

## The Water Curing of a Polyurethane Resin Used as a Wool Fiber Coating

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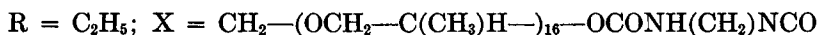
### Synopsis

In the industrial application of polyurethane resins to form surface coatings on wool fabrics, the prepolymer resin Synthappret is cured by reaction with water, either as steam or as atmospheric water vapor, to form the rubber network. This paper examines changes in the mechanical properties of the resin with cure conditions. It is shown for steam-cured resin that the initial modulus, the equilibrium swelling in tetrachloroethylene, the Mooney-Rivlin constant  $C_1$ , and the average molecular weight of chain segments between crosslinks all reach constant values after 1 hr. However, the resin density and the Mooney-Rivlin constant  $C_2$  show a linear dependence on cure time with no indication of reaching an equilibrium value. It is concluded that although the network is substantially complete after 1 hr of steam cure, there is a continuing pattern of reorganization. The mechanical properties of resin produced by air curing, a much slower process, are consistent with those of a network which has had a longer period of reorganization. The density of air-cured resin is significantly higher than that of resin prepared by steam curing. Stereoscan electron micrographs of the resin surface reveal a texture which coarsens with prolongation of cure time and also reveal a difference for the two methods of cure.

### INTRODUCTION

Polyurethanes are materials which find a wide range of applications and have been utilized in the textile processing of wool fibers since about 1932.<sup>1</sup> Produced by the reaction of polyfunctional hydroxyl compounds with polyfunctional isocyanates, they have a great diversity of physical properties, and polymer can be "tailor made" for specific applications. A good deal is now known about the relationship between their mechanical properties and structure and the effect of variation of curing conditions.<sup>2</sup> A satisfactory polyurethane resin treatment is now being used commercially for wool fabrics and makes use of the urethane prepolymer resin Synthappret LKF (registered trademark of Farbefabriken Bayer A.G.). This can be applied to the fabric either from a solution in a mixture of ethyl acetate and tetrachloroethylene or from an aqueous emulsion. Since the molecular weight of the prepolymer is high, there will be little diffusion of the resin into the fiber, so that the cured resin will be formed almost exclusively as a surface layer.

The prepolymer is prepared by the reaction of a triol with a trifunctional diisocyanate and has the composition  $RCX_3$ , where<sup>3</sup>



Curing of the prepolymer to form a crosslinked elastomeric network is by reaction with water, either as atmospheric water vapor (air curing) or with steam (steam curing), each isocyanate terminal theoretically being available to react to produce disubstituted urea linkages and biuret crosslinkages. The relative proportions of these groupings will depend on the conditions of cure.<sup>4</sup>

In this paper, an investigation is reported of the change in the mechanical properties of the resin for various conditions of cure and for prepolymer resins having different isocyanate contents. The structure of the network has been examined in order to characterize the resin since it has been found to have a satisfactory performance as a wool fiber coating.

## EXPERIMENTAL

### Material

Synthappret (Type LKF, Farbefabriken Bayer A.G.) was supplied as a prepolymer resin concentrate in ethyl acetate (83%). During the course of the experimental program stock prepolymer concentrates showed a gradual decrease in isocyanate content and this conveniently provided a range of samples varying in isocyanate content from 3.08% to 4.06% NCO, as determined by titration.<sup>5</sup>

### Resin Sheets

Resin sheet ca.  $5 \times 12 \times 0.1$  cm was prepared using a mold constructed from plate glass. In the steam curing experiments, both the oven and the glass molds were at operating temperature before spreading the resin concentrate so that the cure time was reasonably well defined ( $\pm 2$  min). Mechanical tests, the measurement of density, and swelling were all commenced immediately on completion of the steam cure period. Resin concentrate spread into glass molds at 20°C and 65% R.H. (air curing) took at least ten days to form a coherent sheet.

### Density of the Resin

Measurements were made of the drift velocity of small pieces of resin in aqueous  $ZnCl_2$  solutions of known density at 20°C. The density of the resin was obtained by interpolation of the data to obtain the density of the liquid in which the drift velocity would be zero.

### Swelling of the Resin

Equilibrium swelling measurements were carried out in tetrachloroethylene (Merck Analytical Reagent,  $\rho_r^{20} = 1.623$  g/ml) at 20°C using small blocks of resin ca. 50 mg. The initial and swollen weights  $w_0$  and  $w_s$  were determined using an electromicrobalance (Beckmann, R.I.I.C. Type EMB-1). Before weighing the swollen resin, surface liquid was carefully removed and the resin block wrapped in preweighed aluminium foil. The volume fraction of polymer in the swollen resin,  $v_2$ , was calculated from

$$v_2 = [1 - (\rho_r/\rho_s) + (\rho_r/\rho_s)(w_s/w_0)]^{-1} \quad (1)$$

where  $\rho_r$  and  $\rho_s$  are the densities of the resin and swelling liquid, respectively.

### Mechanical Measurements

**Tensile Strain.** Stress-strain diagrams of resin strips were determined using an Instron tensile testing machine operated at a rate of extension of 30%/min.

**Compressive Strain.** The initial part of the stress-strain diagram was obtained using the Instron testing machine fitted with a compression cell (Type CB), the rate of compressive strain being 1%/min. Dimensions of the specimen were approximately  $0.5 \times 0.1 \times 0.1$  cm, the end faces being cut parallel and the junction between the resin and the surface plates of the compression cell being lubricated with Nujol oil. Swollen resin samples were measured in the same manner except that the test specimen was maintained in a swollen condition by placing a drop of tetrachloroethylene on the Instron cell surface close to the sample.

### Electron Microscopy

Stereoscan electron microscopy (SEM) of the gold-coated resin surface was carried out using a Cambridge Mk II instrument. All samples were examined as a batch several days after preparation so that it is possible for specimens which were given only a short period of steam curing to undergo air cure prior to SEM examination.

## RESULTS AND DISCUSSION

### Characterization of the Resin

Swelling results for Synthapret resin in tetrachloroethylene are shown for various periods of steam cure in the lower part of Figure 1. The results indicate that a minimum of 1 hr is required to effect completion of the rubber network,  $v_2$  reaching a constant value of 0.39. It was found that resin which had been air cured for ten days had a value of  $v_2 = 0.42$ , so that the more rapid method of

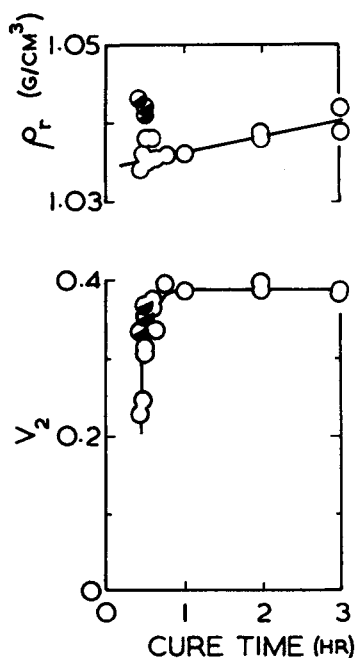


Fig. 1. Dependence of resin density (upper curve) and volume fraction of polymer determined in tetrachloroethylene at 20°C (lower curve) on the period of steam cure: (O) 3.08% NCO; (●) 4.06% NCO.

curing produces a less crosslinked network. Density measurements on the steam-cured samples made immediately on completion of curing are shown in the upper section of Figure 1. These results do not show a correlation with the swelling data and indicate that the density of the resin continues to increase with a linear dependence of time of cure, there being no indication of an equilibrium value. Air-cured Synthappret resin has a significantly higher density of 1.048 g/ml, and this is consistent with the higher value of  $v_2$  which is obtained. Measurements of the density of both steam- and air-cured resin made after a long period of storage in an air-conditioned room show that there is a small increase. This must be attributed to structural changes within the resin as a result of the continuation of the curing process.

### Effect of Cure Time on Initial Modulus

A coherent network is formed shortly after 0.25 hr of steam cure, and resin sheet can be removed from the mold to permit mechanical measurements to be made. In this state the resin is found to have an extensibility of about 250% and a breaking strength of between 0.3 and 0.4 MN/m<sup>2</sup>. Continuation of the curing process produces a marked reduction in extensibility and an increase in breaking strength to about 1.3 MN/m<sup>2</sup>. Little change in the stress-strain diagram occurs after a steam cure of 2 hr.

The changes in mechanical properties accompanying increase in steam cure time are shown in Figure 2 where the initial modulus  $\epsilon$  is shown plotted against cure time. This shows that the initial tensile modulus changes rapidly during the first hour and thereafter becomes independent of cure time. These results correlate with the values of  $v_2$  shown in Figure 1.

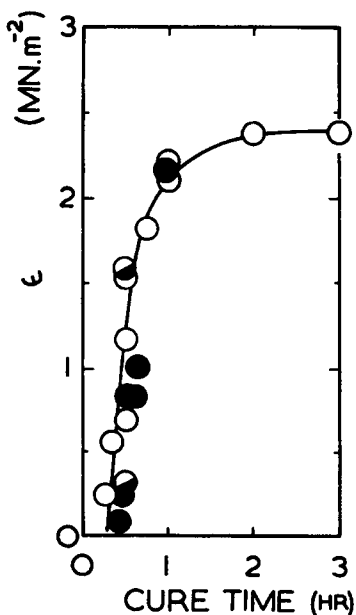


Fig. 2. Dependence of initial modulus on the period of steam cure: (○) 3.08% NCO; (●) 3.29% NCO; (◐) 4.06% NCO.

TABLE I

Change in Initial Modulus and in Mooney-Rivlin Constants with Time of Storage at 20°C and 65% R.H. for Air-Cured Synthappret Resin Prepared from Prepolymer Concentrates Having Different Isocyanate Contents

NCO, %	Time, days	$\epsilon$ , MN/m <sup>2</sup>	$C_1$ , MN/m <sup>2</sup>	$C_2$ , MN/m <sup>2</sup>
3.08	12	2.6	0.56	0.42
...	14	2.7	0.47	0.49
...	15	2.8	0.76	0.38
...	203	3.7	0.76	0.47
3.29	14	2.6	0.69	0.24
3.81	50	2.9	0.43	0.65
4.06	14	3.6	0.93	0.42

Air-cured resin was found to have a distinctly higher initial modulus as shown in Table I, and this is consistent with the resin having a greater crosslink density. Table I shows that there is a continuing change in the mechanical properties on storage. Nakane et al.<sup>6</sup> have also reported changes in the stress-strain diagram for diamine-cured polyurethane elastomers on storage in air at various controlled humidities. There is some indication that the initial modulus of air-cured resin also shows some dependence on the isocyanate content of the prepolymer, which is a measure of its initial reactive condition, but this has not been found for steam-cured resin.

### Calculation of Mooney-Rivlin Constants

The elasticity and structure of polyurethane networks has been examined in some detail by Blokland<sup>7</sup> and Blokland and Prins.<sup>8</sup> It was shown that elastic behavior in the urethane networks derived from reaction between toluene diisocyanate and poly(oxypropylene) glycols of varying functionality deviated substantially from a Gaussian distribution of network chains. In an ideal network, the free energy of deformation is given by

$$\Delta F = (C/2)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - B\nu \ln \lambda_x \lambda_y \lambda_z \quad (2)$$

where

$$C = A\nu kT \langle r^2 \rangle_i / \langle r^2 \rangle_0 \quad (3)$$

$\nu$  being the number of elastically effective network chains per unit volume,  $A$  and  $B$  being numerical constants, and  $\lambda_x$ ,  $\lambda_y$ , and  $\lambda_z$  being the strain ratios. The dimensionless ratio  $\langle r^2 \rangle_i / \langle r^2 \rangle_0$  is introduced to compensate for the average chain dimensions in the undeformed rubber,  $\langle r^2 \rangle_0$  not being identical with those in the strained state,  $\langle r^2 \rangle_i$ . For a unidirectional strain, the force will be given by

$$f_x = (C/L_x)(\lambda_x - \lambda_x^{-2}) \quad (4)$$

where  $L_x$  is the initial length. This equation only partly accounts for the observed behavior and is replaced by an empirical equation of the same form:

$$f_x = C_1(\lambda_x - \lambda_x^{-2}) + C_2(\lambda_x - \lambda_x^{-2})\lambda_x^{-1} \quad (5)$$

where  $C_1$  and  $C_2$  are the Mooney-Rivlin constants. The constant  $C_2$  has been taken to give an approximate measure of the degree of non-Gaussian behavior,<sup>8</sup>

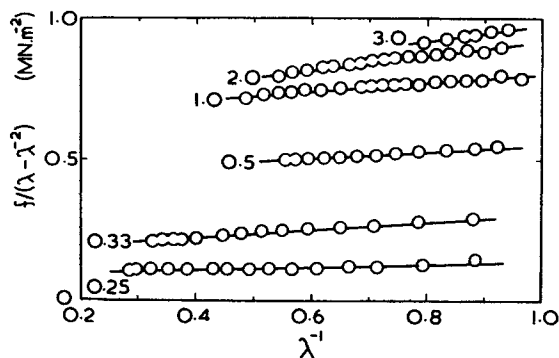


Fig. 3. Mooney-Rivlin plots for unswollen Synthappret resin prepared by steam curing. The period of cure (hr) is indicated against each curve.

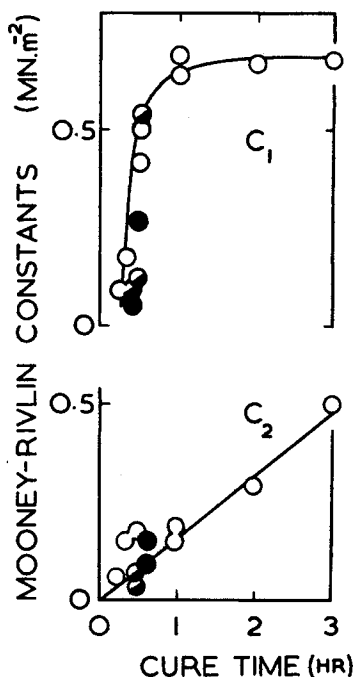


Fig. 4. Derived values of the Mooney-Rivlin constants for steam-cured resin: (O) 3.08% NCO; (●) 3.29% NCO; (◐) 4.06% NCO.

but the observations of Gumbrell et al.<sup>9</sup> show that although  $C_2$  depended on the degree of swelling, it was independent of the type of rubber clearly making this assumption untenable. The parameter  $C_1$  is directly proportional to the degree of crosslinking but may also show a small increase with swelling.

Mooney-Rivlin plots for unswollen Synthappret resin prepared after various periods of steam curing are shown in Figure 3. The constants  $C_1$  and  $C_2$  determined from the intercepts and slopes, respectively, and supplemented by data derived in a similar manner for resins prepared from prepolymer concentrates having different isocyanate contents are given in Figure 4. Errors in  $C_1$  and  $C_2$  are approximately  $\pm 0.02$  MN/m<sup>2</sup>. In the upper set of results, values of  $C_1$  show a correlation with the volume swelling data given in Figure 1 and indicate that crosslink formation can be considered to be almost complete after 1 hr of steam

cure. Values of  $C_1$  for air-cured resin are given in Table I. For the polyurethane networks examined by Blokland and Prins,<sup>8</sup> values of  $C_1$  and  $C_2$  were about 60 and 20 MN/m<sup>2</sup> but decreased to 5 and 0.5 MN/m<sup>2</sup>, respectively, as the number of polypropylene oxide groups between trifunctional junction points in the chain increased from 36 to 102. Thus, values of  $C_1$  can be taken as sensitive indicators of the structure of the resin, and the increasing value of  $C_1$  with the isocyanate content of the prepolymer shown for the air-cured resins in Table I can be taken to indicate that a more highly crosslinked resin is obtained from the 4.06% NCO prepolymer.

In the industrial application of Synthappret resin to wool fabrics, the isocyanate content of the prepolymer resin treatment bath cycles, as a result of the water brought in with the wool, between 4.2% and 2.8% NCO when new resin prepolymer solution is introduced into the equipment. Thus, as judged by the present results, the network structure of the wool fiber coating will show some dependence on the state of the resin treatment bath at the time of application to the fabric.

Blokland and Prins<sup>8</sup> have observed that the ratio  $C_2/C_1$  remains roughly constant. This is clearly not the case with the present data, since  $C_2$  shows a linear dependence on cure time whereas  $C_1$  reaches a constant value. This would suggest that although the network is complete, some structural change continues well after the resin may be judged to be fully cured on the basis of the  $C_1$  and  $\nu_2$  results as given in Figures 1 and 4. It has already been noted that the density of the resin continues to increase.

#### Mooney-Rivlin Constants for Polyurethane Elastomers

In their examination of polyurethane elastomers, Blokland and Prins<sup>8</sup> observed that values of the Mooney-Rivlin constants were dependent on the nature of the applied strain. Thus, typical values of  $C_1$  determined by unidirectional tensile and compressive forces were 0.40 MN/m<sup>2</sup> and 0.98 MN/m<sup>2</sup>, respectively. The increase in  $C_1$  arises from a change of sign of  $C_2$ . Examination of their data, however, shows that  $C_2$  does not show a consistent change of sign and may remain positive for some resins.

The origin of the difference in the Mooney-Rivlin constants can be demonstrated by Figure 5, where  $f/(\lambda - \lambda^{-2})$  has been plotted as a function of  $\lambda^{-1}$

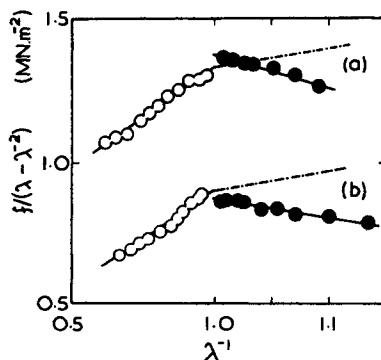


Fig. 5. Mooney-Rivlin plots for unswollen resin prepared by (a) air curing; (b) steam-curing; (O) tensile; (●) compressive data. Broken line indicates the extrapolation of the tensile data assuming no change in the Mooney-Rivlin constants. Note that scale has been enlarged for the compressive data.

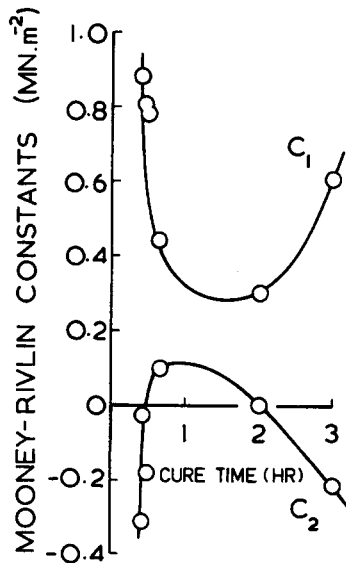


Fig. 6. Dependence of the Mooney-Rivlin constants derived from compressive measurements on steam-cured Synthappret resin on the time of cure.

using data obtained in tensile and compressive measurements on the same resin samples. The scale of the abscissa has been enlarged for  $\lambda^{-1} > 1$ , where  $\lambda^{-1} = 1$  corresponds to the unstrained state. In Figure 5, the broken lines have been drawn to indicate the continuation of the tensile results assuming no change in the Mooney-Rivlin constants. In the region  $\lambda^{-1} \cong 1$ , values of the ordinate become increasingly inaccurate so that it is not practicable to examine the continuity of data from the tensile to the compressive strain regions. Blokland and Prins<sup>8</sup> have reported a marked discontinuity at  $\lambda^{-1} = 1$ , but this has not been corroborated by the present work.

Values of the compressive Mooney-Rivlin constants determined for steam-cured Synthappret resin are shown in Figure 6 and are in marked contrast to the corresponding data reported in Figure 4. Values of  $C_1$  go through a deep minimum at a steam cure time approximating to that at which the tensile value of  $C_1$  indicates that the network had been almost completed.  $C_2$  takes both positive and negative values. The apparent inconsistencies of sign in the Blokland and Prins<sup>8</sup> results may have a similar origin although they only examined fully cured resins. For air-cured resin, corresponding value of  $C_1$  and  $C_2$  are 1.69 and  $-0.24$  MN/m<sup>2</sup> and are consistent with data for resin steam cured for more than 3 hr.

In the phenomenological theory of Rivlin,<sup>10</sup> it is shown that for an isotropic incompressible rubber undergoing deformation with three principal deformation ratios  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , the stored energy function  $w$  will be given in general by

$$W = \sum_{i=0, j=0}^{\infty} C_{ij} (I_1 - 3)^i (I_2 - 3)^j \quad (6)$$

where

$$\left. \begin{aligned} I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 &= \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} \end{aligned} \right\} \quad (7)$$



In the case of a unidirectional deformation with strain ratio  $\lambda$ , the force of retraction is given by<sup>11</sup>

$$f = 2(\lambda - \lambda^{-2})(\partial W/\partial I_1 + \lambda^{-1} \partial W/\partial I_2). \quad (8)$$

This equation is formally identical to eq. (5) taking  $C_1 = 2\partial W/\partial I_1$  and  $C_2 = 2\partial W/\partial I_2$ . In an extensive investigation of the stored energy function for vulcanized rubbers, Rivlin and Saunders<sup>11</sup> plotted  $\partial W/\partial I_1 + \lambda^{-1}\partial W/\partial I_2$  as a function of  $\lambda^{-1}$  for data obtained both in extension and compression to give equivalent plots to those shown for Synthappret resin in Figure 5. In these plots, the compression data for vulcanized rubbers also showed a negative slope. Thus, the results of Blokland and Prins<sup>8</sup> and also the present data, while being experimentally correct, simply show that the Mooney-Rivlin equation should be restricted to the interpretation of tensile results. The dependence of the Mooney-Rivlin constants on the nature of the strain is an artifact and certainly not of intrinsic interest in the study of polyurethane elastomers.

It is in fact found that the present results are in better agreement with eq. (4), that is setting  $C_2 = 0$ . For example the steam-cured data given in Figure 5b may be fitted to eq. (4) by taking  $C/L_x$  to be 0.8 MN/m<sup>2</sup> for the tensile results and 0.9 MN/m<sup>2</sup> in compression. Although linear plots of  $f$  against  $(\lambda - \lambda^{-2})$  were obtained over the range  $-0.4 < (\lambda - \lambda^{-2}) < 0.2$ , there remained a small but detectable difference between the two constants.

### Compression Measurements on Swollen Resin

In the swollen state, Synthappret resin was found to be extremely fragile, and considerable care had to be taken in handling the samples for mechanical measurements. It was not practicable to determine the stress-strain diagram in extension on swollen resin and so mechanical measurements in this case were carried out entirely using the compressive mode. Cluff et al.<sup>12</sup> have made use of a compressive test for the evaluation of urethane elastomers, and their work, in which they were able to make both tensile and compressive measurements on the resin, showed a reasonable comparison between values of the effective network chain concentration as determined from data in extension and in compression.

In the examination of the compression data obtained for Synthappret, eq. (4) has been used in the form given by Flory and Rehner<sup>13</sup>:

$$f = (RT \rho_r/M_c v_2^{-1/3}) (\lambda - \lambda^{-2}) \quad (9)$$

where  $R$  is the gas constant and  $M_c$  the average molecular weight of chain segments between crosslink junctions. Defining the initial modulus  $\epsilon$  as the slope of the stress-strain ratio plot at  $\lambda = 1$ , then from eq. (9),

$$M_c = 3RT \rho_r/\epsilon v_2^{1/3}. \quad (10)$$

The dependence of the average molecular weight of the chain segments in the network on the conditions of cure are given in Table II. This shows the early stage of the cure process is accompanied by a large decrease in  $M_c$  to a value of 4400 which is independent of cure time. The results indicate that formation of the network is substantially complete after 1 hr of steam curing. From the structural formula for the prepolymer, the molecular weight of each branch is about 1060. If it is assumed that each isocyanate terminal reacts to produce a disubstituted urea linkage; then the molecular weight between crosslink junc-

TABLE II  
Dependence of Average Crosslink Molecular Weight  
on Conditions of Cure for Synthappret Resin

Time	$M_c \times 10^3$
Steam cure	
0.42 hr	125
0.50 hr	16.3
0.58 hr	12.8
0.75 hr	5.7
1.0 hr	4.8
2.0 hr	4.4
3.0 hr	4.4
Air cure	
10 days	4.0

tions is about half of the value of  $M_c$  for the fully cured resin. A value of  $M_c$  for air-cured resin, given in Table II, is significantly lower, indicating a still tighter network structure. This is consistent with the higher density and initial modulus and also the lower degree of swelling in tetrachloroethylene which has been observed.

### Surface Texture of the Resin

Blokland and Prins<sup>8</sup> have made light-scattering measurements on fully cured polyurethane resins and revealed an angular dependence of the  $H_v$  component of the scattered light. It was found that the anisotropy showed a dependence on the preparative history of the sample and also on the number of propylene oxide groups in the chain between junction points, the anisotropy becoming greater as the number of such groups was reduced. They concluded that the polyurethane network consisted of Gaussian chains together with a small proportion of inelastic bundles of chain segments which were responsible for the optical anisotropy. Evidence of a texture which could account for the optical results was obtained in electronmicrographs taken of the cleaved resin surfaces, especially if the exposed surface had been plasma etched.

In the present study, stereoscan electron-microscopic examination of the resin surface has shown a textural pattern which correlates with the method and duration of cure. SEM photographs taken at the same magnification for some of the resin surfaces are given in Figure 7. The top three photographs show an increasing granularity with prolongation of the steam cure period. Air-cured resin has a distinctive texture as shown in Figure 7d and comprises a coarse pattern on a much finer granular background. The large items shown in Figures 7c and 7d are granular residues obtained when cutting the resin sheet and are difficult to remove entirely from the surface.

Microdensitometer scans have been made of the SEM negatives, but these were not easy to quantify. They showed the presence of more than one type of periodic structure which is obvious in Figure 7d but not immediately apparent in Figure 7c. The SEM pictures given in Figures 7a and 7b show a similar textural pattern to the transmission electron micrographs of cleavage surface replicas reported by Blokland and Prins.<sup>8</sup> SEM examination of the surface of other wool resins, i.e., Hercosett resin, generally show a much finer textural pattern

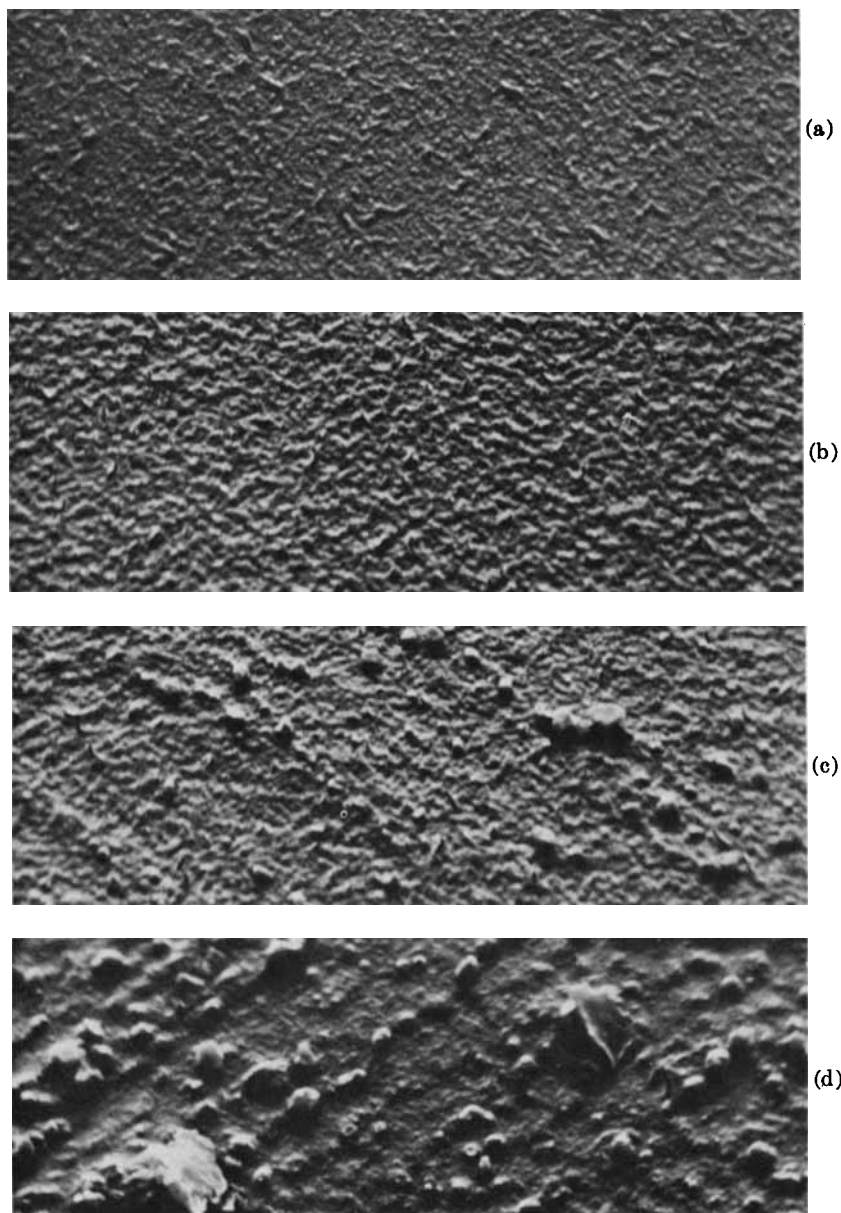


Fig. 7. Stereoscan electron micrographs of the surface of Synthappret resin for different conditions of cure. Steam cured for (a) 0.27 hr; (b) 0.58 hr; (c) 0.95 hr; and air-cured (d).

which is only revealed under much higher magnification. The coarse surface textural pattern shown in Figure 7 is certainly a feature of the polyurethane resins.

The surface texture gives a strong indication that the body of the resin comprises aggregates of network chains and it is reasonable to expect that it is the reorganization of these structural entities which account for the change in density

and mechanical properties on storage. The mechanical weakness of the swollen resin and the presence of fine granular residues when cutting unswollen resin sheet is also consistent with the presence of larger structural units.

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