Polymerization of Organic Compounds in an Electrodeless Glow Discharge. X. Internal Stress in Plasma Polymers

H. YASUDA, TOSHIHIRO HIROTSU,* and H. G. OLF, *Polymer Research Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*

Synopsis

Owing to the unique mechanisms operative in plasma polymerization, a thin layer of plasma polymer deposited on the surface of a substrate shows a tendency to expand, indicating an internal stress in the layer. This stress, σ_s, has been estimated from the observed curling of composite membranes in which the thickness of the plasma coating, d, is much smaller than the thickness of a flexible substrate, D, according to the relation

$$\sigma_s = ED^2/6Rd$$

where R is the radius of the roll into which the composite films curl up and E is the modulus of the substrate polymer. The stress σ_s is found to depend on the kind of monomer used and to be of the order of magnitude 10^8–10^9 dynes/cm^2 with most of the monomers here employed.

INTRODUCTION

When a thick layer (i.e., 1 μm or thicker) of plasma polymer of styrene is deposited on a rigid surface such as a glass plate, the layer of plasma polymer tends to buckle and crack.[1] This phenomenon was thought to be due to absorption of moisture from the atmosphere and consequent swelling of the layer.[1] More recently, it has been observed that a composite film consisting of a thin layer of plasma polymer deposited on a flexible polymeric substrate such as polyethylene often shows a marked tendency to bend and to curl up. This curling is observed even during plasma polymerization. It may be attributed to an internal stress arising in the plasma layer during polymerization.

In all cases of curling observed in such composite membranes, the direction of bending was such that the membrane was convex toward the side of the layer. This is the situation schematically indicated in Figure 1. This sense of bending is in marked contrast to that expected if the layer were deposited by conventional polymerization. As is well known, conventional polymerization proceeds, with
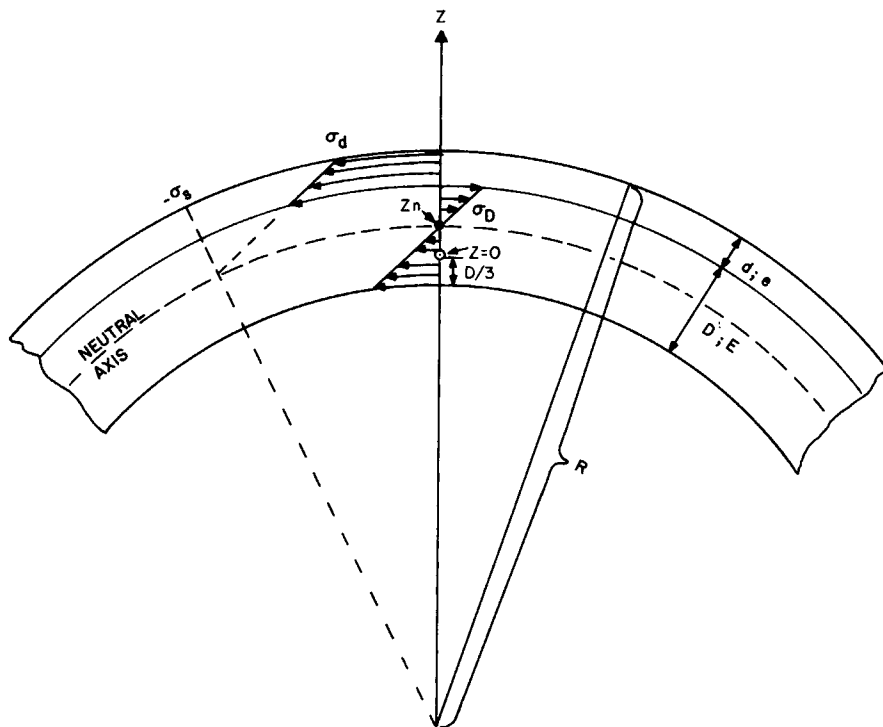
Fig. 1. Model of a composite membrane, bending because of a stress σ_s in the thin layer deposited by plasma polymerization onto a flexible polymeric substrate. Layer and substrate have thicknesses d and D and Young's moduli e and E, respectively.

very few exceptions, under volume decrease: the specific volume of the polymer is smaller than that of the (liquid) monomer. A thin film of liquid monomer polymerized on top of a flexible substrate would contract and cause bending concave toward the side of the layer, i.e., in the direction opposite to that obtained with plasma polymerization.

We conclude that the internal stress in the plasma-polymerized layer is an expansive one. The origin of this stress is largely a matter of speculation, but the following intuitive picture may provide a useful rationalization. Reactive species—such as ions of either charge, excited molecules, and free radicals—are continuously formed in the plasma and impinge onto the already laid-down plasma polymer,[2] which contains a great number of radicals also.[3] These highly reactive species, in attaching themselves to the polymer, are imagined to become frequently wedged between existing polymer chain segments. This wedging effect is thought to give rise to the observed expansive stress.

In this study, an attempt is made to estimate the internal stress, which builds up in the plasma polymer, from the extent of curling of composite films prepared by depositing a layer of plasma polymer on low-density polyethylene film.

CALCULATION OF INTERNAL STRESS

Our purpose is to derive a relationship between the radius of curvature of the curling membrane and the stress causing it.

Figure 1 represents the model on which the calculation will be based.   The substrate has thickness D and Young's modulus E; the plasma-polymerized layer has, correspondingly, d and e.   If the substrate were constrained to its original shape, a "swelling stress," σ_s, would develop in the plasma-deposited layer.   This stress exerts a bending moment which is partly relieved when the membrane is allowed to bend.   Bending creates reactive stresses in the substrate, and equilibrium will be reached when the moment of the stresses in d is opposite and equal to the moment of the stresses in D,

$$M_d + M_D = 0$$

where the moments are those with respect to the neutral axis (see Fig. 1).   A second equilibrium condition is that the stress integrated over the cross section perpendicular to the neutral axis must be zero, as no external force is applied.   These two equilibrium conditions are sufficient to calculate the location of the neutral axis and to derive the desired relationship between the swelling stress σ_s and the radius of curvature of the composite membrane.   This is done first for the general case where d can assume any value and subsequently for the special case that d is small compared with D.

General Case

For purposes of calculation, we assume a coordinate axis z perpendicular to the membrane and put the origin, $z = 0$, at a distance $D/3$ from the bottom of the composite membrane (Fig. 1).

The strain ϵ is assumed to vary linearly with distance from the neutral axis:

$$\epsilon = k(z - z_n)$$

where k, a constant which determines the strain, will be dependent on σ_s and where z_n is the coordinate of the neutral axis.   The stress in d will be given by

$$\sigma_d = -\sigma_s + ek(z - z_n)$$

and in D by

$$\sigma_D = Ek(z - z_n)$$

Since the membranes are thin compared to their lateral dimensions, shear stresses may be ignored.   Application of the two mentioned equilibrium conditions yields the dependence of the strain constant k on stress and the material constants and the location of the neutral axis z_n:

$$k = \frac{\sigma_s d}{[(ED^2/6)(1 + 4ed/ED + 3ed^2/ED^2) - (ED + ed)z_n]} \tag{1}$$

$$z_n = (d/6)\{1 - (d/D) + [d^2/D(D + d)](E - e)/E\} \tag{2}$$

The radius R of the roll into which the membrane curls up (Fig. 1) is given by

$$R = (1/k) + \Delta \tag{3}$$

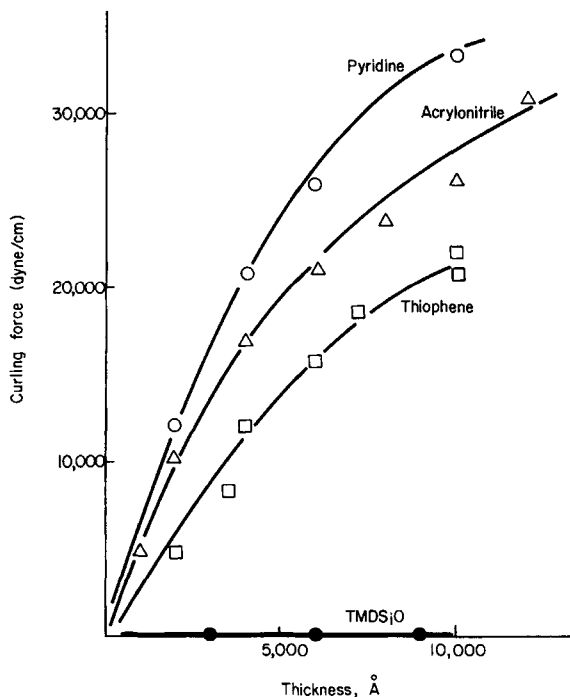where $\Delta = (2D/3) + d - z_n$ is the distance of the neutral axis from the upper surface of the membrane.

Fig. 2. Curling force $\sigma_s d$, which is the product of the internal stress (σ_s) and the thickness (d) of the plasma-deposited layer, is plotted vs d. The three curves correspond to layers obtained by plasma polymerization of the indicated monomers.

Special Case $d \ll D$

In all the membranes used, the plasma-polymerized layer has a thickness d very much smaller than D, the thickness of the substrate. As d approaches zero, z_n also becomes zero, eq. (2).

If it is assumed that $d \ll D$ and that e and E are of the same order of magnitude, we get from eq. (2)

$$z_n \simeq d/6$$

and from eq. (1)

$$k \simeq 6\sigma_s d/(ED^2)$$

With all our membranes, D is always less than 1% of R, so $D \ll R$ and, a fortiori, $\Delta \ll R$. Hence, we have according to eq. (3)

$$R \simeq 1/k \simeq ED^2/(6\sigma_s d)$$

This yields the desired estimate of σ_s from a measurement of R:

$$\sigma_s = ED^2/(6Rd) \tag{4}$$

At a given radius of curvature R, the stress σ_s is directly proportional to Young's modulus of the substrate and to the square of its thickness, and inversely proportional to the thickness d of the plasma polymer layer.

EXPERIMENTAL

Preparation of Composite Films

A strip (1 cm × 8 cm) of low-density polyethylene film ($D = 5 \times 10^{-3}$ cm, $E = 10^9$ dynes/cm^2) was used as the substrate. A plasma coating was deposited on this film by the usual method, which was described elsewhere.[1] The coating thickness was estimated from the known deposition rate of each polymer. Most strips curled in the course of the coating; therefore, in order to prevent curling and to obtain a uniform coating, the strip was supported on a stiff film (Mylar A) by means of aluminum foil fixed at both ends.

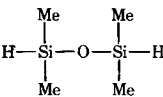### Measurement of the Radius of Curled Films

After polymerization, the strip was taken off from the supporting film, and the uncoated portion (under the aluminum foil) was cut off. The film was kept in air at room temperature for approximately 24 hr before the measurement of curling was taken. The radius of the curled film was measured by a caliper with a vernier scale.

RESULTS AND DISCUSSION

The force per unit width of film which causes curling is given by the product of stress σ_s and layer thickness d, i.e., $\sigma_s d$. This curling force was measured with plasma coatings of different thicknesses and with different monomers. The results, appearing in Figure 2, show that the curling force in a layer of plasma polymer increases with increasing layer thickness.

At small values of the layer thickness, the curling force $\sigma_s d$ increases linearly

TABLE I
Internal Stress of Plasma Polymer (thickness = 4000 Å;
reaction conditions: 30 μm Hg monomer pressure and 80W power)

Monomer	Structure	σ_s, dynes/cm^2
Thiophene		2.7×10^8
Pyridine		5.2×10^8
Acrylonitrile	$CH_2{=}CH{-}C{\equiv}N$	4.3×10^8
Furan		7.0×10^8
Styrene	$CH_2{=}CH$	4.3×10^8
Acetylene	$CH{\equiv}CH$	3.8×10^8
2-Methyloxazoline	CH_3	0
Tetramethyldisiloxane	$H{-}\overset{Me}{\underset{Me}{Si}}{-}O{-}\overset{Me}{\underset{Me}{Si}}{-}H$	0

with d; this means that σ_s is independent of layer thickness and is a material constant.   The curling force tends to deviate from this linear dependence on d at a greater coating thickness; the stress σ_s decreases with increasing thickness of the layer.   This seems to be related to cracking of the layer, which has been observed to occur in relatively thick layers and will certainly relieve a part of the internal stress.   Figure 2 indicates that a meaningful value of σ_s can be determined from eq. (4) if the coating thickness is limited to values of 4000 Å or less.

Although only one kind of substrate polymer of a given thickness was used in this study, it is clear that the method can be adapted to cover a wide range of internal stress by suitable changes of thickness and modulus of the substrate.

The values of internal stress measured at 4000 Å coating thickness for some plasma polymers are listed in Table I.   All plasma polymer coatings were prepared under an arbitrarily chosen set of conditions.   The results may, therefore, not be unique as the internal stress may also depend on the conditions of plasma polymerization.   The possibility of such a dependence is being studied further.

The data in Table I show that most monomers give layers having internal stress in the range of 10^8–10^9 dynes/cm^2.   The two monomers 2-methyloxazoline and tetramethyldisiloxane, however, gave layers with no observable bending and, hence, zero internal stress.

The detailed characterization of the structure and properties of plasma-polymerized layers is difficult and lags far behind their technologic exploitation. Accordingly, it is not possible at present to interpret the significance of the results in Table I in terms of polymerization mechanisms or structure of the layer.   The purpose of this communication is to show that an expansive stress of considerable magnitude exists in certain plasma-deposited polymeric layers and to propose the simple method employed here for the measurement of that stress.   It is hoped that this approach will contribute to the further study and understanding of the structure and properties of these layers.

References

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3. H. Yasuda, M. O. Bumgarner, H. C. Marsh, and N. Morosoff, *J. Polym. Sci., Polym. Chem. Ed.*, 14, 195 (1976).