

achieve the best chemical durability involves manipulation of variables in a direction away from development of best toughness.⁷ Reconciling the opposing trends is a problem of compromise which needs to be solved for each particular end usage.

EXPERIMENTAL PROCEDURES

Preparation of Polyester Resins

A series of hydroxyl terminated, linear polyesters (acid number less than three) of varying number average molecular weight were prepared by the fusion process from neopentyl glycol (2,2-dimethyl-1,3-propanediol) and adipic acid (hexanedioic acid).

The number-average molecular weights of polyesters were determined by endgroup analysis, deduced from hydroxyl number.

The resins, as analyzed by the Karl Fischer method¹⁸ had a water content between 0.01 to 0.05%. These were used without further drying.

Preparation of Polyester-Diisocyanate Adducts

One number-average mole of each was reacted with 2 moles of 2,4-toluene diisocyanate (Mondur TDS, supplied by the Mobay Chemical Company) of minimum 99% purity, as checked by the "amine equivalent" method.¹⁴ Because of the higher reactivity of the *p*-NCO group of 2,4-toluene diisocyanate, the principal result is the reaction of one molecule of the diisocyanate with each terminal hydroxyl group on the polyester chain.

The polyester was weighed into a dried flask, and reagent grade benzene (dried over activated alumina) was added in sufficient amount to dilute the final adduct to a 50% nonvolatile content. The diisocyanate was then added to the resin solution with thorough mixing. A cold-water condenser was attached to the flask, and the reaction mixture was allowed to stand for 1/2 hr. After an induction period, exothermic heat raised the temperature to 40–50°C. The reaction mixture was then refluxed on a steam cone for 1 hr. and cooled to room temperature. When catalyst was used, it was added to the cooled adduct. The catalyzed mixture was used immediately for film preparation.

Preparation of Free Films

The films were prepared by casting on mercury. Mercury, which had been cleaned by passing through a fine silica sand filter, was poured over the flat-bottom of a rectangular pyrex dish. Five milliliters of dried benzene were poured over the

mercury, and the dish was covered with a piece of heavy paper and allowed to stand for a few minutes to accumulate an atmosphere of benzene vapor. The 50% benzene solution of the adduct was then poured over the mercury in an amount sufficient to form a dried film about 0.01 in. (10 mils) thick, and the dish was again covered with a piece of heavy paper and allowed to stand undisturbed.

Tack-free films without bubbles could be obtained in this manner with relatively few failures. The development of films clouded with small bubbles was not an uncommon occurrence. Such defective films were rejected, and new trials were made until optically bright films were obtained. Although atmospheric water is required to obtain tack-free films from adducts of this type, it is necessary to keep the water vapor pressure and reaction rate relatively low so that the carbon dioxide formed by some reactions can diffuse out of the film without nucleating bubbles. Once the exposed surfaces were tack-free, greater variations in post-curing conditions could be made without developing obvious film faults.

The term "curing," when used in this paper, will refer to the processes occurring on mercury when only one film surface was exposed. The term "aging" refers to the process history which followed after the films were removed from the mercury surface and supported with both faces exposed to the ambient environment selected for the aging process.

The mechanical tests were conducted in accordance with the specifications of ASTM Designation: 882-56T—"Tensile Properties of Thin Plastic Sheets and Films,"⁵ with the exception that the prescribed period of constant temperature-humidity conditioning of the specimens before testing was modified. Unless otherwise specified, the specimens were conditioned for 24 hr. at $23.4 \pm 1.5^\circ\text{C}$. and $50 \pm 3\%$ R.H.

The tensile test specimens were 1/2 in. by 4 in. strips cut from the film stock with a sheet metal cutter. A thin sheet of tin plate was used as a backing for the film during the cutting operation.

The tensile properties were determined with a modified Instron tensile testing machine equipped with a Sanborn Model 150 recorder. Stress-time curves were recorded at constant rates of jaw separation up to 20 in./min. A straining rate of 1000%/min. was used with initial jaw separation at 2 in.

By use of the data from the stress-time Sanborn recorder curve and the known constant rate of jaw

separation, the stress-strain curves could be constructed on rectangular coordinate paper. Samples of typical curve forms are shown in Figure 2.

The energy of rupture, which is defined as the area under the stress-strain curve, was calculated by graphical integration. The calculation of the other mechanical properties was by standard procedures.⁵ For calculation of true tensile strengths, it was assumed that deformation occurred without change in volume. The values reported are averages obtained from three or four specimens. The population standard deviation, as estimated from the range of values, was usually less than 5%.

Determination of Solvent Properties

The degree of swelling of the films by various swelling media was determined volumetrically by employing the principle of solvent displacement. The apparatus and experimental procedure are described by Hauser, Walker, and Kilbourne.¹⁵ Because many of the swollen polymers were too fragile to withstand unsupported suspension in the solvents, cylindrical sample holders formed from 325-mesh, 316 stainless-steel screen were used to contain the test specimens, which had a dry weight of 0.10–0.15 g.

All of the swelling measurements were made at $30 \pm 0.5^\circ\text{C}$. with reagent grade solvents. With the exception of 1,4-dioxane, which was redistilled before use, the solvents were used without further purification.

Solvent extraction tests on the polymeric materials were performed also. For this purpose, a number of 0.7–1.0 g. specimens of each film were immersed in 25 ml. of the solvents in individual containers at $30 \pm 0.5^\circ\text{C}$. After intervals of soaking, the solutions were drained from the swollen film into tared aluminum foil dishes, evaporated to near dryness on a steam cone, and finally dried under vacuum to constant weight at room temperature. Blanks with solvent alone were run and corrections were made for solvent residues when such were significant. When extraction rates were studied, the drained solvent was replaced with fresh solvent, and the sample was returned to the thermostat until another test.

The intrinsic viscosity in redistilled 1,4-dioxane was determined for the dioxane extracts by successive dilutions in a size 50 Cannon-Ubbelohde dilution-type viscometer at a temperature of $30 \pm 0.02^\circ\text{C}$. The initial polymer concentrations were determined gravimetrically as described above.

The specific viscosities, determined at four or

more concentrations, were used to calculate the intrinsic viscosity and k' values according to the Huggins viscosity equation:¹⁷

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

A PRELIMINARY CHARACTERIZATION OF SOLUBILITY PROPERTIES

A series of swelling measurements were made with solvents of variable solubility parameter in order to determine the solubility parameters of the polymers.

The films used for the preliminary tests were from stock cured without added catalyst for 48 hr. at 75°C . and aged for three months under room conditions. Figure 1 shows that this type of film reaches a steady-state after approximately two months of aging.

When films were immersed in the solvent, two competing processes followed, the swelling of the film (which was rapid), and extraction of solubles (a slower process); hence the swelling ratio passed through a maximum with time. The swelling ratio at the time it had its maximum value is referred to here as the maximum swelling ratio, $(V/V_0)_{\text{max}}$. This number was the most consistent factor which could be determined for any particular film from several rate curves for the swelling process. The rate of swelling per unit time up to the maximum value did not change much for different polymers in the same solvents. The maximum swelling ratios obtained with a typical film in a series of solvents are given in Table I. Maximum swelling developed in less than 1 hr. The solubility parameters of the one-component solvents are those given by Burrell.¹⁰ The solubility parameters for the binary solvent systems were calculated by the method proposed by Small.²⁴ Table I includes only the values for those binary compositions which exhibited the greatest swelling powers.

The maximum swelling ratio as a function of composition for the benzene–nitromethane and

TABLE I
Maximum Swelling in Various Solvents

Solvent	Solubility parameter	$(V/V_0)_{\text{max}}$
Ethyl acetate	9.1	3.1
Benzene	9.2	2.6
Benzene–isopropanol	9.8	4.6
Dioxane	9.9	6.2
Acetone	10.0	5.6
Benzene–nitromethane	10.2	4.3
Isopropanol	10.5	1.3

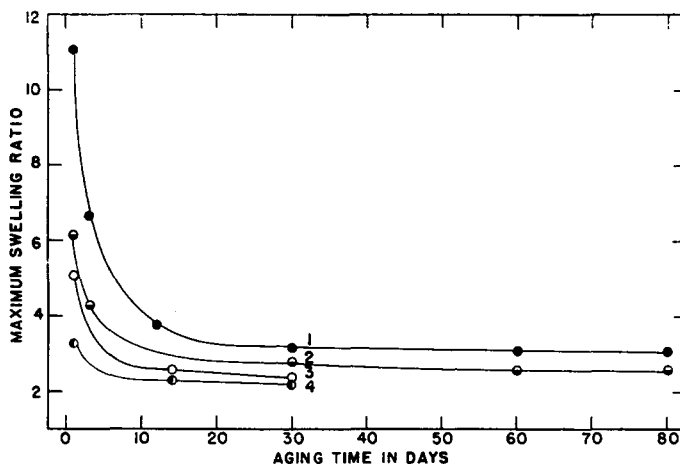


Fig. 1. Maximum swelling for noncatalyzed films cured at 75°C. for 48 hr. vs. aging time under room conditions: (1) polyester MW = 1150, swelling in ethyl acetate; (2) polyester MW = 1150, swelling in benzene; (3) polyester MW = 850, swelling in ethyl acetate; (4) polyester MW = 850, swelling in benzene.

benzene-isopropanol mixtures for two polymers formulated from polyester resins of different molecular weights are given in Tables II and III. Maximum swelling of both films occurred at a calculated solubility parameter of 9.7 ± 0.1 with benzene-isopropanol mixtures and 10.2 ± 0.1 with benzene-nitromethane mixtures. This difference might not be significant because the assumptions involved in the calculation introduce considerable error.¹³ Particularly doubtful is the assumption that no volume change occurs with mixing.

The results of these tests indicate that the solubility parameter of these particular polymers is approximately ten, and that the solubility parameter is relatively insensitive to the polyester molecular weight.

The results of swelling measurements with films

TABLE II
Maximum Swelling in Benzene-Isopropanol Mixtures

Mole fraction isopropanol	Calculated solubility parameter	$(V/V_0)_{max}$	
		R-3 ^a	R-2 ^a
0.0	9.2	2.8	2.2
0.1	9.4	—	3.1
0.2	9.6	4.2	3.7
0.3	9.8	4.5	3.5
0.4	10.1	4.2	3.3
0.5	10.3	3.9	3.2
0.6	10.5	3.6	2.8
0.7	10.7	2.9	2.6
0.8	11.0	2.5	—
1.0	11.5	1.3	1.2

^a Polyester molecular weight: R-3 = 1150; R-2 = 850.

TABLE III
Maximum Swelling in Benzene-Nitromethane Mixtures

Mole fraction nitromethane	Calculated solubility parameter	$(V/V_0)_{max}$	
		R-3 ^a	R-2 ^a
0.0	9.2	2.8	2.2
0.1	9.4	3.3	—
0.2	9.7	3.5	2.8
0.3	9.9	3.7	2.9
0.4	10.2	4.3	3.2
0.5	10.5	4.0	3.0
0.6	10.9	3.9	2.9
0.7	11.3	—	—
0.8	11.7	3.5	—
1.0	12.7	2.4	2.2

^a Polyester molecular weight: R-3 = 1150; R-2 = 850.

of widely differing behavior are given in Table IV. These results show that the relative order of swelling efficiency in this series of solvents remains the same for all the films. Dioxane exhibits maximum swelling power in this liquid series tested, and large decreases in dioxane resistance are coincident with increased swelling and/or extraction by the weaker solvents. This behavior indicates that the solubility parameter of the polymer is not altered significantly by such variances in molecular architecture as were developed in the polymers here tested, even though the polymers differ considerably in swelling behavior.

The solubility tests conducted with dimethylformamide at a later time showed that most of the films of Tables II-IV were completely soluble.

TABLE IV
Maximum Swelling of Films by a Spectrum of Solvents

Film No. ^a	Polyester mole. wt.	Benzene		Ethyl acetate		Benzene-nitromethane		Benzene-isopropanol		1,4-Dioxane	
		(V/V_0) _{max}	Extract in 2 hr., %	(V/V_0) _{max}	Extract in 2 hr., %	(V/V_0) _{max}	Extract in 2 hr., %	(V/V_0) _{max}	Extract in 2 hr., %	(V/V_0) _{max}	Extract in 2 hr., %
1A	1150	2.8	3	3.2	5	4.3	4	4.5	4	6.2	10 ^b
2A	850	2.2	2	2.4	3	3.2	3	3.7	3	—	—
1B	1150	5.6	12	4.8	70	—	—	—	100	—	100 ^c
2B	850	3.2	6	5.0	50	—	—	4.2	85	—	100 ^c
2C	850	2.5	3	—	—	5.8	7	10.0	11	14.0	20

^a Description of films: Series A: no catalyst; precure, 48 hr. at 75°C.; aging, 3 months at room conditions. Series B: 2½% *N*-methylmorpholine, ½% added before adduct formation; precure, 48 hr. at room temperature; aging, 3 months at room conditions. Series C: 2½% *N*-methylmorpholine; precure, 24 hr. at room conditions plus 24 hr. at 75°C.; aging, 2 weeks at 30°C. and 79% R.H.

^b Extraction time: 200 hr.

^c Extraction time: 1 hr.

Solution occurred in a short time with very little preliminary swelling. The only exception were some heat-cured, noncatalyzed films and some covalently crosslinked films formulated from polyester resins and 2,4-toluene diisocyanate-trimethylolpropane (2-ethyl-2-hydroxymethyl-1,3-propanediol) adducts. These films were moderately swelled, and the degrees of extraction were less than 2% after immersion for one week in dimethylformamide. No swelling could be detected at all with the weaker solvents.

Apparently, limitation of solubility in dimethylformamide can be used to indicate the presence or absence of covalent crosslinking. However, if covalent crosslinking is absent, then dimethylformamide is too strong a solvent to respond to such differences in molecular architecture as effect the behavior of weaker solvents.

The fact that in many cases gels were obtained with other relatively strong solvents even though the polymers were inherently soluble in dimethylformamide suggests that relatively strong bonding forces of less permanent nature operate to cause effective crosslinking at least at isolated spots along the chains. Moreover, preliminary tensile tests showed that all of these swellable films had high extensibility with relatively no permanent set. By analogy from experience with other polymers, such behavior is best explained as the result of a loosely crosslinked structure.¹² Reversible associations strong enough to yield bonds that retard compliance to mechanical stress but which may be broken down with specific solvents have been observed in other types of polymers. These are explained as due to either crystallites or to local-

ized regions of high hydrogen-bonding densities along the chains.^{16,25}

For materials of this type the heat of mixing is not a simple function of the cohesive energy densities;¹⁰ therefore, the behavior of solvents with these polymers should deviate from what is predicted from solubility parameter considerations alone. The results of swelling tests with a proper choice of solvents show a behavior which must be related to crosslink density, and the response to different solvents can distinguish crosslinks which can be reversed by solvation from stable covalent crosslinks. The utility of such an approach to discriminating the qualitative character of intermolecular forces in polymer networks is suggested implicitly in much of the solubility and swelling studies which have been published.^{2,9,10,19,25}

RESULTS AND DISCUSSION OF MECHANICAL TESTS

Tensile Properties

The mechanical properties of films formulated from polyesters of varying number average molecular weights with a constant NCO/OH ratio of 2/1 are listed in Table V. These films were cured without added catalyst at 75°C. for 48 hr., and aged for five months under room conditions.

These results do not necessarily represent the optimum mechanical properties obtainable with films of this type, but they are an indication of the great importance of the molecular weight of the polyester on the behavior of the films obtained. As the molecular weight is decreased, the form of the stress-strain curve, Figure 2, changes from that of

TABLE V
Mechanical Properties of Films Formulated from Polyesters of Varying Molecular Weights

Polyester molecular weight	Yield point		Ultimate elongation, %	Tensile strength, psi	True tensile strength, psi	Energy of rupture, ft.-lb./in.
	Stress, psi	Elongation, %				
690	5260	5	300	6320	25,300	1110
850	560	10	370	4880	22,900	690
1150	20	10	420	1900	9,880	190

an elastomeric material exhibiting stress-induced crystallization toward something more characteristic of a high modulus, fibrous material. The initial resistance to deformation increases and the rate of elastic response after removal of the stress decreases. The empirical relationships demonstrated here between tensile properties and molecular structure confirm the general principles of theory set forth by Alfrey and Gurnee⁴ and Hill and Walker.¹⁶

To show whether different curing conditions can have comparable effects on the molecular architecture and the related mechanical properties, several series of films were prepared for extensive testing.

The results of the mechanical tests for uniformly aged films cured with various catalysts are listed in Table VI. The most significant feature is the relative uniformity of the values obtained with all catalysts except such as function also as copolymerizing monomers. Only the lead-catalyzed,

heat-treated samples deviated to a significant degree, showing the common reinforcing effect of lead soaps in polar polymers.

Significant variations in the shape of the stress-strain curve and the stress relaxation times suggest that the molecular architecture varies from film to film, depending upon what catalysts were used. However, these variations are not of such a nature as to alter the conditions required for induction of crystallization. In all cases a secondary yield point, more or less well defined, was noted at approximately 300%, at which point the specimen turned opaque. This behavior is characteristic where extreme crystallization is induced.^{1,11}

The adducts catalyzed with hydroxyl-containing methyldiethanolamine yield films of lower strength and the strength decreases as the catalyst concentration is increased. This reduction in strength is to be expected as the introduction of hydroxyl groups reduces the NCO/OH ratio compared to the other polymers of the series.

The mechanical properties of films at various age levels for films catalyzed with 2½% *N*-methylmorpholine are given in Table VII, and those for films catalyzed with 0.1% cobalt plus 1.0% lead in Table VIII.

All films for each series were prepared from the same adduct (polyester molecular weight = 730 and NCO/OH ratio = 2/1). After a cure of 42 hr. at room temperature, the films were removed from the mercury surface and suspended by wire fasteners in the aging ovens. Two sets of aging conditions were used. The first was a temperature of 30°C., and 79% R.H. (atmosphere in equilibrium with a saturated ammonium chloride solution) and the second, 100°C., and 56% R.H. (atmosphere in equilibrium with a saturated potassium iodide solution). The relative humidity at the elevated temperature varied to some extent as equilibrium was difficult to maintain, and the actual humidity was probably less, at least during some intervals of aging.

At the start, the amine-catalyzed films were clear

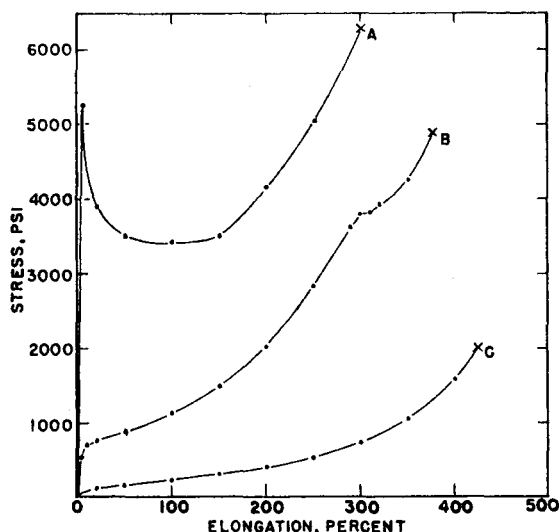


Fig. 2. Stress-strain response of polyurethane films formulated from polyester resins of varying molecular weights (A) polyester MW = 690; (B) polyester MW = 850; (C) polyester MW = 1150.

and colorless. Very little discoloration occurred in the lower temperature aging environment. However, similar samples aged at 100°C. turned pale yellow. The cobalt-lead catalyzed films were clear but already discolored at the time of removal from the mercury surfaces, and these became progressively darker with further aging, even at 30°C.

The mechanical properties of the films aged at

30°C. changed slowly with time toward the same limits as were approached more quickly by aging similar films at 100°C. The apparently lesser strength and toughness of low temperature aged films may not be real, because probably they were plasticized with more water than the freshly heat-aged samples which were conditioned before testing for only 1 hr. under ASTM test conditions (23.4 ± 1.5°C., and 50 ± 3% R.H.). The high yield

TABLE VI
Effect of Catalysts on the Mechanical Properties of Resulting Films

Film no.	Description of Film ^a		Yield stress, psi	Tensile strength, psi	True tensile strength, psi	Ultimate elongation, %	Energy of rupture, ft.-lb./in. ³
	Catalyst	Curing conditions					
1	None	96 hr., room cond.	1650	7620	40,100	440	1270
2	2% <i>N</i> -methylmorpholine	24 hr., room cond.	980	7190	44,600	520	1280
3	2% <i>N</i> -methylmorpholine	25 hr., room cond. + 2 hr., 90°C.	1010	7260	44,300	510	1330
4	0.1% cobalt + 1.0% lead	48 hr., room cond.	1380	7260	44,300	510	1350
5	0.1% cobalt + 1.0% lead	48 hr., room cond. + 2 hr., 90°C.	1420	7080	41,400	485	1250
6	1.0% lead	48 hr., room cond.	1410	7380	40,200	450	1260
7	1.0% lead	48 hr., room cond. + 2 hr., 90°C.	1780	8170	49,400	505	1520
8	0.2% cobalt	48 hr., room cond.	1210	7090	39,000	450	1130
9	0.2% cobalt	48 hr., room cond. + 2 hr., 90°C.	1000	7120	40,600	470	1130
10	2½% methyl-diethanolamine	24 hr., room cond.	1370	6340	38,000	500	1170
11	5% methyl-diethanolamine	24 hr., room cond.	1080	4190	24,700	490	810

^a Aging conditions: 30°C. and 79% R.H.; Film No. 1 aged for 90 days, all others 14 days.

TABLE VII
Mechanical Properties of Films Catalyzed by 2½% *N*-Methylmorpholine at Various Age Levels

Aging time ^a	Film thickness, mils	Yield stress, psi	Ultimate elongation, %	Tensile strength, psi	True tensile strength, psi	Energy of rupture, ft.-lb./in. ³
0	12-13	100	520	990	6,140	175
1h	11-12	1700	510	8480	51,700	1620
2h	10-12	2290	490	8030	47,300	1550
3h	11-12	1650	460	8050	45,100	1530
5h	12-14	2280	510	6840	41,700	1570
12h	12-14	2710	490	7190	42,400	1660
24h	12-14	2590	480	7100	41,200	1570
72h	10-12	1930	480	7830	45,400	1520
216h	11-12	1960	470	6950	39,600	1380
2d	10-12	260	440	2910	15,700	450
5d	12-14	330	470	3290	18,800	550
9d	13-14	470	470	4270	24,400	700
16d	11-13	600	450	4650	25,600	780
23d	10-11	1250	440	6360	34,400	1050
40d	13-14	1120	480	5880	34,100	1100

^a (h) denotes time in hours at 100°C.; (d) denotes time in days at 30°C.

TABLE VIII
Mechanical Properties of Cobalt-Lead-Catalyzed Films at Various Age Levels

Aging time ^a	Avg. film thickness, mils	Yield stress, psi	Ultimate elongation, %	Tensile strength, psi	True tensile strength, psi	Energy of rupture, ft.-lb./in. ³
0	11.5	175	430	2500	13,300	270
1h	11.5	1950	460	7620	42,700	1380
2h	11.5	2620	470	8120	46,300	1630
3h	12.5	2640	450	7690	42,300	1490
5h	12.5	2320	450	6960	38,000	1340
10h	12.0	2950	420	6340	33,000	1260
24h	12.0	3020	440	6340	34,200	1310
1d	12.5	250	450	3510	19,500	460
2d	12.5	350	480	4280	24,900	600
7d	12.5	525	460	5960	33,400	820
14d	13.0	625	470	6420	36,600	940
21d	13.0	790	480	6750	39,200	1080
35d	12.0		450	7340	40,400	1210

^a (h) denotes time in hours at 100°C.; (d) denotes time in days at 30°C.

stresses of the films aged at 100°C., which led to high rupture energies, were probably due to the fact that they did not reach equilibrium saturation with water vapor between oven time and time of testing. The yield values of these heat-aged films decreased after several days of storage at 23°C. and 50% R.H. until properties approached those for specimens aged at room temperature. Hence, the optimum mechanical properties obtained with the two sets of thermal aging conditions cannot be considered to be significantly different. Although rates of increase of strength with time differed at high and low temperatures, the steady state prop-

erties developed after film stabilization using either morpholine or metal catalysts were very much alike.

As the aging time increased, the shape of the curve changed from the rubbery type (type C, Fig. 2) to the more fibrous type (type A, Fig. 2). However, throughout aging history, both the ultimate elongation, and also the minimum elongation required to induce crystallization opacity remained nearly constant for all specimens.

The significance of the variation of mechanical properties with aging time will be discussed again later along with the solubility properties.

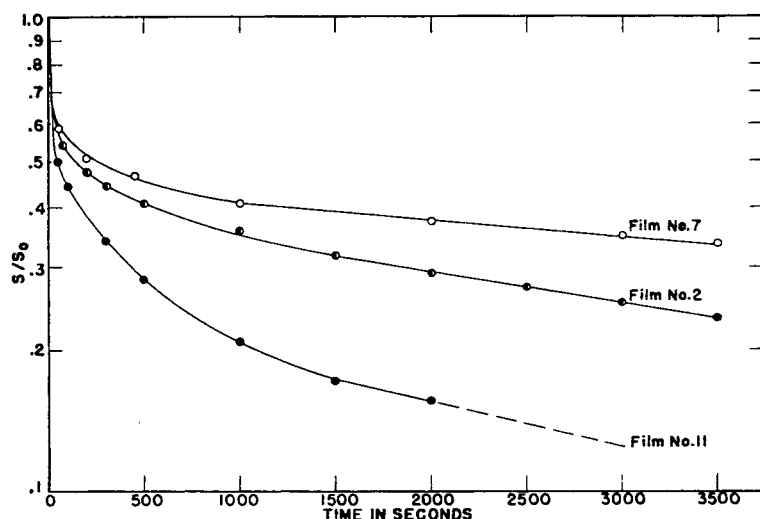


Fig. 3. Range of stress-relaxation response for films described in Table VI: logarithm of stress vs. time.

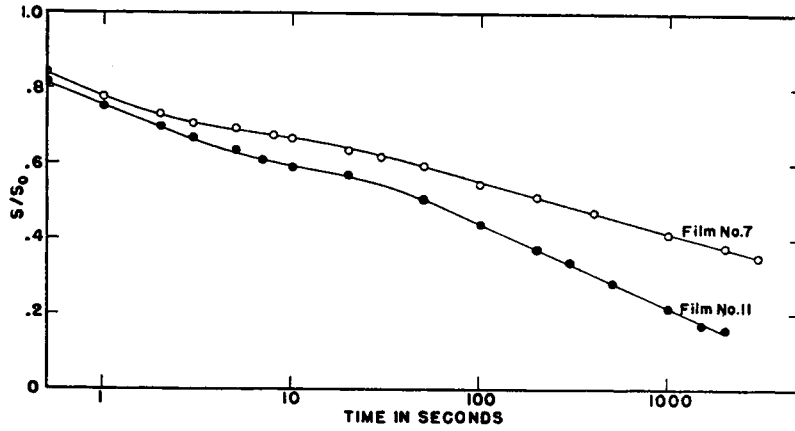


Fig. 4. Range of stress-relaxation response for films described in Table VI: stress vs. logarithm of time.

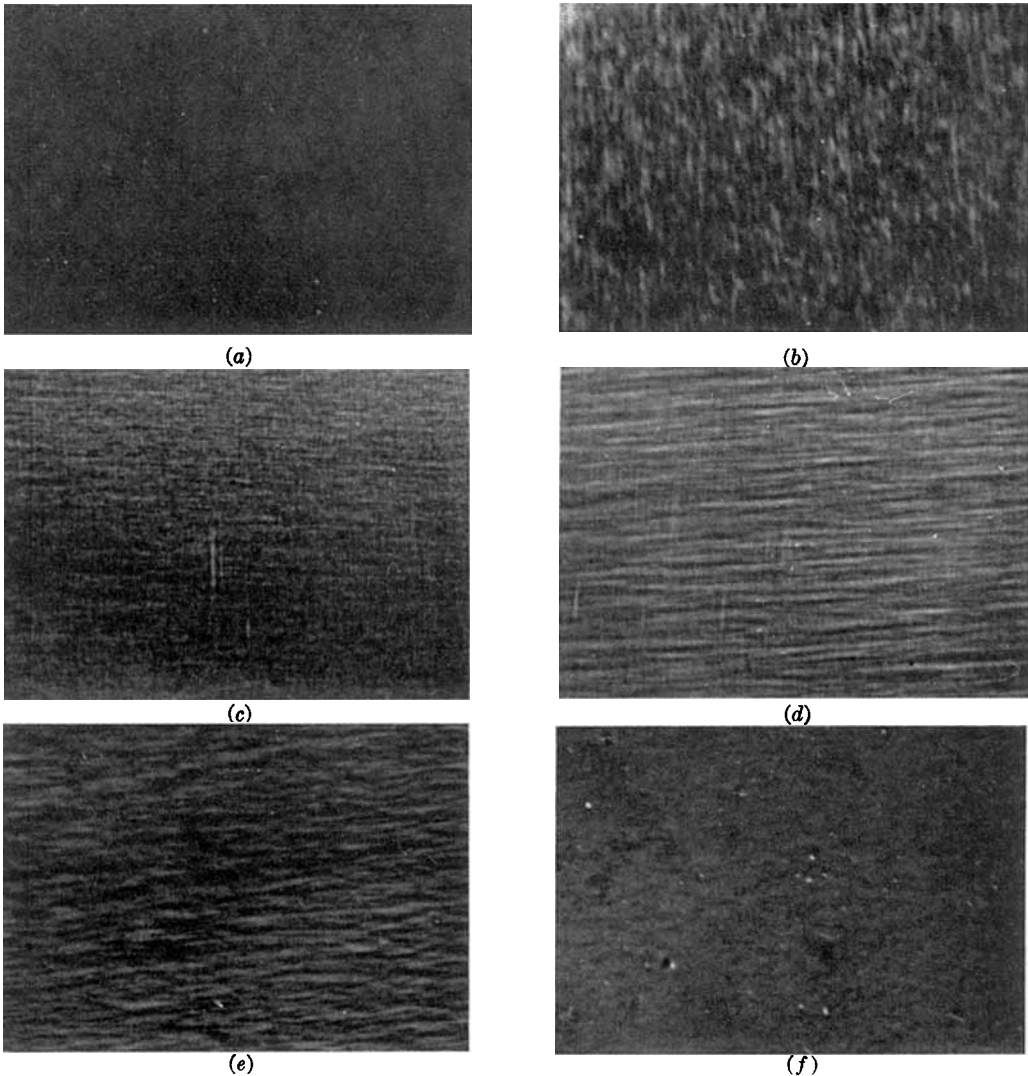


Fig. 5. Photomicrographs of morphological changes during stress relaxation: (a) initial unstrained specimen; (b) after 15 min. stress relaxation; (c) after 2 hr. stress relaxation; (d) after 4 hr. stress relaxation; (e) 30 min. after release of strain; (f) 24 hr. after release of strain. Magnification: 200 \times .

Relaxation Phenomena

The relaxation behavior of a representative series of films (described in Table VI) was determined with the same equipment as was used for the tensile tests. These tests were conducted to determine the general nature of response and whether property changes suggesting variations in molecular architecture could be detected. Some examples of typical stress relaxation curves are shown in Figures 3 and 4. Rapid responses are usually determined by the chemical composition of the polymer, while the slower mechanisms of response are more sensitive to molecular architecture and composition.⁴

When the stress on the specimens was released following a relaxation period of 1 hr. at constant strain, the recovery of original dimensions was essentially complete over a period of the next several hours. During the process of recovery of shape, the specimens recovered also their original optical transparency. This indicates a recovery of the original unoriented state.

Specimens strained to extensions of even less than that required to develop incipient opacity showed the same highly retarded relaxation and creep recovery processes.

A series of photomicrographs taken with a dark field, phase-contrast microscope at intervals during

stress relaxation at a constant strain of 400% are given in Figure 5. The specimens were extended to 400% at a straining rate of 1000%/min.

These photomicrographs show that considerable changes in the gross structure resulted from the relaxation processes. As the diffuse pattern disappeared, the specimens became clear which indicates that induced crystallinity is unstable even in strained specimens. A few hours after stress release, the permanent set seemed to be less than 10%. This nearly complete recovery of original dimensions, despite the fact that considerable morphological changes had occurred during straining seems to be an unusual and possibly unique property of polyurethanes.

SIGNIFICANCE OF THE SOLVENCY TESTS

Effect of Catalysts on Solvent Properties

The results of the swelling and extraction tests for a series of films cured with various catalytic systems are given in Table IX. The maximum swelling ratios obtained with dioxane for the cobalt- and/or lead-catalyzed films (Films No. 4 to 9) were within the range of 18 ± 4 . This range of variation is considerably greater than can be explained by experimental error.

TABLE IX
Effect of Catalysts on the Solvent Properties of Resulting Films

Film no. ^a	Catalyst	Benzene		Ethyl acetate		1,4-Dioxane			
		$(V/V_0)_{\max}$	Extract in 300 hr., %	$(V/V_0)_{\max}$	Extract in 300 hr., %	$(V/V_0)_{\max}$	Extract in 300 hr., %	50% extraction time, hr.	95% extraction time, hr.
1	None	2.7	3.0	4.5	15	7.5	100	3	72
2	2% <i>N</i> -methylmorpholine	2.2	3.8	3.4	18	13	71	8	700 ^b
3	2% <i>N</i> -methylmorpholine	2.3	4.2	3.7	24	14	70	7	700 ^b
4	0.1% cobalt + 1.0% lead	2.8	5.7	4.2	28	21	100	12	110
5	0.1% cobalt + 1.0% lead	2.7	6.3	4.4	31	22	100	12	100
6	1.0% lead	2.5	6.1	4.3	26	19	98	5	110
7	1.0% lead	2.5	6.4	4.0	30	15	98	3	120
8	0.2% cobalt	2.6	4.1	4.4	24	17	100	3	110
9	0.2% cobalt	2.4	4.2	4.1	28	14	100	2.5	100
10	2½% methyl-diethanolamine	2.8	3.6	5.0	37	4.2	100	0.2	0.5
11	2½% methyl-diethanolamine	2.6	5.1	3.0	100	2.6	100	0.2	0.5

^a Description of films given in Table VI.

^b 75% extraction time.

In correlation with the parallel extraction tests, the maximum swelling ratio increased as the time requirement increased for extraction of half the soluble polymer in the film. The rates of extraction as determined from the static extraction tests are not the same as those encountered during the swelling measurements because of variable agitation and concentration factors. For this reason accurate values of the true maximum swelling ratios could not be calculated by using these independent extraction data to correct the swelling data. If one considers the time required to extract 50% of the solubles as an indication of the initial extraction rate, it is clear that the true swelling ratios, which might be obtained by correcting the volume of the swelling specimen for the amount of extracted material, could differ from each other to a lesser degree than do the uncorrected maximum values here reported. The disparity of swelling and initial extraction rates between polymers which do not differ much in total extract, suggests that the polymers may differ considerably in molecular weights. Such differences may influence rates of solubility to a greater extent than they do equilibrium solubility values or solubility parameters.

The maximum swelling ratios and degrees of extraction obtained with benzene and ethyl acetate and the 95%-extraction times in dioxane for most of the metal catalyzed films seemed to be essentially alike; the differences shown in Table IX may be due entirely to experimental error.

The behavior of the *N*-methylmorpholine-catalyzed films (Films No. 2 and 3) differed from the pattern for the metal-catalyzed films in the following ways: the maximum swelling ratios in dioxane were lower than expected on the basis of correlation with the initial extraction rates; the maximum swelling by benzene and ethyl acetate was lower; the degree of extraction by dioxane was considerably lower.

The results were out of order for films cured with the hydroxyl-source catalyst, methyldiethanolamine. These films dissolved quickly and completely in dioxane, and the solubility in ethyl acetate was much greater. Because this gain in solubility and loss in strength increases with increasing amounts of methyldiethanolamine, it can be surmised that this catalyst is a copolymerizing monomer which creates a new polymer compared to others of this series.

The results of these solubility tests suggests that molecular architecture can be varied greatly by changing catalysts. If this is so, it might be

expected that variations should occur also in mechanical behavior.

The tensile properties of these films are listed in Table VI. The tensile strengths and toughness of the methyldiethanolamine-catalyzed films are lower. This is what might be expected, because their higher solubility in ethyl acetate indicates a lesser degree of intermolecular attractive forces. However, some considerable variance of mechanical properties should also be expected for the other polymers because of the considerable variance in their solubility behavior. Such expected differences did not develop. Apparently, some factors which can alter solubility exert only a minor influence on tensile behavior.

Effect of Aging on Solubility Properties

The results of the swelling and extraction tests with dioxane for films at various age levels are given in Figure 6.

Considering only the cobalt-lead-catalyzed films aged at 100°C. (Fig. 6a) one observes the following trends as the aging time increased: the rate of extraction increased; the intrinsic viscosity of the extracts from any given sample decreased during storage of the solution extract. All of these trends indicate that the main effect of aging was to degrade the polymer and this degradation continues even for polymer molecules in solution.

Data for similar films at 30°C. (Fig. 6b) show that the properties remained largely unchanged for 14 days of aging. Only a small increase in the extraction rate and a small decrease in the intrinsic viscosity resulted from increased aging times.

The data for the *N*-methylmorpholine-catalyzed films aged at 100°C. (Fig. 6c) showed the following trends as the aging time increased: the maximum swelling ratio decreased; the rate of extraction and the extent of extraction decreased. The intrinsic viscosity of the extract did not change after 14 days storage of the solution. Here, unlike the situation with cobalt-catalyzed films, no appreciable degradation of the polymer extract occurs in solution during the time intervals used to make this extraction test.

The results for the samples aged at 30°C. (Fig. 6d) were somewhat irregular, but they followed the same general pattern described above for the samples aged at 100°C. However the magnitudes of the variations were much smaller.

These results indicate that the main mechanism of aging for films catalyzed with *N*-methylmorpholine is such as to upgrade the polymer.

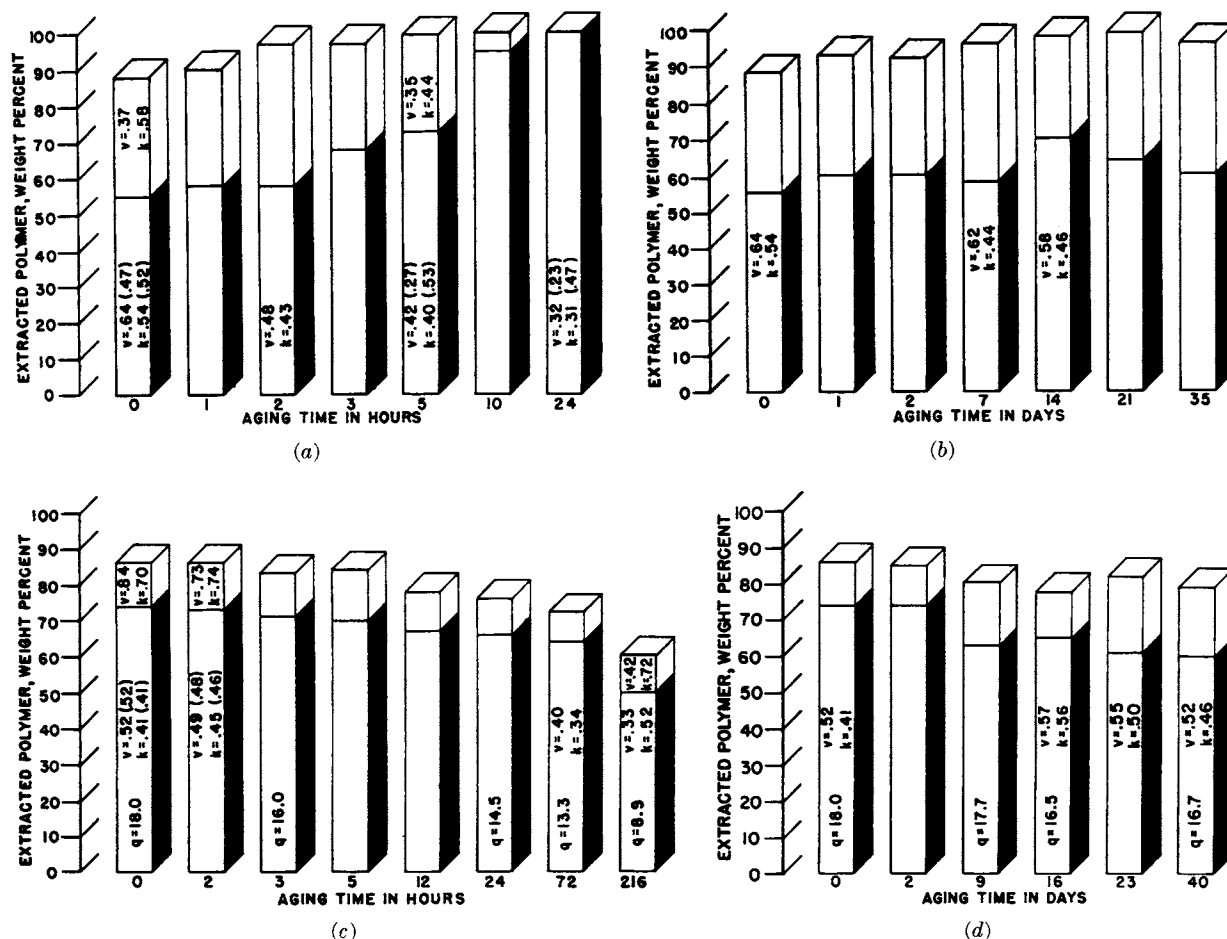


Fig. 6. Effect of aging on dioxane resistance of films: (a) catalyzed with cobalt-lead, aged at 100°C.; (b) catalyzed with cobalt-lead, aged at 30°C.; (c) film catalyzed with *N*-methylmorpholine, aged at 100°C.; (d) catalyzed with *N*-methylmorpholine, aged at 30°C. Shaded bar heights represent the degree of extraction after 72-300 hr. immersion; unshaded bar heights represent the degree of extraction after 2-5 hr. immersion; v denotes the intrinsic viscosity of the extracted polymer; k denotes the Huggin's k' value of the extracted polymer; the values in parentheses are the respective v and k' values after two weeks additional aging in solution at room conditions; q denotes the maximum swelling ratio.

This is the reverse of the behavior observed with the cobalt-lead-catalyzed films.

In the interpretation of the results of these tests it must be remembered that the incompletely age-cured films contained unreacted isocyanate groups and reactive hydrogen atoms. In addition traces of water were present in the test solvent. Therefore polymerization reactions could occur during the extraction tests, especially with such highly undercured films as may be encountered in the earlier stages of aging at low temperatures. If such reactions occur to an appreciable extent the characteristics of the polymer prevailing after long periods of solvent extraction could be appreciably different from what existed when the extrac-

tion tests were started. In this case the extraction data would be of less value than the more rapid swelling measurements as an index of solubility properties at early stages of the aging history. For well aged and well cured films, however, the extraction data are probably reliable and useful in characterizing the state at the time the films were entered into solubility tests.

Very few correlations were apparent between the mechanical properties of these polymers (see Tables VII and VIII) and their solubility behavior. The general decrease in true tensile strengths of the cobalt-lead-catalyzed films after aging 2 hr. at 100°C. indicates that side reactions which degrade solvent resistance will also damage strength. For

other nondegraded films, the differences in solubility properties can be very great without a parallel effect of some sort showing in the mechanical properties.

SUMMARY AND CONCLUSIONS

The results of the solvent tests show that the polymers here studied are inherently soluble in very strong solvent (dimethylformamide). This indicates that covalent crosslinking is either absent or present to only a slight degree. The swelling behavior with respect to solvents of lesser solvency power argues for the existence of crosslinking through secondary bonding forces of a semipermanent nature. Since the specimens swell appreciably, these crosslinks must occur at relatively infrequent intervals along the linear chains.

Variation of the swelling and solubility behavior of different films toward polar solvents having a solubility parameter near 10 shows that variations of the molecular structure must have resulted from modifications of the film aging process through the use of different catalysts. However, these vari-

ations had very little effect on the mechanical properties, except where the catalyst was a copolymerizing type which contributed parts to the polymer chains.

The mechanical behavior of the films is viscoelastic throughout the complete range of deformation. The highly retarded nature of the response indicates a high internal viscosity. The secondary creep mechanisms are so slow that no permanent deformation occurred during limited time intervals of a few hours even at strains beyond the tensile yield value.

The relaxed specimens were bright and transparent. This suggests a continuous amorphous phase. However, crystallization seemed to be induced by straining. This was indicated by increased opacity and increased modulus. The crystallization process appeared to be completely reversible, because the specimens become transparent again after stress relaxation at constant strain or after the stress was removed following a short period at high strain. These morphological changes caused by straining the specimens for

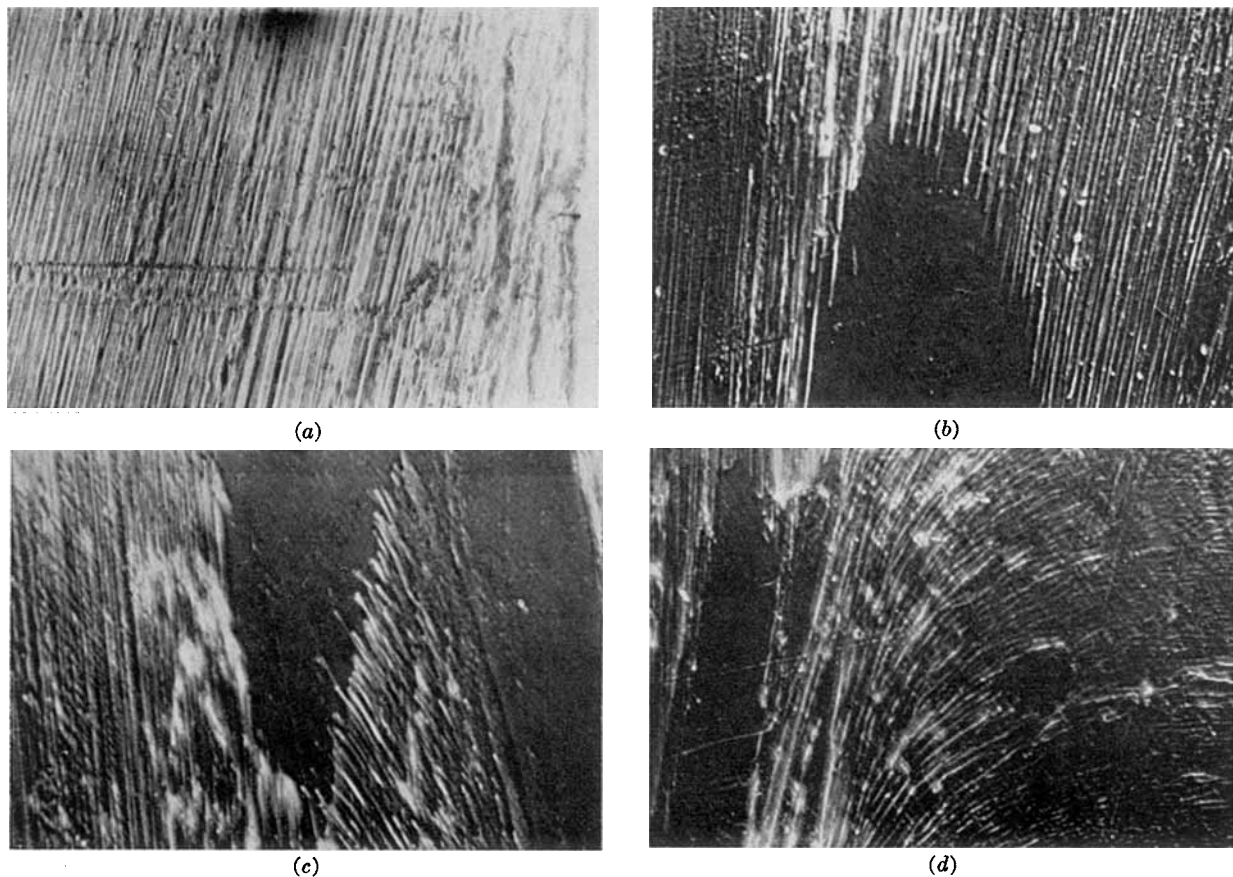


Fig. 7. Photomicrographs of transverse cracking developed in typical ruptured tensile specimens. Magnification: 150 \times .

either short or long periods seemed to produce very little permanent set.

The minimum strain required to induce opacity in polymers of fixed composition was independent of such variations in molecular structure as resulted from modifications of the curing conditions. The strain-induced cloud point and ultimate elongation did not depend upon degree of aging of the films even though other tensile properties changed.

It can be inferred that polymers derived from these isocyanate-modified polyesters possess a low degree of long range order. The polymer chains are heterogeneous with long polyester segments joined by relatively short segments of highly polar urethane and substituted urea linkages. The importance of the polyester molecular weight, i.e., the length of the polyester segment, on the mechanical properties has been shown. Apparently the separation interval of the polar urethane and urea linkages along the chain largely determines the mechanical behavior of the resulting films, and other modifications of the structure which can result from varying curing conditions have a negligible effect on mechanical properties.

Since the behavior at high extensions is fiberlike (true tensile strengths up to 50,000 psi), the mechanism of ultimate failure postulated for fibers can be expected to apply to these polymers. Ultimate failure of a fibrous material is considered to be a failure in tear which begins at the weakest spots and propagates transversely through the sample as a result of stress accumulation at the edge of the crack. Chain ends in an amorphous region represent weak spots as they are free to slip and form holes. If the chain ends are embedded in a crystalline region, strong intermolecular forces would tend to prevent slippage and hole formation; therefore, the specimens should develop more resistance to tearing under tension as the degree of crystallization is increased.

The high strength and toughness of the isocyanate-modified polyesters seems to be the result of their ability to resist the propagation of transverse cracks. Inspection of the relaxed segments of ruptured tensile specimens disclosed always large numbers of transverse cracks of varying lengths at numerous intervals throughout the previously stressed sections of the specimens (see Fig. 7)

On the basis of this study it is plausible to assume that the high strength and toughness of these materials result from the formation during stressing of a large number of minute "crystallites" which are probably composed of a small number of

imperfectly arranged chain segments. The driving force toward formation of these crystallites is such that a wide variation of other details of molecular architecture, such as moderate covalent crosslinking or other imperfections of order, does not appreciably affect their formation. The driving forces for the crystallization process apparently lie in the high dipole attractive forces between structural elements along the chains formed by the isocyanate reactions. Because of the extended length of the flexible polyester chain segments and their relatively disordered arrangement, the crystalline phase is unstable and requires the mechanical assistance of directional stress application to exist for even a transient period. The stress relaxation process involves in part the melting of the crystallites, causing the structure to return to the more stable amorphous or disordered condition. Because of the very low internal mobility of these polymers, these relaxation processes are slow, and the crystalline phase may persist for relatively long periods in films in the strained states.

The rapidity of formation of such an ordered state upon stress application and its slow decay explain the fact that these polymers resemble permanently crystalline types in their mechanical behavior even though they seem to be amorphous when the relaxation process comes to equilibrium with the thermal environment for all levels of strain which can be imposed on the material. This behavior resembles that of natural rubber and some other synthetic elastomers, but is found only rarely in condensation-type polymers at room temperature.

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Synopsis

Although the necessary conditions are known for formation of tough films from polyurethane intermediates, the chemistry is too complex to allow certain predictions of how variances in the polymerization process effect molecular structure and polymer properties. This research examined the hope that a correlated study of solubility and mechanical behaviors might show the effect of different catalysts and environments on crosslinking or other structural features which can modify film quality. Films (0.01 in. thick) were cast on mercury of intermediates derived from reaction in solvent of 2 moles of diisocyanate per mole of hydroxyl terminated polyesters, catalysts like *N*-methylmorpholine, methyldiethanolamine, and cobalt and/or lead ions being used to promote film-forming reactions. The films, when dry, were aged at different levels of temperature and humidity. The solubility behavior was rated by measuring swelling ratios, rates of extraction, and intrinsic viscosity of extracts. Mechanical properties were rated by measuring tensile and stress relaxation behavior. The stress-induced microstructure and fracture process were observed microscopically in a few typical specimens. The data support the theory that hydrogen bonding provides a strong crosslinking mechanism which dominates even the effects of moderate covalent crosslinking. Polymers derived from the same intermediates show very similar mechanical properties, even though significant differences in solubility properties suggest variances in other details of molecular structure.

Résumé

Bien que l'on connaisse les conditions nécessaires à la formation de films durs provenant de polyuréthanes, la chimie est trop complexe pour permettre quelques prévisions à propos des variations dans le processus de polymérisation affectant la structure moléculaire et les propriétés du polymère. Les recherches rapportées ici ont été entreprises dans l'espoir qu'une étude se rapportant en même

temps à la solubilité et aux comportements mécaniques puisse révéler les effets des différents catalyseurs et de leurs entourages sur le pontage ou d'autres caractéristiques structurales qui peuvent modifier la qualité du film. On prépare sur du mercure des films de 0.01 pouce d'épaisseur au départ de produits intermédiaires provenant de la réaction, dans un solvant, de 2 moles de diisocyanate par môle, de polyesters terminés par des hydroxyles en utilisant des catalyseurs comme la *N*-méthyl-morpholine, la méthyldiéthanolamine et des ions de cobalt et/ou de plomb pour favoriser les réactions de formation du film. Les films, une fois séchés, sont soumis à vieillissement à différents degrés de température et d'humidité. La solubilité est évaluée en mesurant des rapports de gonflement, le taux d'extraction et la viscosité intrinsèque des extraits. Les propriétés mécaniques sont évaluées par des mesures de tension et de relaxation à la tension. La microstructure et le processus de rupture de quelques spécimens typiques sont observés par microscopie; les données expérimentales confirment la théorie suivant laquelle une liaison hydrogène fournit un mécanisme de pontage important qui surpasse même les effets d'un pontage moyen par covalence. Les polymères dérivés des mêmes intermédiaires montrent des propriétés mécaniques très similaires bien que des différences significatives dans les propriétés de solubilité suggèrent des différences dans d'autres détails de la structure moléculaire.

Zusammenfassung

Obwohl die zur Bildung von zähen Filmen aus Polyurethanzwischenprodukten notwendigen Bedingungen unbekannt sind, so ist doch der Chemismus zu komplex, um über die Beeinflussung der Molekülstruktur und der Polymereigenschaften durch Änderungen der Polymerisationstemperatur bestimmte Voraussagen zu machen. Die vorliegende Arbeit wurde in der Hoffnung durchgeführt, dass eine gemeinsame Untersuchung der Löslichkeit und des mechanischen Verhaltens den Einfluss verschiedener Katalysatoren und des Milieus auf die Vernetzung und andere Strukturmerkmale, die die Filmqualität beeinflussen können, erkennen lassen wird. Film (0.01 in. dick) aus Zwischenprodukten, die aus der Reaktion von 2 Molen Diisocyanat und einem Mol Polyester mit endständiger Hydroxylgruppen unter Verwendung von Katalysatoren wie *N*-Methylmorpholin und Methyldiäthanolamin stammten, wurden, mit Kobalt- oder Bleiionen zur Beschleunigung der Filmbildungsreaktion, auf Quecksilber gegossen. Die getrockneten Filme wurden unter verschiedenen Temperatur- und Feuchtigkeitsbedingungen gealtert. Das Löslichkeitsverhalten wurde durch Messung des Quellverhältnisses, der Extraktionsgeschwindigkeit und der Viskositätszahl der Extrakte, die mechanischen Eigenschaften durch Messung des Dehnungs- und Spannungsrelaxationsverhaltens untersucht. Bei einigen typischen Proben wurden die spannungsinduzierte Mikrostruktur und der Bruchvorgang mikroskopisch beobachtet. Die erhaltenen Ergebnisse bilden eine Stütze für die Ansicht, dass Wasserstoffbindungen einen wirksamen Vernetzungsmechanismus liefern, der sogar den Einfluss einer mässigen kovalenten Vernetzung überwiegt. Polymere, die aus den gleichen Zwischenprodukten erhalten wurden, zeigen sehr ähnliche mechanische Eigenschaften, obwohl deutliche Unterschiede in den Löslichkeitseigenschaften auf Abweichungen in Feinheiten der Molekülstruktur hinweisen.

Received December 27, 1960