain curves for pure isoprene rubber at room temperature.

Cracking in Pt/PET

An increase in temperature resulted in transitions in the mechanism of the cover cracking in Pt/PET composites. Cover cracking was different in the regions of glass state of the polymer (I in Fig. 2), glass transition region (II), region of rubberlike state (III), and in the region of PET crystallization (IV). Figures 4–7 show SEM micrographs of Pt/PET after elongation to 100% strain at 18, 75, 90, and 115°C. Figure 4 shows the surface of Pt/PET composite after elongation in the arrowed direction at 18°C when PET is in the glass state region. The coating fractures on thin elongated fragments appear lighter on the photograph. Darker regions are PET between cracked cover fragments. Cover fragments are uneven, oriented preferably perpendicularly to the tension direction, and form a two-dimensional network.

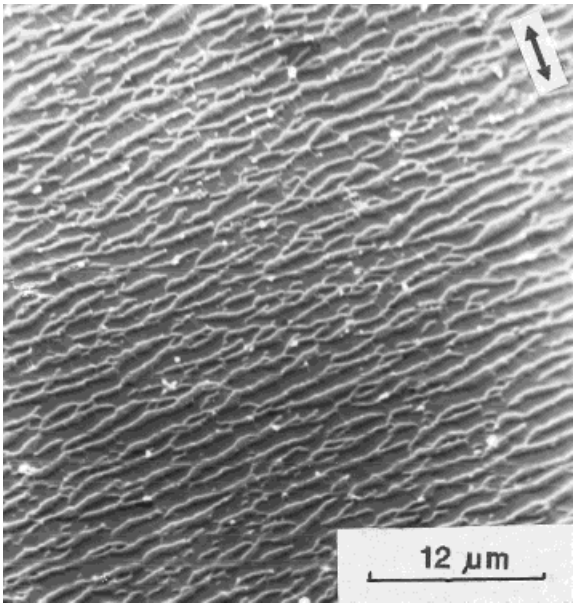

Figure 4 SEM micrograph of Pt/PET composite after elongation to 100% strain at 18°C. The direction of elongation is shown by the arrow.

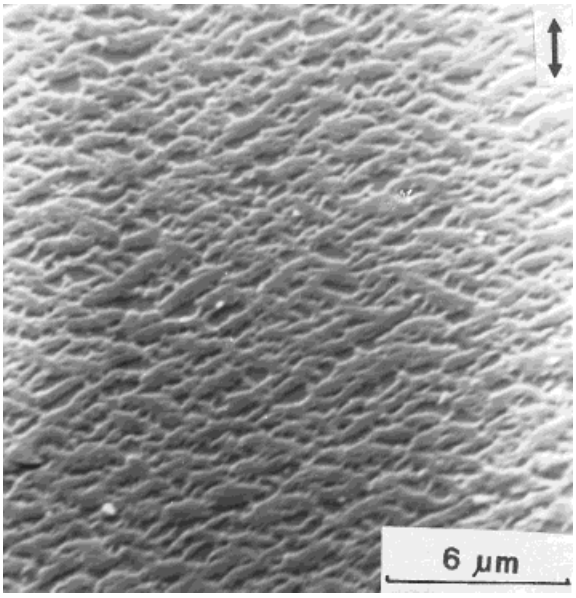

Figure 5 SEM micrograph of Pt/PET composite after elongation to 100% strain at 75°C.

Figure 5 shows the surface of Pt/PET composite after elongation at 75°C, in glass transition region of Pt substrate (II in Fig. 2). The coating fragments are oriented under an angle of ±30-35° to the elongation direction. This allows to assume that on the microscopic level, PET yields in shear slip lines despite yielding is uniform on macroscopic level.

Figure 6(a) shows an SEM micrograph of the Pt/PET elongated at temperature of 90°C, in the rubber-state region of the substrate. The cover fractures on bands oriented perpendicularly to the elongation direction. The Pt bands are broader than in Figure 4. In addition, a periodic wavelike pattern is observed on the surface. The wave appears both on the metal and the polymer separating the cracked metal bands. Cooperative deformation of the substrate and the cover indicates that the cover is well adhered to the polymer. Appearance of the wave on an originally smooth surface is caused by mechanical buckling instability of the cover under compressive force arising in the lateral direction.[4,5] The volume of PET in the rubberlike state does not change at elongation, and the specimen is contracted in the

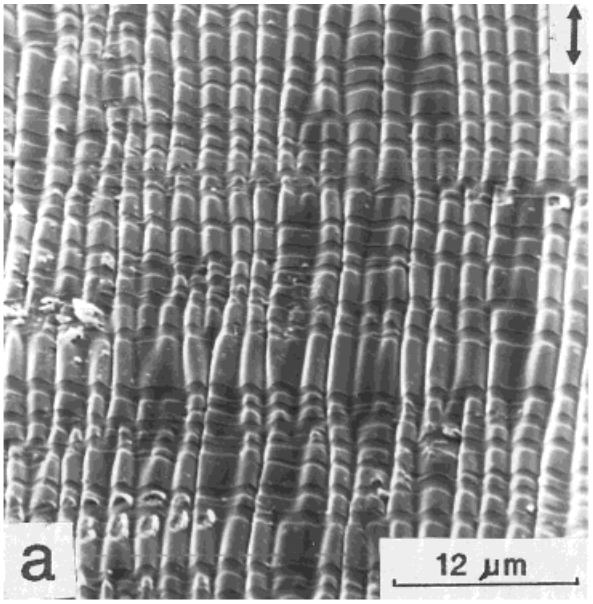

Figure 6 (a) SEM micrograph of Pt/PET after elongation to 100% strain at 90°C; (b) schematic drawing illustrating the surface wave.

lateral direction. This contraction leads to compression of the cover. Figure 6(b) illustrates schematically the mechanism of appearance of the surface wave.

Figure 7 shows an SEM micrograph of the Pt/PET elongated at 115°C. The coating fragments form a continuous network as in Figure 4. The cover fragments are comparatively uniform in width. Their width is smaller than in Figure 6(a). The surface of the specimen is wavy.

Figure 8 shows the average width of the platinum fragments in Pt/PET composite plotted against temperature of elongation. The dependence reflects temperature transitions described in Figure 2. The width of metal fragments in the

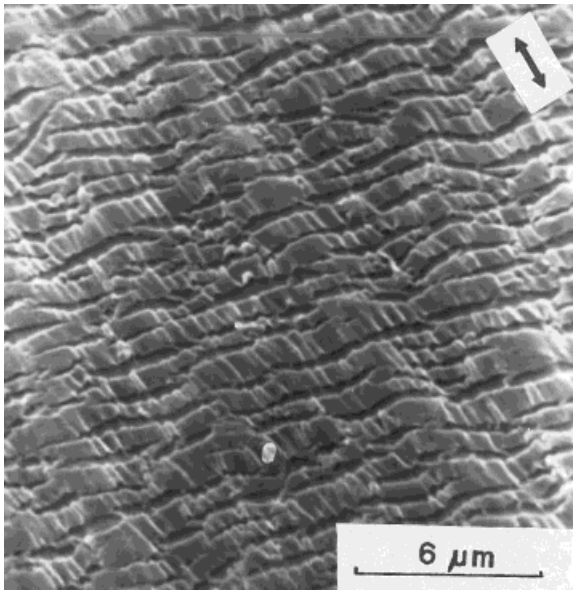

Figure 7 SEM micrograph of Pt/PET after elongation to 100% strain at 115°C.

glass state region slowly increases with increasing temperature. In the glass transition region, the width of the metal fragments increases abruptly with temperature. In the rubber-state region, the width of metal bands increases moderately with increasing temperature. Finally, crystallization of PET leads to an abrupt decrease in the width of the platinum fragments.

Comparison of Figures 8 and 2 shows that the width of the cover fragments and the elasticity modulus of PET substrate are related. The width of the cover fragments increases with decreased elasticity modulus of the substrate and vice versa.

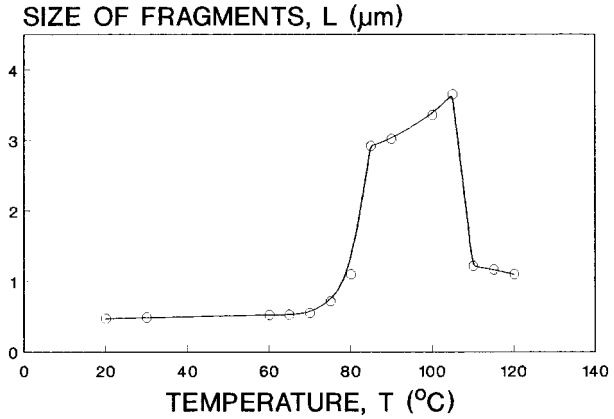

Figure 8 The width of cover fragments in Pt/PET composite L plotted against temperature of elongation T.

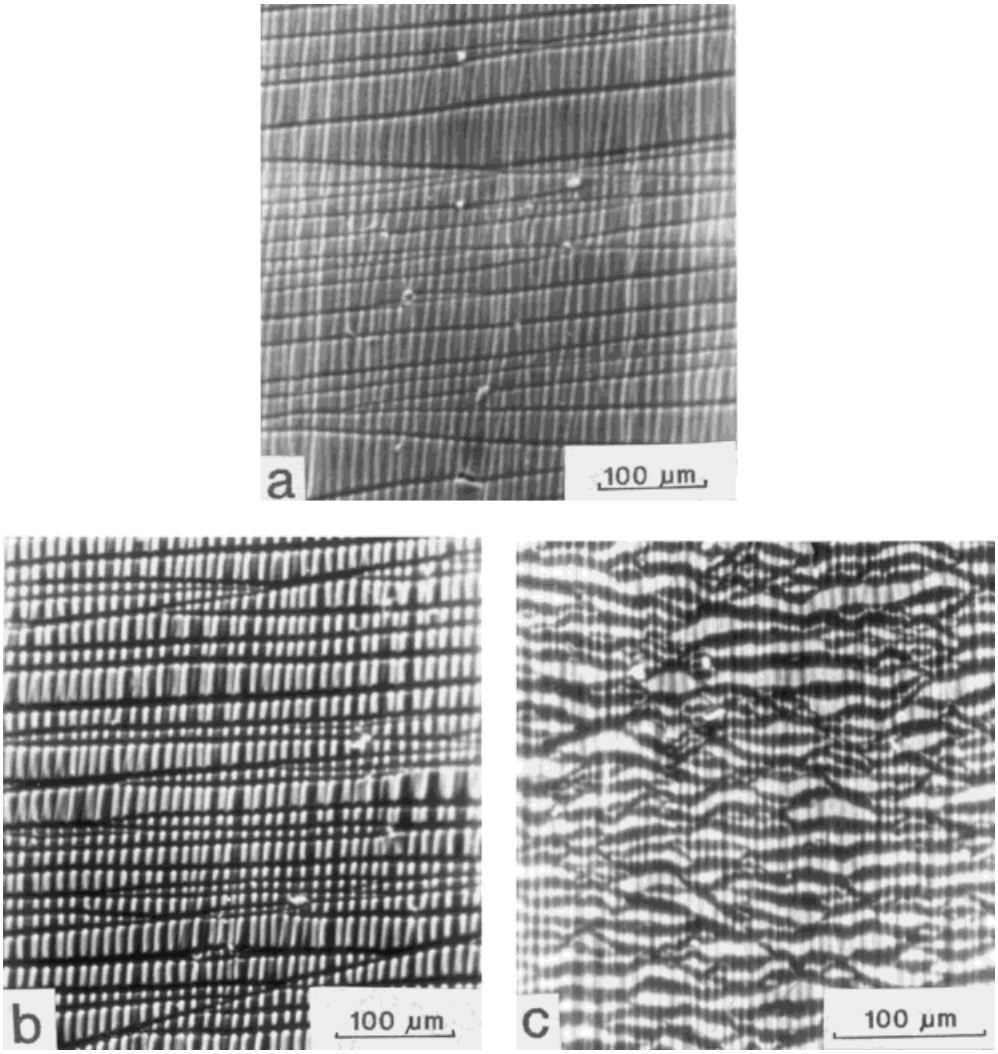

Figure 9 SEM micrographs of isoprene rubber coated by Pt after elongation in the vertical direction to 25% (a), 100% (b), and 400% (c) at room temperature.

Thus, cracking of the cover depends on mechanical properties of the substrate.

Cracking in Pt/Isoprene Rubber

First cracks in the Pt/rubber composites were observed at strain of 2%. Figure 9 shows SEM micrographs of a Pt/isoprene rubber after elongation to strains of 25% (a), 100% (b), and 400% (c) at room temperature. Cracking of the Pt cover at 25 and 100% strain is similar to that in the Pt/PET composite when the polymer substrate is in a rubberlike state [Fig. 6(a)]. The cover in Figure 9(a) and (b) is fractured on long bands oriented perpendicularly to the loading direction. The texture of the surface is wavy, and the wave crests are parallel to the loading direction. At a strain of 400% [Fig. 9(c)], the cover fragments are uneven and limited in length due to progressive cracking of the cover. The Pt cover fragments at 400% strain resemble Pt fragments in Pt/PET after elongation at temperatures of 18 and 115°C.

The first cracks in the Pt/rubber composite were observed at strain of 2%. Hence, initially Pt film behaves as a quasi-brittle material. Deformation of the cover at 100% elongation [Fig. 6(b)] was estimated by measuring the total width of band along the loading direction. The total length of the deformed cover was determined and divided into the initial length of the specimen. The average tensile strain of the cover is 55%; fracture strain of Pt in bulk is 45%.[6] Thus, the cover film on a nanoscale level remains ductile, and its frac-

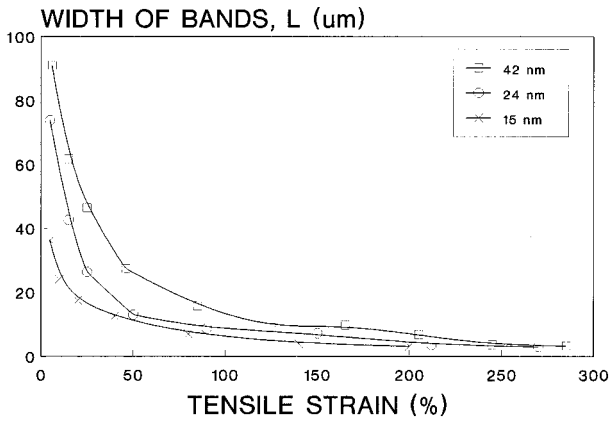

Figure 10 Width of cover fragments in Pt/SR, L, plotted against tensile strain for thickness of the cover layers of 15, 24, and 42 nm.

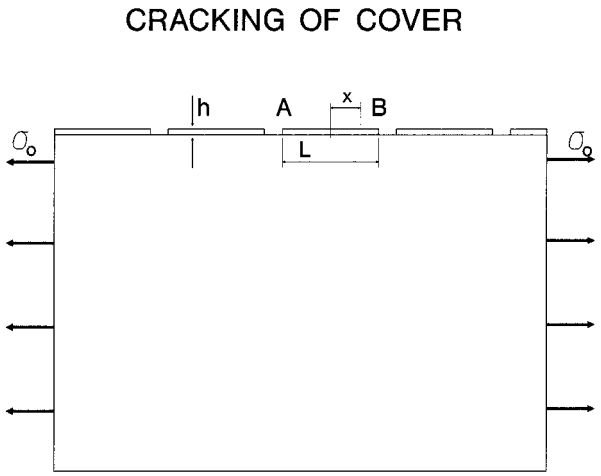

Figure 12 Schematic drawing illustrating cracking of the cover.

ture strain is close to that in bulk. Behavior of the cover is different at low strains, possibly due to defects in the cover.

Figure 10 shows the width of platinum fragments plotted against tensile strain for Pt/SR composites with three different thickness of the cover layer. The average width of the cover fragments gradually decreases with an increase in tensile strain up to 200%. At strains exceeding 200%, the width of the metal band is almost independent of strain, and the cracking rate reduces. The mechanical behavior of PET and NR is quite different. Despite this, the effect of tensile stress in the substrate on the width of the cover fragments is similar. An increase in stress leads to a decrease in fragment width for both rubber and PET substrates.

Figure 11 shows the average width of the cover bands in Pt/SR plotted against the thickness of cover at tensile strain of 30%. The average width of the cover bands is proportional to the thickness of the cover. Thus, multiple cracking of the rigid cover at tension is determined by mechanical characteristics of the polymer substrate, thickness of the deposited Pt layer, and tensile strain of the specimen.

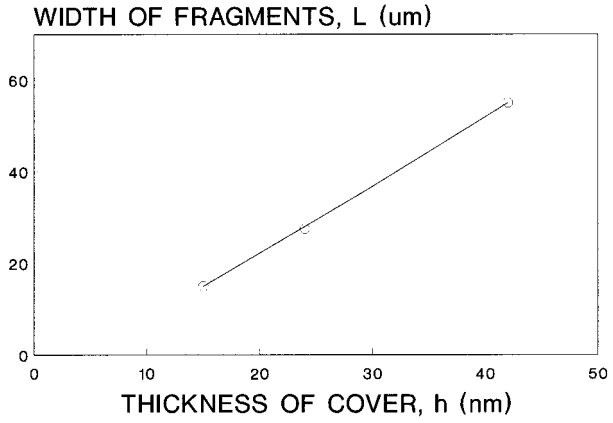

Figure 11 Width of cover fragments in Pt/SR, L, plotted against the thickness of the cover, h.

Theory

Here the theoretical solution for the average width of the cover bands is found. The phenomenon is analyzed by using the model shown schematically in Figure 12. The upper surface of the cover is free, and its lower surface is well adhered to an elastic semiplane. The coordinate system is defined so that the X-axis is oriented along the surface. After cracking, the stress in the cover in the points A and B in Figure 12 is equal to 0. Due to adhesion with the substrate, the stress in the cover increases when the distance from the crack increases. Stress distribution in a single band, adhered to a linearly elastic semiplane, was found approximately in assumption of small deformations,[7]

$$\sigma_f = \frac{\sigma_0}{2h(1 + d/\sqrt{2})} \sqrt{L^2/4 - x^2} \qquad (1)$$

where σ_f is the tensile stress in the cover, σ_0 is the stress in the substrate, h is the thickness of the cover, x is the distance from the midpoint of the band, L is the width of the band, d is the dimen-

sionless coefficient equal to $LE/4hE_f$, and E and E_f are elastic moduli of the substrate and the cover. It is worth mentioning that this equation considers singularity of stress near the band end.

Tensile stress is maximum at $x = 0$, in the midpoint of the cover band. For the foregoing composites, the thickness of the cover is 10–40 nm, the width of the cover bands is 1–10 μm (Figs. 4–7), and the ratio of moduli E/E_f is $\approx 10^{-5}$. For such E/E_f ratios, the coefficient d is negligible in comparison with unity in the denominator of eq. (1). Considering $d \ll 1$, the maximum stress at the midpoint of the cover band is

$$\sigma_f = \frac{\sigma_0 L}{4h} \tag{2}$$

Assuming that the band fractures when the stress σ reaches the ultimate strength of the cover material σ^*, the width of the band is given by

$$L = \frac{4h\sigma^*}{\sigma_0} \tag{3}$$

Equation (3) describes progressive cracking of the cover into smaller fragments with increasing applied stress in the substrate σ_0. At the qualitative level, this equation describes the foregoing experimental data. It explains a direct proportionality between the size of the cover bands and the thickness of the deposited cover film, and the decrease in the band width with an increase in applied stress σ_0. In addition, it explains why the width of the cover bands is sensitive to transitions in the polymer state.

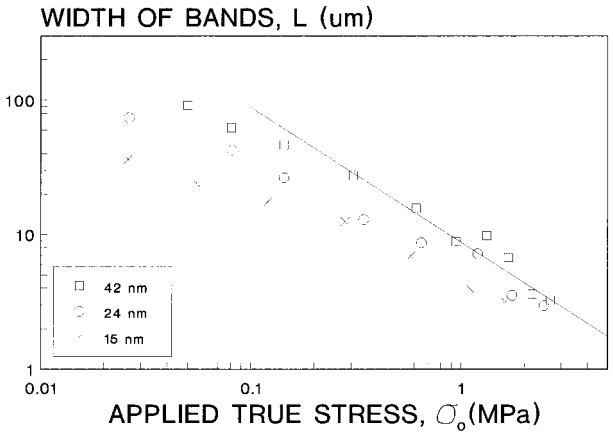

Figure 13 Width of cover fragments in Pt/SR, L, plotted against true stress in the rubber substrate σ_0.

Figure 13 shows the average width of the Pt bands plotted against the true stress in the SR substrate in double logarithmic coordinates. At equal applied stress, the width of the bands increases with thickness of the deposited cover. At $\sigma > 0.15$ MPa (tensile strain $> 40\%$), experimental data are described by the straight line with the slope of -1. In double-log plots, the straight line describes a power function with an index equal to the slope of the straight line. Thus, at strains $\varepsilon > 40\%$, $L \sim 1/\sigma_0$, in agreement with eq. (3). At low stress, $\sigma_0 < 0.15$ MPa, the curves deviate from the straight line and hence from the reverse proportionality between the width of the bands and the stress in the substrate. At low strains, the thickness of the cover bands is lower than expected from eq. (3). This may be caused by defects in the cover.

The straight line in Figure 13 shows the dependence predicted by eq. (3) for a 15-μm thick cover. To calculate the width of the cover band, the ultimate fracture strength of the cover ($\sigma^* = 145$ MPa[6]), thickness of the cover ($h = 15$ nm), and applied stress (σ_0) were substituted into eq. (3). The strength of the cover film was assumed to equal the strength of the platinum in bulk. This assumption is based on the conclusion that Pt film is ductile at comparatively high strains.

The theoretical curve is a straight line with the slope equal to -1. Experimental values of the band width (x) at $\varepsilon > 40\%$ are approximately two times lower than the theoretical estimates. Therefore, experimental data are better described by the following semiempirical equation:

$$L = \frac{2h\sigma^*}{\sigma_0} \tag{4}$$

Such agreement between experimental data and theory is satisfactory, especially considering assumptions made in the derivation of eq. (2) and the assumption that the strength of platinum film is equal to the strength of platinum in bulk. At low strains this assumption is not fulfilled, and deviation from the reverse proportionality between the width of the bands and the stress in the substrate is observed.

DISCUSSION

Here the mechanism of multiple cracking of the cover is discussed. Platinum in bulk is ductile

metal, and its fracture strain is 45%.[6] However, multiple cracking of the Pt cover is observed at a strain of 2%. This may be caused by defects in the cover. Further deformation leads to an increase in fracture strain of the cover. Platinum films on the nanometer scale level are ductile.

On the first sight, multiple cracking of the cover in two-layer composite with a soft substrate resembles multiple breakage of fibers in fiber-reinforced plastics. However, there is a difference in the mechanisms of cracking. To demonstrate this difference, the mechanism of fiber breakage is reviewed.

Figure 14 shows typical stress distribution in a fiber embedded in an epoxy matrix and loaded along the fiber direction. The fiber length is L. The stress at the fiber ends is equal to 0 and increases with distance from the fiber end. Far from the fiber ends, the magnitude of stress asymptotically approaches the stress in an infinite unbroken fiber. This stress is given by Hook's law: $\sigma_f = E_f\varepsilon$, where E_f is the Young's modulus of the fiber. Near the fiber ends, the stress is essentially less than σ_f. The length of the end parts is called the ineffective length of fiber L_c.[1,7]

In fiber-reinforced plastics, ineffective length is usually shorter than fiber length, $L_c \ll L$. Brittle fibers have scattering in their strength, related to the presence of defects. The fiber breaks when the applied stress reaches its strength in some weak point. Multiple breakage of a fiber is caused by an increase in applied stress and presence by defects. When the fiber breaks to length equal to the double ineffective length $2L_c$, cracking stops.

Mechanism of cracking in two-layer composites with soft substrates at high strain is different.

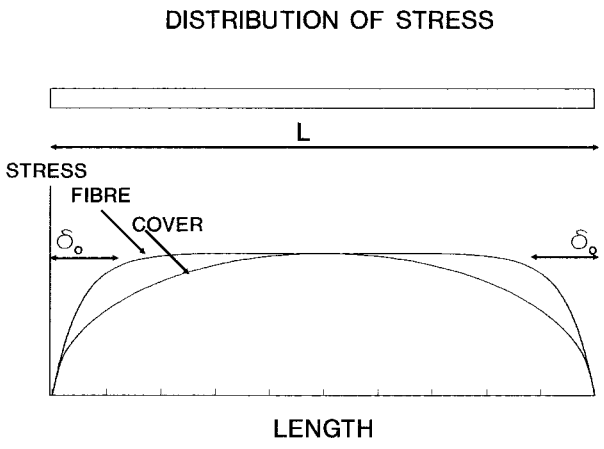

Figure 14 Schematic drawing showing distribution of stress in a fiber in fiber-reinforced composite and in a cover adhered to a polymer substrate.

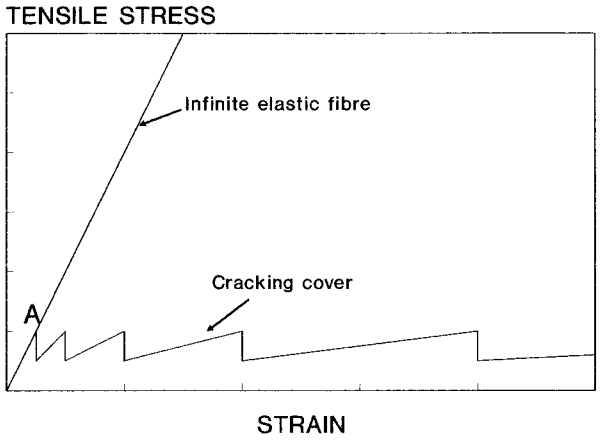

Figure 15 Schematic drawing showing tensile stress in an infinite fiber and in the midpoint of a cover plotted against tensile strain. Drops in load are caused by cracking of the cover on 2, 4, 8, 16, etc. parts.

The distribution of stress in a cover layer is presented in Figure 14. The stress in the midpoint of a band at low strain is close to that in an infinite band. The coefficient d in the denominator of eq. (1) is much >1. Considering $d \gg 1$ the maximum stress at the midpoint of the cover band is

$$\sigma = \frac{2^{1/2}\sigma_0 E_1}{E} \tag{5}$$

where σ_0/E is the strain in the substrate and eq. (5) is similar to Hook's law for the cover. The coefficient $2^{1/2}$ is caused by inaccuracy of eq. (1). (In an exact equation this coefficient should = 1.) The case $d \gg 1$ corresponds to the initial stage of the cover cracking, when the band ends do not reduce the stress in the midpoint of the band. At some strain, the width of the cover bands decreases, so that the coefficient d in the denominator of eq. (1) = 1. In this case the band ends (cracks) affect stress even in the midpoint of the bands. The critical width of the cover bands is found considering $d = 1$ as

$$L_c = \frac{4hE_f}{E} \tag{6}$$

The length L_c is analogous to a fiber's ineffective length in fiber-reinforced composites. Moreover, eq. (6) determines the ineffective length for composites with extremely low fiber contents. For Pt/NR and Pt/PET composites, typical values of L_c are estimated as 0.5–5 mm. At $L < L_c$, the

effect of the ends of the cover band on the entire width of the band cannot be neglected. Hence, in this case cracking of the cover is determined primarily by the ability of the substrate to load the cover, rather than by defects and statistical nature of the cover strength.

Figure 15 shows schematically the stress in the midpoint of the cover band plotted against applied tensile strain. At low strains, cracks do not affect the stress in the band midpoint, and the stress is described by Hook's law, eq. (5). In the point A, the band width decreases to $L = L_c$, and the band fracture leads to drop in stress. Following deformation leads to loading of the cover, its cracking, and drops in load. The stress in the cover in this case is much lower than it should be in a continuous uncracked cover.

CONCLUSIONS

1. In Pt/PET and Pt/NR composites, the platinum cover fractures on several fragments elongated perpendicularly to the loading direction. The width of the platinum fragments depends on the thickness of the deposited layer and the tensile stress in the polymer substrate.
2. A theoretical equation describing the average width of the cover fragments was obtained.
3. The width of cover bands L is determined mainly by the ability of the substrate to transfer load to the cracked cover. L is reversely proportional to the stress in the substrate. This behavior is typical for narrow bands when their width is lower than the cover ineffective length given by eq. (6).
4. The appearance of a periodic wavy pattern on an originally smooth surface of composites with rubberlike polymer substrate was observed. The mechanism of the appearance of this surface wave is a mechanical buckling instability of the cover under compressive force.

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