

NOTES

Mechanical Anchoring of Polymer Layers on Polymer Substrates with an Open-Porous Surface Structure

INTRODUCTION

A general requirement of organic coatings and adhesives is that sufficient adhesion is secured at the interfaces, especially in multilayer film systems consisting of different polymer material. In principle, the adhesion between two polymer films can be provided by intermolecular forces and/or by a mechanical connection between both layers, ranging from the molecular scale, as in chain entanglements, to supermolecular dimensions as given by various degrees of surface roughness.

Above the glass transition temperature of a polymer substrate, a molecular interpenetration by the liquid polymer material brought upon it is rather improbable. In some exceptional cases, valence bonds may be formed which then connect both layers under favorable circumstances. Generally, however, the bonding at the interface is essentially due to adsorption forces.¹

Molecular interactions will certainly be facilitated when the substrate is above its glass temperature and/or is swollen by any component of the liquid polymer material to which it should adhere. According to Voyutskii,² in such cases the adhesion may be promoted by diffusion phenomena. As the molecular chains of the upper polymer layer may penetrate into the upper region of the polymer basis layer, interfacial bond formation may be enhanced if the systems are compatible. In this case the interface may exhibit a bonding strength comparable to the cohesive strength of either bulk polymer.

The improvement of adhesion by increasing the surface roughness of the substrate³ is predominantly mechanical, because the contact area is increased and some interlocking is effected by the penetration of the liquid polymer into the cavities and crevices of the substrate. This principle has found considerable application in metal-plated plastics.⁴ If the basic polymer material consists of two phases with different polymers, a surface roughness may be attained by the dissolution and extraction of the disperse phase in the uppermost layer of the substrate. The holes thus produced enable excellent adhesion between the metallic layer and the polymer substrate covered by the electroplating process. In the following, a method for obtaining a special porous surface structure will be described.

EXPERIMENTAL

The polymer material for the basic layer consisted of a vinylchloride-vinyl acetate (VCVA) copolymer (9:1). For films having a surface layer with an open-porous structure of microvoids, a ratio by weight of methylisobutyl ketone:3-methoxybutanol = 3:2 was used as solvent mixture. The liquid films were applied on a glass or tin foil substrate, corresponding to 45 μm dry film thickness. During that application and film formation, the relative humidity was 80% at 23°C. After additional eight days at 45% R.H. and 23°C, the films were detached from the substrate and after one day at 23°C overcoated by a layer of an epoxy resin (Epikote 815) cured with a polyamide resin (Versamid 140).

Films from the same VCVA copolymer have also been prepared with a closed microvoid structure. In this case, phase separation took place throughout the whole layer somewhat later during film formation at 20°C and only 45% R.H.

Mechanical Interlocking by Porous Surfaces Layers of Polymer Films

In contrast to a heterophase system consisting of different polymers, the improvement of adhesion by mechanical interlocking of polymer layers can also be realized in suitable homophase polymer systems. This may be demonstrated with a vinyl acetate-vinyl chloride copolymer of the specification given.

With usual formulations and under normal conditions of drying, the films, obtained after evaporation of the solvent, are transparent and homogeneous. If, however, the film formation takes place in an atmosphere containing high relative humidity, the film shows a white, opaque appearance. This so-called blushing phenomenon is a well-known defect, which is caused by the condensation of water at the drying film surface due to the temperature decrease involved in rapid evaporation processes. The condensation of water leads to a phase separation within a thin surface layer. The discontinuous phase consists of tiny droplets of solvents mixed with water. The more volatile organic solvents continue to evaporate preferentially. Finally, after the less volatile components have also evaporated, a porous structure consisting of interconnected microvoids remains in the upper section of the film. A cross section of such a film, prepared by the fractographic method of electron-microscopic preparation,⁵ is presented in Figure 1.

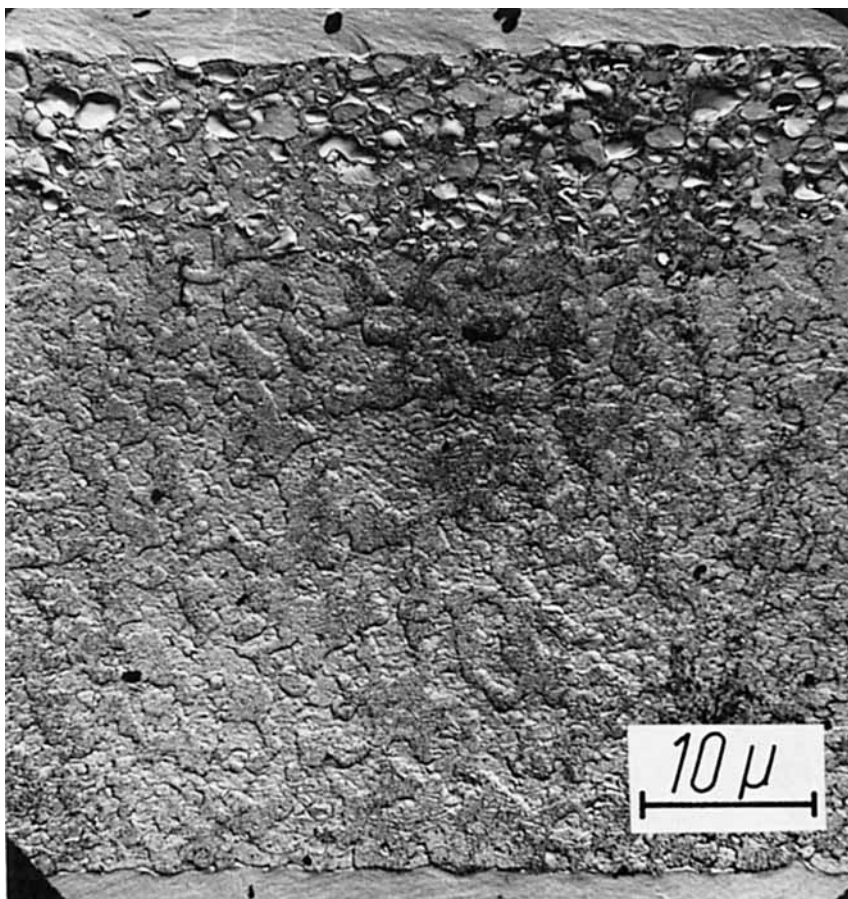


Fig. 1. Complete cross section of VCVA copolymer film with open-porous top region. Film is covered on both sides by epoxy resin layers.

The total film thickness was about $45\ \mu\text{m}$. With the exception of a surface region, the film exhibits a dense, homogeneous structure, with only some pattern produced by the process of fracture. However, the surface region obviously has a porous structure with a depth of about $11\ \mu\text{m}$.

From Figure 2 it is very obvious that most of the microvoids existing in the surface region of the VCVA film are filled up with just the same epoxy resin material which covers the surface of this film. Therefore the epoxy resin, while still being in the liquid state, must have been able to penetrate into the microvoid system. This is only possible if the microvoids are interconnected by capillaries, forming a surface layer with open pores. The mechanical interlocking between both polymer layers may therefore be considered as virtually optimal.



Fig. 2. Open-porous top region of VCVA copolymer film, covered by epoxy resin layer that has penetrated into the microvoids.

To a certain degree, the adhesion is substituted by cohesive forces even in the very interfacial region. It must be emphasized that obviously the intrinsic adhesion of the system discussed is fairly poor. This can be shown from the even separation of both materials at the surface of the microvoids after the fracture has occurred. The bonding strength at the interface would therefore be very low were it not for the root-like penetration of the substrate by the epoxy resin.

Closed Microvoids Without Interlocking Effect

Not all kinds of microvoids will support adhesion in the way just described. Microvoids generated in a different way with a closed structure, though virtually having the same shape, may not be filled up with resin from the initially liquid top layer. This condition prevails in a VCVA film shown in Figure 3. The fracture surface of the whole section of this film is very similar to that of the surface region of the former film. However, both the special solvent composition and conditions of drying used in this case leads to a structure in which the microvoids, though extending through the whole cross section of a film, are obviously not interconnected. Such films with a closed microvoid structure, which are also known as "bubble coatings" or "pitted" paint films,⁶

have a white appearance as if being pigmented. As is known, the optical effect has already been utilized on a fairly broad scale.⁷ Films containing microvoids of smaller dimensions than necessary for obtaining such optical effects exhibit peculiar mechanical properties,⁸ particularly a high ultimate elongation.

Microvoids of films prepared by phase separation at later stages of film formation at low humidity are obviously predominantly closed and therefore cannot be filled up by the epoxy resin, as is indicated by the interfacial region shown in Figure 3.

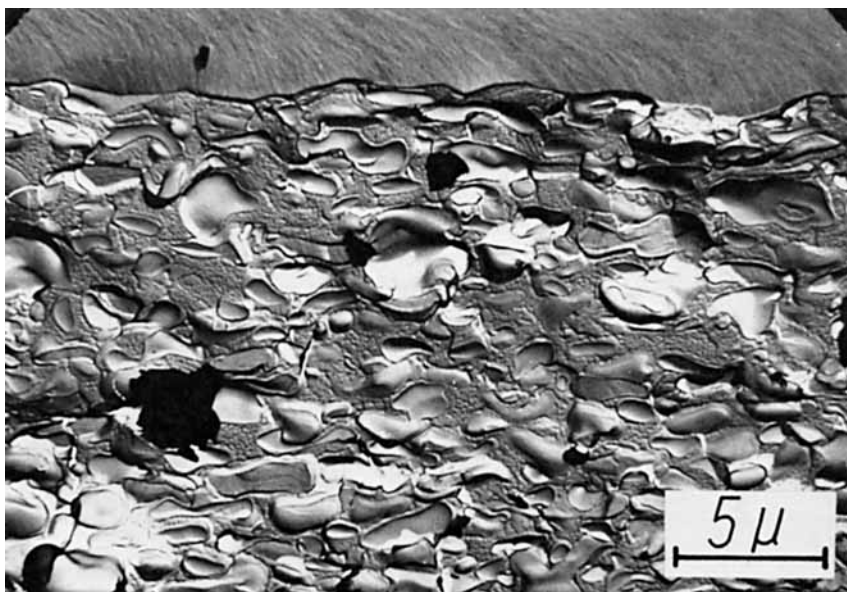


Fig. 3. Structure of the VCVA copolymer film with closed microvoids.

It may therefore be concluded that the specific way of film formation involved in this case of a polymer solution containing solvent/nonsolvent mixtures is different from the former case. The solvent components left back after phase separation obviously evaporate by molecular diffusion through the thin walls of binder separating the individual microvoids. Though the optical effect, namely, the white appearance or blushing is exactly the same in both cases and cannot be distinguished by visual inspection, the closed microvoids obtained in the procedure just described may not be expected to promote adhesion between polymers.

CONCLUSIONS

By phase separation occurring in physically drying polymer films under special conditions which involve a water condensation at the surface, films may be obtained which have an open-porous structure of microvoids in their surface region. These microvoids may be filled up by the polymer from an initially liquid top layer. The penetration provides the mechanical anchoring of this layer to the base layer. By this mechanism, multilayered film systems may be prepared of which a markedly improved interlayer adhesion can be expected.

We are indebted to the Deutsche-Forschungsgemeinschaft e.V. for supporting these investigations.

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Received August 4, 1972
Revised September 11, 1972