

A Rigid Coating on a Soft Substratum Polymer–Polymer System¹

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Abstract—Two procedures for the preparation of a rigid coating on a soft substratum polymer–polymer system were advanced. According to the first procedure, a thin film of a rigid-chain polymer (NC) is deposited onto a surface of a thick film of a flexible-chain polymer (PI and PET). In the second procedure, a rigid coating is formed by the chemical modification of a thin-surface PS layer. As was shown, the uniaxial stretching of the as-formed polymer systems is accompanied by multiple fragmentation of the rigid coating and the development of a regular microrelief. Similar phenomena have been observed earlier when studying a rigid coating on a soft substratum system based on a polymer with a deposited low-molecular-mass coating. The regular fragmentation of the coating and the development of a regular surface relief represent a characteristic property of a rigid coating on a soft substratum system, independently of its nature.

INTRODUCTION

In recent years, a new scientific direction related to study of the structural mechanical behavior of polymer films with a rigid coating has been intensively developed [1, 2]. As has been shown, the deformation of such systems is accompanied by a certain mode of surface structuring, and this approach offers a simple means for preparing polymer films with a regular surface microrelief. In this connection, the above systems seem to be attractive from the viewpoint of the preparation of polymer films with valuable optical properties [3], as well as for the formation of new types of polymer substrates capable of orienting liquid crystals [4]. The above structural mechanical features of polymer films with a rigid coating open new routes for the preparation of new types of advanced shatter-resistant polymeric screens for displays of various sizes. Therefore, the search for new polymer–coating systems which make it possible to prepare new types of polymeric materials is of particular importance.

Let us mention that all specific features of a unique surface structuring phenomenon have been illustrated through the deformation of polymers with a rigid low-molecular-mass coating (metals, carbon, oxides, etc.) [1–4]. This work aims at preparation of a rigid coating on a soft substratum polymer–polymer system and characterization of its structural mechanical behavior.

EXPERIMENTAL

In this work, we used commercial films of an amorphous unoriented PET with a thickness of 100 μm . The films of isoprene rubber (thickness 500 μm) were prepared by crosslinking 100 wt parts of a raw rubber with 1.5 wt parts of dicumyl peroxide at 150°C. Isotropic PS films with a thickness of 90–110 μm were prepared by molding a granulated PS at 150°C as disks with a diameter of 7 cm. The above films were cut into dumbbell-shaped samples with a gage size of 6 \times 22 mm.

Currently, two approaches for the preparation of a rigid coating on a soft substratum polymer–polymer system are advanced. The first approach involves the deposition of a thin layer of a rigid-chain polymer on the surface of a polymer substrate. Actually, we deal with a well-known procedure for the preparation of thin supported films for transmission microscopy [5]. The calculated quantity of a 1% solution of nitrocellulose (colloxylin) in isoamyl acetate was deposited onto the surface of distilled water. Upon solvent evaporation, a thin NC film was formed on the water surface. The amount of NC solution was selected so that the thickness of the as-formed film was \sim 1 μm . Prior to this procedure, rubber or PET samples were placed onto the bottom of a laboratory vessel filled with water. Once the film was formed, water was carefully decanted; as a result, a thin NC film was deposited on the surface of the polymer samples. Upon further drying, one may obtain samples of flexible-chain polymers with a thin coating based on rigid-chain polymer.

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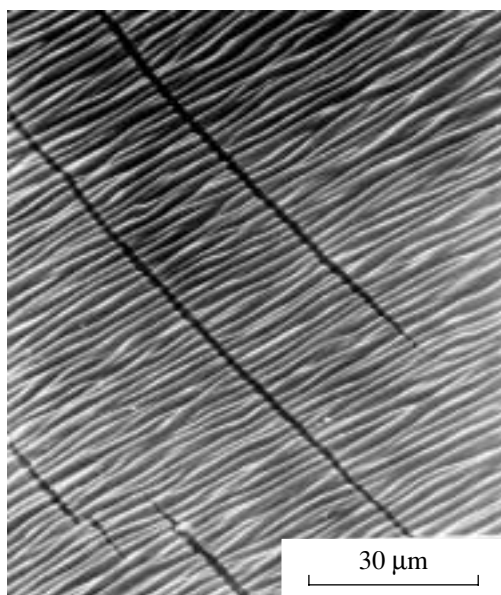


Fig. 1. Scanning electron micrograph of the surface of the PET film with a thin ($\sim 1 \mu\text{m}$) NC coating. The film was stretched at 90°C to a tensile strain of 70% at a strain rate of 1 mm/min.

The second approach to the preparation of a rigid coating on the surface of polymer film involves the chemical modification of a thin surface polymer layer. Such surface modification of polymers may be carried out via either their chemical [6] or plasma treatment [7].

In this work, a PS film was treated with a nitration mixture ($\text{H}_2\text{SO}_4 : \text{HNO}_3 = 1 : 1$) at $30\text{--}60^\circ\text{C}$ for 2–60 s. As a result of the treatment, the surface is coated with a thin nitrated polystyrene layer and the thickness of this layer depends on the temperature and time of exposure. The as-prepared sample was then treated with a reducing agent at 40°C for 30 min. Under the action of the reducing agent, nitrated polystyrene on the surface layer is transformed into aminated polystyrene, which appears as a rigid infusible film on the PS surface. As reducing agents, we used hydrazine, hydrogen sulfide, a basic solution of hydroquinone, *in statu nascendi* hydrogen, etc. By varying the duration and temperature of nitration, the nature of the reducing agent, and the reduction regime, one may control the thickness and properties of the surface film.

The as-prepared samples were stretched to a given tensile strain (PET and PS samples were drawn on an Instron-1122 tensile machine at $90\text{--}110^\circ\text{C}$; rubber samples were stretched using hand-operated clamps at room temperature). Electron microscopic studies were performed on a Hitachi S-520 scanning electron microscope. The samples for electron microscopic studies were prepared according to a standard procedure and decorated with platinum.

RESULTS AND DISCUSSION

PET samples with a thin NC coating were prepared according to the first procedure. The as-prepared samples were stretched to a given tensile strain at tempera-

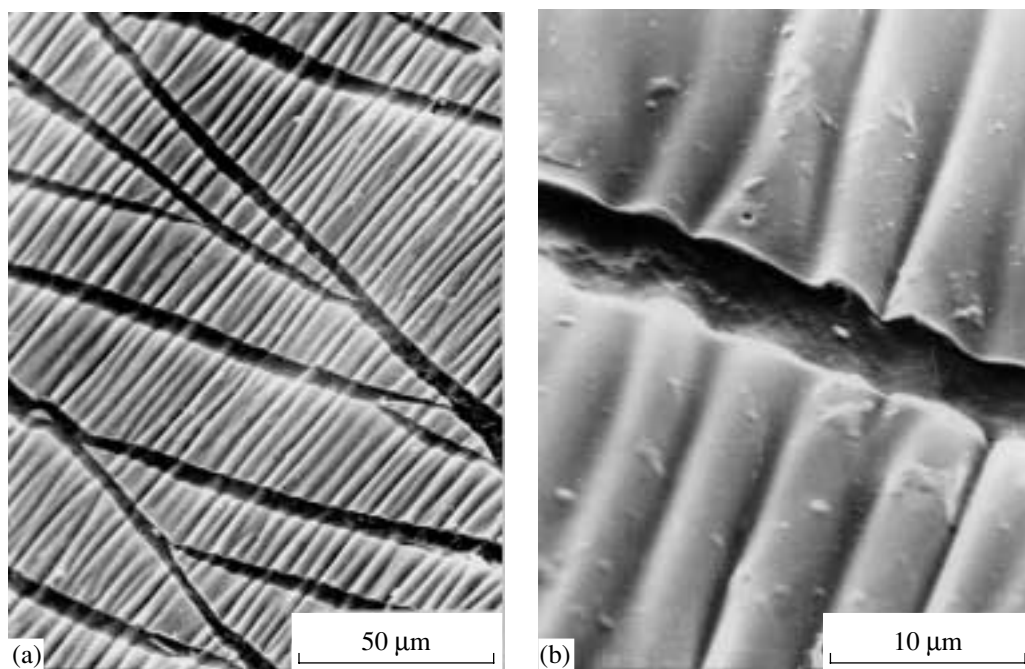


Fig. 2. Scanning electron micrographs of the surface of PI films with a thin ($\sim 1 \mu\text{m}$) NC coating. The film was stretched at room temperature to a tensile strain of 70%. Comments are given in the text.

tures above the glass transition temperature of PET (90°C); then, the samples in their drawn state were cooled down to room temperature and examined using a scanning electron microscope. Typical results of this study are presented in Fig. 1. As follows from Fig. 1, the deformation of polymer-coated polymer films is accompanied by the same structural rearrangements as the deformation of the polymer film with a coating of any other nature [1–3]. Upon tensile drawing, a thin NC coating on the PET surface is seen to produce a regular periodic relief. The identity period of this relief is ~2–2.5 μm . Figure 1 also shows that the deformation of the coated polymer leads to nucleation and growth of the cracks in the direction perpendicular to the drawing axis. In this case, even though tensile strains of the test sample are rather high, cracks do not cross the entire polymer surface as is usually observed upon tensile drawing of other a rigid coating on a soft substratum system [1–3]. The as-formed cracks are characterized by different lengths, which vary from several microns to tens of microns.

Similar results were obtained when studying deformed samples of synthetic rubber with a NC coating. In this case, the polymer sample was stretched at room temperature to a given tensile strain; the as-stretched sample was then placed into a special holder. As follows from Fig. 2a, a regular microrelief is also formed on the polymer surface and fragmentation of the coating occurs. Note that, despite a principal similarity of the above results, the nature of the polymer support has a certain effect on the character of the coating fragmentation. One may easily see that the propagation of cracks in the coating is not linear and the as-formed fragments have no regular shape. The dimensions of fractured fragments of the coating vary in a wide range (from 3 to 30 μm).

This behavior is typical of fragmentation of a brittle coating upon deformation of a rubber support. As was shown in [8], upon tensile drawing of the rubber support, a brittle carbon coating breaks down into fragments with an irregular shape; however, an amazingly regular surface relief also forms. Presently, the reasons for this similarity are not evident because the NC coating cannot be considered as brittle as a carbon coating. Note that the adhesion of the NC coating to the rubber support is far from ideal. At high magnifications (Fig. 2b), one may easily see that the edges of fractured fragments of the NC coating are separated from the rubber surface. This behavior is not exactly unexpected because the thin film of a polar polymer (NC) is located on the hydrocarbon support of the isoprene rubber. Nevertheless, despite this partial separation, this rigid coating on a soft substratum polymer-polymer system shows all its characteristic properties.

Let us consider now the structural mechanical behavior of rigid coating on a soft substratum polymer-polymer system prepared via chemical modification of the surface of a polymer film. Evidently, in this case,

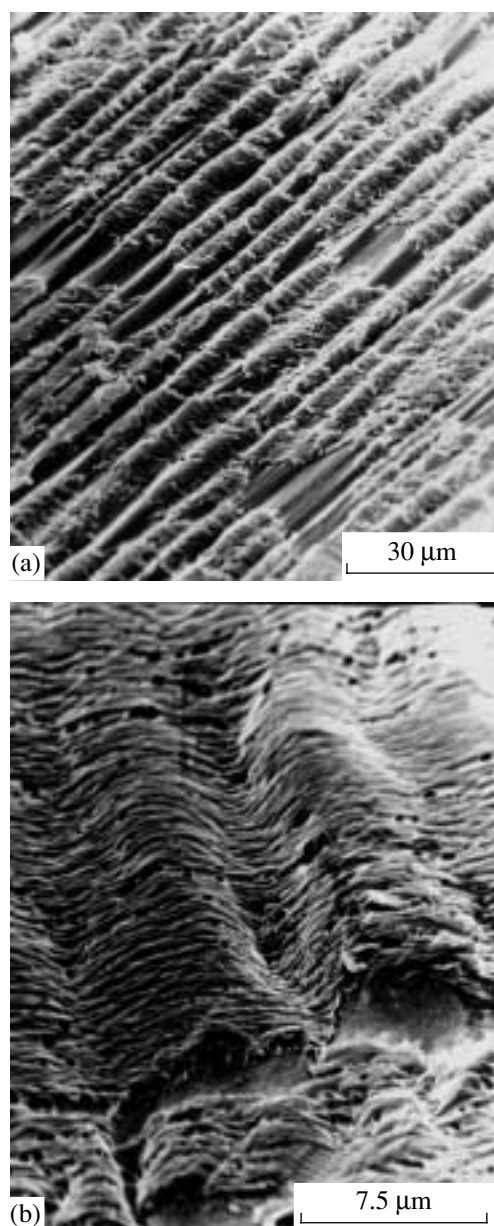


Fig. 3. Scanning electron micrographs of the surface of PS films with a thin modified layer of amino polystyrene. The film was stretched at 110°C to a tensile strain of 100%. Comments are given in the text.

adhesion between a rigid surface layer and a soft polymer matrix is close to ideal. Figure 3a shows the SEM image of the surface of the chemically modified PS film as prepared according to the procedure described in the previous section. This film was stretched to a tensile strain of 100% at 110°C. At this temperature, an unmodified PS core exists above its glass transition temperature, whereas the reinforced surface layer remains rigid and brittle. As can be clearly seen, upon tensile drawing, a rigid surface layer breaks down into fragments with an irregular shape; as a result, the sur-

face of the unmodified PS is cropped out. Note that, under such conditions, the preserved coating fragments, in turn, contain numerous microscopic cracks which are oriented perpendicular to the drawing axis (Fig. 3b). At the same time, the deformation of this system leads to the development of a well-pronounced regular microrelief with a wavelength of $\sim 6\text{--}7\ \mu\text{m}$.

In summary, the feasibility of preparing a rigid coating on a soft substratum polymer–polymer system is shown. The deformation of the above systems is accompanied by similar structural rearrangements in their surface layer characteristic of such systems, such as multiple fragmentation of coating and the development of a regular microrelief.

REFERENCES

1. Volynskii, A.L., Bazhenov, S.L., and Bakeev, N.F., *Russ. Khim. Zh.*, 1998, vol. 42, no. 3, p. 57.
2. Volynskii, A.L., *Nauka Ross.*, 2002, no. 3, p. 4.
3. Bakeev, N.F., Belyaev, V.V., Volynskii, A.L., Ivanov, S.A., Kononov, V.A., Muravskii, A.A., Min'ko, A.A., Chistovskaya, L.V., and Yakovenko, S.E., *Opt. Zh.*, 2001, vol. 68, no. 9, p. 89.
4. Voronina, E.E., Yaminskii, I.V., Volynskii, A.L., and Bakeev, N.F., *Dokl. Akad. Nauk*, 1999, vol. 365, no. 2, p. 206.
5. Fischer, E., *Newer Methods of Polymer Characterization*, Ke, B., Ed., New York: Wiley, 1964.
6. Phuvanarturuks, V. and McCarthy, T.J., *Macromolecules*, 1998, vol. 31, no. 6, p. 1906.
7. Cohn, D. and Stern, T., *Macromolecules*, 2000, vol. 33, no. 1, p. 137.
8. Volynskii, A.L., Voronina, E.E., Lebedeva, O.V., Bazhenov, S.L., Ozerin, A.N., and Bakeev, N.F., *Polymer Science, Ser. A*, 1999, vol. 41, no. 9, p. 921.