

# Effect of Humidity and Elevated Temperatures on Physical Properties of UV-Cured Polymers\*

DONALD A. BOLON, GARY M. LUCAS, DANIEL R. OLSON, and  
KAREN K. WEBB *General Electric Company, Corporate Research and  
Development Center, Schenectady, New York 12301*

## Synopsis

Many UV-cured acrylates, epoxides, and thiol-enes suffer a dramatic, reversible loss of tensile strength during exposure to moisture and/or elevated temperatures. Certain formulations are especially sensitive and lose up to 95% of their dry tensile strength in a humid environment. Glass transition temperatures of these materials are also much lower in high humidity than they are in low humidity. It is proposed that these losses of physical properties in high humidity are due to reduced intersegmental attractions of polymer chains caused by preferential hydrogen bonding to water.

## INTRODUCTION

In applications where specific physical or electrical properties are important, polymers must generally maintain these properties over a wide range of temperature and environmental conditions. Long-term weathering of many polymers can lead to an irreversible loss of physical properties through chemical degradation. However, short-term exposure to high temperatures and/or high humidity can also be devastating to certain polymers, even in the absence of chemical degradation.

The tensile strengths of a number of polymers have been measured at various temperatures. Generally, the tensile strengths of amorphous thermoplastics decrease with increasing temperature,<sup>1,2</sup> with the loss being especially severe near the glass transition temperature ( $T_g$ ).<sup>3,4</sup> Brendly implied that a polymer's  $T_g$  influences the shape of a plot of its tensile strength versus temperature, but specific data were not presented.<sup>5</sup> On the other hand, some thermosetting polymers increase in tensile strength with increasing temperature.<sup>6</sup> This phenomenon has been ascribed to unequal stress distribution in the crosslinked matrix which causes premature rupture unless it is relaxed as the temperature rises.

The effect of humidity on the tensile strengths of polymers has received relatively little attention. Lawton and co-workers found that an increase in relative humidity from 0 to 90% decreased the tensile strengths of cellulose acetate and cellulose nitrate by 20 to 25%.<sup>7</sup> Gorelov and his co-workers reported that a 70% increase in relative humidity causes only a 7% decrease in the tensile strength of poly(methyl methacrylate).<sup>8</sup> Browning recently reported that absorbed moisture plasticizes a crosslinked epoxy resin system causing the  $T_g$  to be lowered and the relaxation modulus to shift to shorter times.<sup>9</sup> Recent studies have shown

\* A portion of this work was presented in a paper at the National ACS Meeting, Miami Beach, September 1978, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.*, **39**, 512 (1978).

that humidity depresses the  $T_g$  of epoxy matrix materials<sup>10</sup> and influences the tensile strength of composite structures which contain epoxy resins.<sup>11</sup> In a practical application, it was found that the chief environmental hazard affecting the strength of epoxy adhesives is humidity.<sup>12</sup>

In the course of developing UV-cured crosslinked polymers for use under a wide variety of temperature and humidity conditions, a striking effect of humidity on tensile strength of these crosslinked polymers was noted. The present study was undertaken to investigate systematically the effect of humidity on the tensile strengths of a variety of UV-cured polymers both at ambient and at elevated temperatures. Several classes of polymers of general interest in UV-curing applications were included in this study—acrylated urethanes, thiol-enes, and epoxies. These types of polymers are being used in a variety of commercial applications.

## RESULTS

### The Effect of Humidity on Stress-Strain Behavior at Ambient Temperature

Materials that maintain high tensile strengths in both dry and humid environments were of particular interest during this study. In order to screen for such properties, the stress-strain behavior at ambient temperature was determined for polymer films that were either stored in a desiccator or kept at room humidity (30–50% relative humidity) to simulate a dry environment (“dry” film) and stored at 97% relative humidity for 15 hr to simulate a humid environment (“wet” film). Little difference was noted between physical properties of wet and dry thermoplastic materials such as ionomer resins, polycarbonate, or plasticized cellulose acetate. Figure 1 shows the stress-strain behavior found for plasticized cellulose acetate. The observed 20% loss in tensile strength at high humidity agrees with the results of Lawton and co-workers.<sup>7</sup>

Stress-strain testing of UV-cured films made from thermosetting resins revealed that humidity frequently has a drastic effect on these materials. For

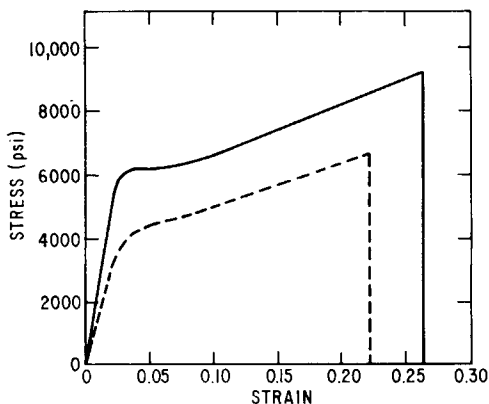


Fig. 1. Stress-strain behavior of wet (---) and dry (—) cellulose acetate films plasticized with diacetone alcohol.

TABLE I  
Effect of Humidity on Tensile Strengths of UV-Cured Epoxy Resins

Epoxy resin	Dry tensile strength, psi	Wet tensile strength, psi
30 pbw Niax Polyol 0200 70 pbw CY 179 <sup>a</sup>	6400	1500
30 pbw Niax Polyol 0200 <sup>b</sup> 70 pbw Epon 828 <sup>c</sup>	5000	2800
30 pbw Niax Polyol 0200 70 pbw DEN 431 <sup>d</sup>	6200	3100

<sup>a</sup> Cycloaliphatic epoxy resin available from Ciba Geigy.

<sup>b</sup> Caprolactone diol, average molecular weight 530, hydroxyl number 212, Union Carbide.

<sup>c</sup> Epoxy resin available from Shell Chemical Co.

<sup>d</sup> Epoxy novolak resin available from Dow Chemical Co.

example, some UV-cured epoxies suffered 50% or more loss of tensile strength when wet (see Table I and Fig. 2). Ultraviolet-cured acrylics frequently had an even larger loss of strength with 80 to 90% loss being common (Table II and Fig. 3). A third class of UV-cured resins, the thiol-enes, was also found to suffer loss of tensile strength when exposed to moisture (Table III). A thiol-ene resin designated 611AG (W. R. Grace Co.) was found to be somewhat sensitive to moisture as shown in its stress-strain behavior illustrated in Figure 4.

### Stress-Strain Behavior at Elevated Temperatures

Not only does humidity have a pronounced effect on tensile strength, but the temperature at which a polymer is tested also affects its tensile strength, especially if the material is wet. Figure 5 shows the tensile yield as a function of temperature of a wet and dry UV-cured thiol-ene film. This was one of the better thiol-ene materials since at 25°C it lost only 50% of its tensile strength after humidity conditioning. However, when it was tested at 40°C, it lost 90% of its tensile strength after humidity conditioning (Fig. 5).

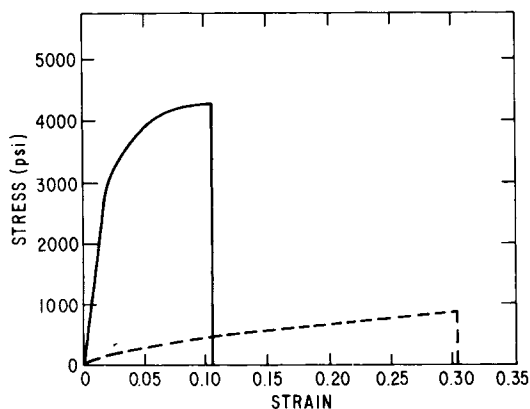


Fig. 2. Stress-strain behavior of wet (----) and dry (—) UV-cured epoxy films consisting of 50 pbw CY-179 and 50 pbw of Dow 741.

TABLE II  
 Dry and Wet Tensile Strengths of UV-Cured Formulations of  $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}(\text{CH}_3)-\text{O}_2\text{CNHC}_4\text{H}_9$ , HPABI, Crosslinked with Decreasing Amounts of Diacrylates

Diacrylate	Dry tensile strength, psi	Wet tensile strength, psi
IPDI-2HPA <sup>a</sup>		
50 wt %	10 000 <sup>b</sup>	7 800 <sup>b</sup>
35 wt %	8 500 <sup>b</sup>	3 500
20 wt %	4 000	200
TDI-2HPA <sup>c</sup>		
50 wt %	10 000 <sup>b</sup>	8 300 <sup>b</sup>
30 wt %	7 000	1 900
15 wt %	1 100	100

<sup>a</sup> Diacrylate obtained from reaction of 2 moles hydroxypropyl acrylate with 1 mole isophorone diisocyanate.

<sup>b</sup> Value recorded is stress at fracture,  $\sigma_y$ .

<sup>c</sup> Diacrylate obtained from reaction of 2 moles hydroxypropyl acrylate with 1 mole toluene diisocyanate.

A UV-cured epoxy film prepared from a commercial epoxy novolac (DEN-431)<sup>13</sup> and a hydroxy functional polyester (Rucoflex F 1016)<sup>14</sup> was humidity conditioned, and its tensile strength was measured as a function of temperature. Figure 6 shows that this material does not suffer as large a loss in tensile strength as the thiol-enes.

The properties of several acrylics were examined for their sensitivity to humidity and elevated temperatures. A UV-cured composition made from the following acrylated urethanes was tested:

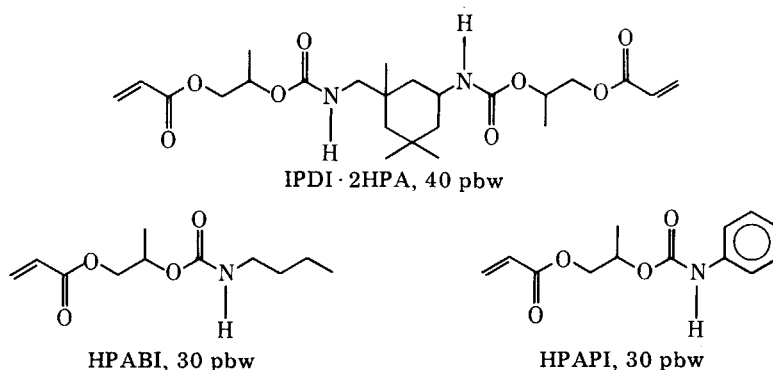


TABLE III  
 Dry and Wet Tensile Strengths of UV-Cured Thiol-ene Resins

Resin	Dry tensile strength, psi	Wet tensile strength, psi
70 pbw 611 AE, <sup>a</sup> 30 pbw 3861-C <sup>a</sup>	2600	1100
60 pbw 611 AE, 40 pbw 9386-14 <sup>a</sup>	2500	1000
35 pbw 611 AE, 65 pbw 7261 <sup>a</sup>	3300	900
9386-12 <sup>a</sup>	1100	700
9386-14 <sup>a</sup>	1500	800

<sup>a</sup> Thiol-ene resin available from W. R. Grace Co.

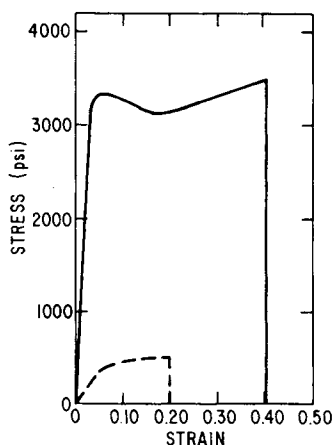


Fig. 3. Stress-strain behavior of wet (---) and dry (—) UV-cured acrylic films consisting of equal parts of Pierce and Stevens' H3908X-1 and H9309X.

As shown in Figure 7, a significant loss in properties occurred when the film was conditioned in humidity. In another composition, the monoacrylate HPAPI was replaced by ethylhexyl acrylate (EHA). The lower set of curves in Figure 7 shows the stress-strain behavior of this UV-cured composition. The overall lower tensile strength of both the wet and dry films of this second composition is probably caused by the plasticizing effect of the ethylhexyl group. In this case, the drop in tensile strength in high humidity was much less than in the first formulation and may be due to the hydrophobicity of the ethylhexyl group.

The degree of cure of a UV-curable resin was found to have a large effect upon the resultant polymer's tensile properties. For example, an acrylic film made from 100 pbw of diacrylate TMHMDI · 2HEA and cured for two different times,

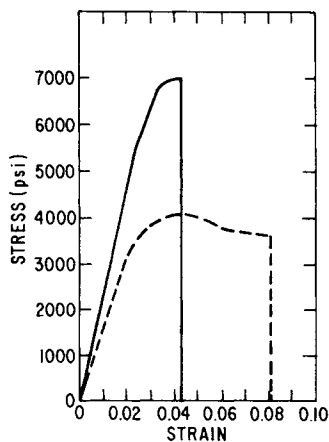
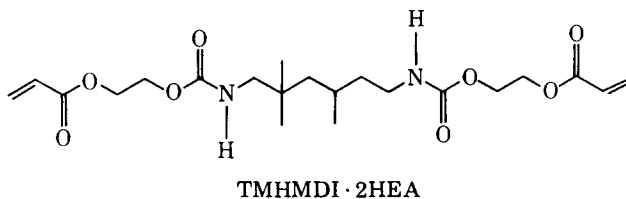


Fig. 4. Stress-strain behavior of wet (---) and dry (—) UV-cured thiol-ene 611AG films.

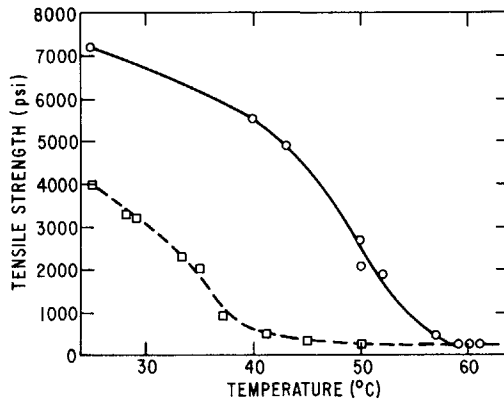


Fig. 5. Effect of temperature on tensile strength of wet (---) and dry (—) UV-cured thiol-ene 611AG films.

10 sec and 5 min, has the tensile properties illustrated in Figure 8. It appears that a higher degree of cure improves the resistance of this material to moisture and/or temperature.

### Glass Transition Temperature

In an attempt to understand why humidity has such a detrimental effect on the tensile strength of UV-cured resins, the glass transition temperatures of wet and dry films were determined using differential scanning calorimetry (DSC).

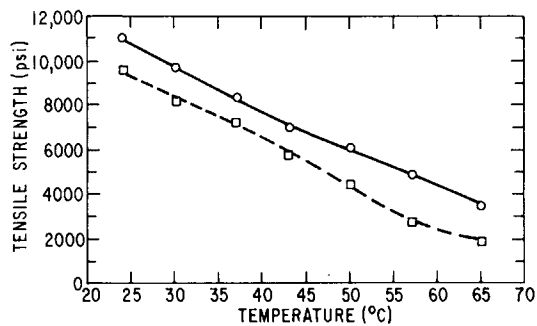


Fig. 6. Effect of temperature on the tensile strength of wet (---) and dry (—) UV-cured epoxy films consisting of 70% DEN 431 and 30% Rucoflex Polyester F 1016.

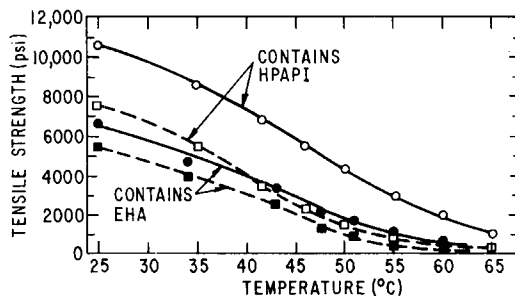


Fig. 7. Effect of temperature on tensile strengths of wet (---) and dry (—) UV-cured acrylics.

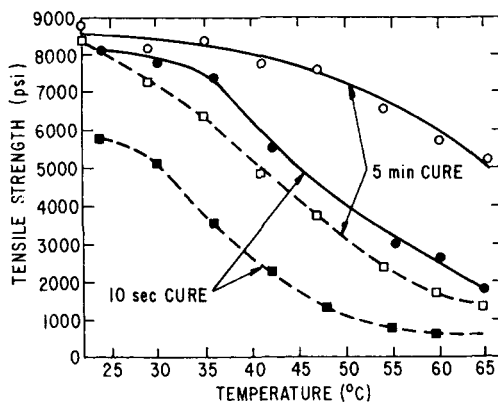


Fig. 8. Effect of temperature on tensile strengths of wet (---) and dry (—) UV-cured diacrylate TMHMMDI-2HEA films cured for two different times.

Table IV shows the apparent glass transition temperatures of selected wet and dry materials.<sup>15</sup> It can be seen that the  $T_g$  values of wet films are considerably lower than those of the corresponding dry film.<sup>16</sup> The lowering of the  $T_g$  is reversible since it was found that several hours of drying causes the “wet”  $T_g$  to return to the “dry” level.

## DISCUSSION

While certain thermoplastic materials such as cellulose acetate suffer some loss of tensile strength in a humid environment, the change is small compared to that observed for UV-cured thermosetting polymers. During stress-strain

TABLE IV  
Glass Transition Temperatures of UV-Cured Thermosetting Polymers

Polymer	$T_g$ , °C	
	Dry	Wet
Thiol-ene 611AG <sup>a</sup>	58	33
Epoxy { 70% DEN-431 <sup>13</sup> 30% Rucoflex F 1016 <sup>14</sup>	60	32
Acrylics		
50% IPDI-2HPA, <sup>b</sup> 50% HPABI <sup>b</sup>	66	43
35% IPDI-2HPA, <sup>b</sup> 65% HPABI <sup>b</sup>	48	23
20% IPDI-2HPA, <sup>b</sup> 80% HPABI <sup>b</sup>	28	8
50% TDI-2HPA <sup>b</sup> , 50% HPABI	67	44
30% TDI-2HPA <sup>b</sup> , 65% HPABI	44	20
40% IPDI-2HPA, 30% HPABI, 30% HPAPI	58	33
100% Diacrylate TMHMMDI-2HEA		
10-sec cure	48	36
5-min cure	84	44
Plasticized cellulose acetate	110	100

<sup>a</sup> W. R. Grace Co.

<sup>b</sup> See footnotes in Table II.

testing of thermoplastic materials, the polymer chains can either slide past each other or experience a discontinuous jumping action from one position in the lattice to another.<sup>17</sup> The ease of either depends on the nature of the groups on the polymer chain and the forces that exist between them. Intermolecular hydrogen bonding is likely to contribute to the overall strength of a polymer such as cellulose acetate. As stretching proceeds, hydrogen bonds are broken, and stress is redistributed to polymer chains held together by carbon-carbon bonds.<sup>6</sup> When water is present, it will be attracted to hydrophilic sites and most likely will break up any intermolecular hydrogen bonding that might exist at such sites.<sup>18</sup> The somewhat lower tensile strength of wet cellulose acetate is probably due to this. But most of the tensile strength is retained, due to orientation and concomitant distribution of stress over many molecules which can still occur during stretching.

With a plausible mechanism for the stress-strain behavior of wet and dry cellulose acetate, the question then arises as to why UV-cured thermosetting polymers behave so differently. Chemical degradation by hydrolysis could conceivably occur during exposure to high humidity. However, this can be ruled out since the effect of humidity was found to be reversible—samples of these materials that had been exposed to high humidity showed a full recovery of their tensile strengths after being dried. Absorbed water must then play some role in the tremendous loss of tensile strength. Furthermore, this behavior does not appear to be related to the amount of water absorbed since cellulose acetate that has been humidity conditioned contains 5.3% water while thio-enes contain 1–2%, the epoxies contain 1–2%, and the acrylic formulations contain 1–3%.

The strength of a dry, crosslinked polymer film is partly derived from primary bonds that connect polymer chains (crosslinks).<sup>6</sup> However, secondary forces, such as hydrogen bonding between segments, must be considered for the crosslinked UV-cured materials discussed above. A simple way to think of this is to consider it crosslinking by hydrogen bonding. This crosslinking, whether from primary chemical bonds or hydrogen bonds, provides a mechanism for distribution of stress among a number of chains, thereby increasing the polymer's strength.

When water is absorbed in these crosslinked polymers, it will likely be attracted to hydrophilic sites breaking up hydrogen bonding and reducing intersegmental attractions which can occur in its absence.<sup>18</sup> With reduced intersegmental hydrogen bonding, the strength of the polymer would rely on chains connected by primary bond crosslinks. This effectively means that the amount of crosslinking would be reduced.

In order to see the effect of reduced crosslinking by primary chemical bonds, successively smaller amounts of diacrylates were added to the monoacrylate  $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}_2\text{CNHC}_4\text{H}_9$ , as shown in Table II. As expected, increasing amounts of diacrylate led to higher strength materials. It is interesting to note that the tensile strength of the dry formulation containing 20% diacrylate is about the same as the tensile strength of the wet formulation containing 35% diacrylate. The same is true for dry formulations containing 35% diacrylate and wet formulations containing 50% diacrylate. These data indicate that these materials have lower tensile strengths when the amount of crosslinking is reduced and that water lowers their tensile strengths. Although not unequivocal, they are at least consistent with a mechanistic interpretation which argues that hy-



drogen bonding occurs in these dry materials, contributing to their tensile strength, while water destroys intersegmental hydrogen bonding, leading to a reduction in tensile strength. An attempt was made to lend further support to this mechanism by monitoring hydrogen bonding using infrared spectroscopy. Unfortunately, the O-H region was broad and ill defined for both wet and dry samples.

Thermoplastic materials such as cellulose acetate are dependent upon a relatively high molecular weight for their strength, while UV-cured thermosets depend upon a relatively high amount of crosslinking for their strength. The data in Table II show that low amounts of crosslinking lead to low tensile strengths for these polymers. The fast and relatively cool cures effected by UV light apparently do not lead to materials with high molecular weights or much tensile strength in the absence of a high amount of crosslinking. This is probably due to relatively low monomer conversions. Evidence for this was recently reported by Moore, who found that monomer conversions in photopolymerizations are significantly lower than they are in thermal polymerizations.<sup>19</sup>

It might be argued that reduction of tensile strength in humidity is not due to reduced intersegmental attractions as a result of preferential hydrogen bonding to water, but rather to a lowered glass transition temperature. However, glass transition temperatures are also thought to be a function of segmental motion, which is a function of intersegmental attractions.<sup>20</sup> It thus seems reasonable to propose that both the glass transition temperature and the tensile strength are lowered because of reduced intersegmental attractions when preferential hydrogen bonding to water occurs.

## EXPERIMENTAL

### Materials

**HPABI.** Hydroxypropyl acrylate (65.5 g, 0.50 mole), butylisocyanate (52.5 g, 0.53 mole), dibutyltin dilaurate (0.01 g), and *t*-butylcatechol (0.1 g) were combined and stirred at 60°C for 17 hr to give *N-n*-butyl acryloxypropyl carbamate (HPABI).

**HPAPI.** Hydroxypropyl acrylate (260 g, 2.00 mole), phenyl isocyanate (246 g, 2.07 mole), 10 drops dibutyltin dilaurate, and 0.5 g *t*-butylcatechol were combined and stirred at 70°C for 17 hr to give *N*-phenyl acryloxypropyl carbamate (HPAPI).

**IPDI 2HPA.** Isophorone diisocyanate (222 g, 1.0 mole), hydroxypropyl acrylate (269 g, 2.07 mole), 0.7 g *t*-butyl catechol, and 40 drops dibutyltin dilaurate were combined and stirred at 65°C for 46 hr to give IPDI 2HPA.

**TMHMDI 2HEA.** Trimethylhexamethylene diisocyanate (40.8 g, 0.20 mole), hydroxyethyl acrylate (50 g, 0.43 mole), dibutyltin dilaurate (0.05 g), and *t*-butylcatechol (0.1 g) were combined and stirred at 75°C for 12 hr to give trimethyl-4,13-dioxo-3,14-dioxa-5,12-diazahexadecane-1,16-diyl-2-propenoic acid (TMHMDI 2HEA). Infrared absorptions (thin film) occurred at 3.0 and 4.87  $\mu\text{m}$ .

### UV-Curable Resins

The UV-curable epoxy resin was formulated by combining 100 parts by weight (pbw) of the epoxy monomers or oligomers with 2 parts by weight of bis(*p*-tolyl)iodonium hexafluoroarsenate.<sup>21</sup> The UV-curable acrylates were prepared by combining 1 pbw diethoxyacetophenone with 100 pbw of the acrylic monomers or oligomers. The thiol-ene resins were obtained directly from W. R. Grace Photopolymer Division and were already sensitized.

### UV Cure

The sensitized resins were placed on glass plates, using a doctor blade technique, in films with a nominal 0.025 cm thickness. Those films sensitive to oxygen inhibition were first cured in a conveyORIZED system where they received, in succession, a medium-pressure mercury arc exposure in air, low-pressure mercury arc exposure in nitrogen, another medium-pressure mercury arc exposure in air, all at 15 in./min, after which the film was given a final cure under a GE H26T8/1 mercury arc lamp at 17.5 cm for 5 min. The latter exposure generated considerable heat in the film. Those resins not sensitive to oxygen inhibition were given only the 5-min hot UV cure. Other resins not subject to oxygen inhibition were cured with a GE-H400AT8 lamp ballasted at 800 W.

### Stress-Strain Testing

The specimens for the testing were cut from the films using the dimension given in ASTM D1708, i.e., a dumbbell-shaped specimen with a gauge length of 0.876 in., a width of 0.187 in., and a thickness of 0.0094–0.0136 in. The stress-strain data on these specimens were obtained on an Instron Corp. universal testing instrument with a cross-head speed of 0.05 in./min.

### Conditioning of Films

The films were tested after conditioning at ambient conditions (between 30 and 50% relative humidity), in dry conditions (18 hr in a CaSO<sub>4</sub> desiccator) or in humid conditions (18 hr at 90°F and 95 to 97% relative humidity). All of the films used to determine tensile strength as a function of temperature were conditioned using the latter two techniques.

### *T<sub>g</sub>* Measurements

Ultraviolet-cured films conditioned in either a desiccator or a humidity chamber, as described above, were sealed in aluminum pans immediately after conditioning.<sup>22</sup> They were scanned in a Perkin-Elmer DSC-2 differential scanning calorimeter at 20°C/min. The onset of the transitions were taken as the *T<sub>g</sub>* values following the method of Tan and Challa.<sup>23</sup>

### Water Absorption Measurements

Water absorption by the various formulations was determined by the weight difference of films after subjecting them to dry and wet conditions. Three samples of each cured formulation,  $6.9 \times 5 \times 0.03$  cm, were stored first in a vacuum desiccator over  $P_2O_5$  at  $22^\circ C$  for five days and then in a Vapor-Temp controlling relative humidity chamber at  $90^\circ F/95\% RH$  for three days. The amount of water absorbed per gram of dry film was calculated and the three values were averaged.

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15. The  $T_g$  values of dry materials were determined from the second or third heating in a differential scanning calorimeter. By necessity, the  $T_g$  values of wet materials are from the first heat; they may not be true values, but they are reproducible to within a few degrees for a given sample.
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Received September 7, 1979