

Estimation of Crosslinking of Diallyl Phthalate Prepolymer. An Investigation by Infrared Spectroscopy

KATSUNARI YOSHIDA and HARUNORI KAMADA, *Central Research Laboratory, Sumitomo Chemical Co., Ltd. Takatsuki, Osaka, Japan*, and JU KUMANOTANI, *The Engineering Research Institute, The University of Tokyo, Tokyo, Japan*

Synopsis

The cure of the diallyl phthalate prepolymer was studied by means of infrared spectroscopy. It was found that the C=C stretching band of the allyl group, which appears at 1647 cm^{-1} in diallyl phthalate monomer, splits into two bands at 1645 and 1651 cm^{-1} in both of the prepolymers and cured resins derived therefrom, the split band being found to be mostly useful to investigate the highly cured resin system of diallyl phthalate. On the basis of the split band, α is defined as a new parameter expressing a degree of residual unsaturation of diallyl phthalate prepolymers as well as highly crosslinked polymers, as revealed experimentally. Further, α proved to correlate closely with other parameters such as the iodine value measured for the prepolymers, and swelling weight ratio or Barcoal hardness (hot) measured for the cured resins, it becoming evidently a convenient parameter to examine the degree of crosslinking of diallyl phthalate resin system. The effect of metal molds employed upon cure of prepolymers was also elucidated from the measured α values.

INTRODUCTION

Diallyl phthalate thermosetting molding materials have been employed as characteristic engineering plastics in electrical and electronic industries. From the study of properties of molding materials of diallyl phthalate on the market, it is found that the properties of the molded materials are much affected by the degrees of crosslinking of diallyl phthalate prepolymer employed, in other words, by the residual amounts of allyl groups in these materials.

Principally, the course of polymerization of diallyl phthalate monomer or cure of diallyl phthalate prepolymers can be studied by infrared spectroscopy; the polymerization of diallyl phthalate monomer to yield its prepolymer has been investigated by determining the intensity in the absorption band at 1645 cm^{-1} , which arises from stretching of the double bond of the allyl group.^{1,2}

While studying the cure of diallyl phthalate prepolymers by infrared spectroscopy, we found that the C=C stretching band of the allyl group,

which appears at 1647 cm^{-1} in the diallyl phthalate monomer, splits into two bands at 1645 and 1651 cm^{-1} in both of the diallyl phthalate prepolymers and cured resins, and that the split band first makes it possible to examine the extent of the highly crosslinking reaction of diallyl phthalate resin system.

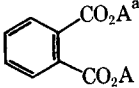
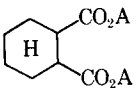
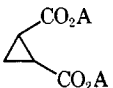
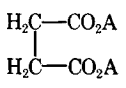
Here, we wish to introduce α , a new empirical parameter concerned with the degree of residual unsaturation of the diallyl phthalate prepolymer-cured resin system, which is derived on the basis of the bands at 1645 and 1651 cm^{-1} . It is also found that α has a close relationship with other parameters of the degree of unsaturation as well as crosslinking of the diallyl phthalate prepolymer such as iodine value, swelling weight ratio, and Barcol hardness (hot), it becoming evident that α can be employed as a convenient parameter for estimation of degree of crosslinking of the diallyl phthalate resin system. The measured α also revealed the influence upon the cure of prepolymers of metal molds used for molding.

EXPERIMENTAL

Materials

Diallyl Phthalate Prepolymer. DAPON-201 used in this experiment is a registered trademark of the Sumitomo Chemical Co. for diallyl phthalate prepolymer, with a molecular weight of ca. 6500 (measured in acetone by v.p.o.). Other DAPON prepolymers with different degrees of cyclization and analogous prepolymers³ were prepared at our laboratory (see Table I).

TABLE I
Prepolymers Prepared from Diallyl Succinate-Type Monomers

Degree of cyclization ^b of prepolymer, %	DAPON							
	201	I	II	III	IV	70	50	51
	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Structure of Monomer</p> </div> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div>							

^a A means allyl group.

^b Measured by the method of Simpson et al.⁴

Cured DAPON Resins. A solution of DAPON-201 (100 parts) and tertiary butyl perbenzoate TBP (3 parts) in acetone (50 parts) was evaporated to dryness. The powder thus obtained was cured between iron molds plated with chrome at a varying temperature and a pressure of 800 kg/cm^2 for a certain time interval, and films of 0.03 mm in thickness were obtained. To examine the influence of metal molds upon cure of the

prepolymers, films were made at 150°C by 1-min cure. The metal molds employed were made of chrome, iron, copper, or stainless steel consisting of 14% chrome, 10% nickel, and 76% iron.

Glass Fiber Forced-Cured DAPON Resins. A mixture of DAPON-201 (100 parts), TBP (3 parts), and glass fiber ($1/4$ in., 100 parts) was blended with acetone (80 parts) in a kneader. The acetone was removed at 60°C in an oven, and the resulting mixture was rolled at 100°C for 4 min to give a composite. Specimens (50 mm in diameter and 3 mm in thickness) were made from this composite, by cure at 150°C and a pressure of 310 kg/cm² for varying time intervals, between the chrome-plated iron molds (see Fig. 1).

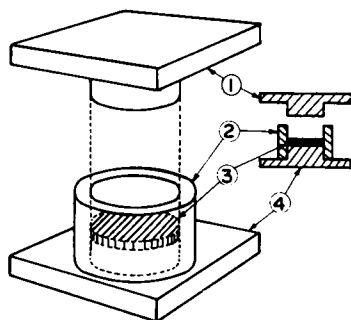


Fig. 1. Schematic diagram of metal molds: (1) upper mold; (2) cavity; (3) specimen; (4) lower molds.

Hydrogenation of Diallyl Phthalate. Diallyl phthalate (2.46 g, 0.01 mole) was hydrogenated with hydrogen (0.02 mole) over 0.2 g of 10% Pd-C as catalyst in 10 ml of ethanol at 25°C for a certain time interval in a shaking apparatus. The product was obtained by removal of the ethanol from the reacting solution from which the catalyst was previously filtrated.

Measurements

Infrared Spectra. Infrared spectra were run on a Hitachi-Perkin Elmer Model 125 spectrophotometer for the films of the cured resin and for the chloroform solutions in a 0.1-mm cell (rock salt) of monomer or prepolymer.

The infrared spectra of the diallyl phthalate monomer and prepolymer are shown in Figure 2. The strong bands at 1725, 1275, and 1125 cm⁻¹ are characteristic of phthalate ester groups; the band (designated as band A) at 1598 cm⁻¹ is due to the aromatic C=C vibration; and the medium bands at 1645, 1420, 1360, 1170, 992, and 935 cm⁻¹ are ascribed to the olefinic bond of the allyl group.

It was found that the stretching band of the olefinic bond, which appears at 1647 cm⁻¹ in the diallyl phthalate monomer, splits into two bands at 1645 and 1651 cm⁻¹ in both the prepolymers and cured resins; these three

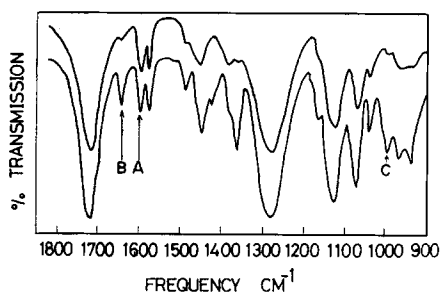


Fig. 2. Infrared spectra of diallyl phthalate prepolymer DAPON-201 (above) and its monomer (below). Scanning speed 3 sec, and scale selector F-1.

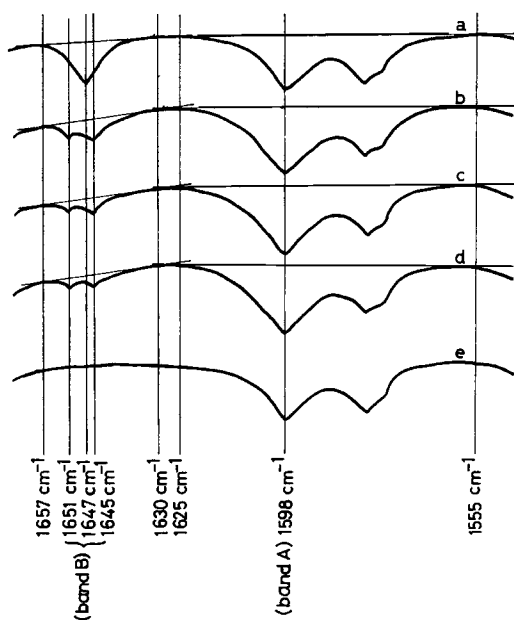


Fig. 3. Infrared spectra of bands A and B of: (a) monomer; (b) prepolymer DAPON-201; (c) hydrogenated monomer with 0.01 mole hydrogen; (d) cured resin (at 150°C for 5 min); (e) diallyl phthalate monomer completely hydrogenated with 0.02 mole hydrogen. Scanning speed 1 sec, scale selector F-1/10.

bands were designated as band B. The infrared spectra involving the details of the split band are shown in Figure 3.

In order to arrive at the character of band B, some infrared spectra were taken for analogous prepolymers, derived from the monomers described in Table I, which exhibited the same type of split bands as mentioned above. The diallyl phthalate monomer that exhibits one band at 1647 cm^{-1} characteristics of the allyl group, upon being hydrogenated (0.01 mole monomer with 0.01 mole hydrogen) shows two peaks at 1645 and 1651

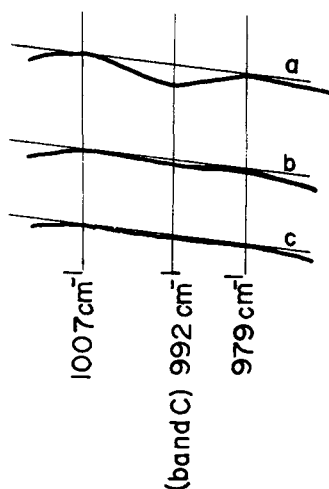


Fig. 4. Infrared spectra of band C (992 cm^{-1}) of: (a) monomer; (b) prepolymer DAPON-201; (c) cured diallyl phthalate resin (at 150°C for 5 min). Scanning speed 1 sec, scale selector F-1/10.

cm^{-1} , whereas the peaks disappear upon complete hydrogenation of the allyl ester (see Fig. 3).

These results indicate clearly that the bands at 1647 cm^{-1} or 1645 and 1651 cm^{-1} arise from the double bond of the allyl group, and the latter two bands can be ascribed to the allyl group of *n*-propyl allyl phthalate, or to the pendant allyl group of the diallyl phthalate prepolymers. Since mono-allyl esters of acetic and caproic acids, as well as diallyl esters of sebacic and adipic acids did not show the same type of split band, the split bands are considered to be closely related to the favorable cyclic configuration of the diesters of succinic acid and its derivatives, which was already established by Simpson and Holt.⁴

In comparing the infrared spectra shown in Figures 2, 3, and 4, it is obvious that the accurate measurement of the amount of allyl groups remaining in the highly crosslinked resin is difficult by the baseline method involving the band at 1647 cm^{-1} (Fig. 3) or the band at 992 cm^{-1} (Fig. 4), whereas such measurement may be carried out favorably with band B.

Degree (α) of Residual Unsaturation of the Diallyl Phthalate Resin System. If U represents the concentration of allyl groups of a prepolymer during crosslinking, it follows from the Lambert-Beer law that

$$\frac{U}{U_0} = \frac{\log T_B}{\log T_{B,0}} = \frac{D_B}{D_{B,0}} \quad (1)$$

where T is the transmission, D is the optical density ($D = \log 1/T$), the subscript B refers to the band B, and the subscript 0 refers to the monomer. The thickness L of the cell or that of the film was in general different from the cell thickness for the monomer determination, L_0 . To obtain the

correct optical density D_B , it is necessary to multiply the observed optical density D_B by the factor L_0/L , as follows:

$$D_B = D_B \left(\frac{L_0}{L} \right). \quad (2)$$

The factor L_0/L can be obtained from the optical density D_A at band A, which does not change during the polymerization and is a function only of cell or film thickness:

$$\frac{D_{A,0}}{D_A} = \frac{L_0}{L}. \quad (3)$$

Combination eqs. (1), (2), and (3),

$$\frac{U}{U_0} = \frac{D_B D_{A,0}}{D_{B,0} D_A}. \quad (4)$$

Therefore, the value of U/U_0 is nothing but the ratio of the degree of residual unsaturation of the prepolymer-cured resin system to that of the monomer. Here, α was defined by

$$\alpha = \alpha_{1645}^* + \frac{1}{2} \alpha_{1651}^* \quad (5)$$

where α_{1645}^* and α_{1651}^* represent the value of U/U_0 for the bands at 1645 and 1651 cm^{-1} , respectively, and are equal to

$$\alpha_{1645}^* = (U/U_0)_{1645} = \frac{D_{1645} D_{1598,0}}{D_{1647,0} D_{1598}}$$

$$\alpha_{1651}^* = (U/U_0)_{1651} = \frac{D_{1651} D_{1598,0}}{D_{1647,0} D_{1598}}$$

Its proof was established experimentally. The variation of the values of α was found to be less than 0.1% when the value was measured by the baseline method. The values of α_{992} were also determined in the same way as the values of the α_{1645}^* or α_{1651}^* (see Table II).

Iodine Value. This value was measured for the prepolymers by the method of Simpson et al.⁵ (see Table III). The number of residual allyl groups of the prepolymer is expressed by $\alpha_{I.V.}$, which is expressed as fraction of the theoretical monomer value.

TABLE II
Values of α of Diallyl Phthalate Prepolymers

Prepolymers	α_{1645}^*	$1/2 \alpha_{1651}^*$	α	α_{992}
DAPON 201	0.297	0.028	0.325	0.321
DAPON I	0.167	0.005	0.172	0.175
DAPON II	0.129	0.034	0.163	0.156
DAPON III	0.094	0.050	0.144	0.138
DAPON IV	0.075	0.036	0.111	0.107

TABLE III
Values of α of Diallyl Phthalate Prepolymers

Pre-polymers	Mol wt	α^*_{1645}	$1/2\alpha^*_{1651}$	α	$\alpha_{I.V.}^*$
(a)	7010	0.243	0.011	0.254	0.255
(b)	4910	0.245	0.039	0.284	0.284
(c)	3360	0.273	0.038	0.311	0.312

* Iodine value.

Curing Test. Barcol hardness (hot) was measured as follows: The composite (6.5 g) was cured at 150°C for varying time intervals between metal molds. The hardness of the upper surface of the specimen in the cavity (shown in Fig. 1) was measured at 150°C 10 sec after taking off the upper mold with a Barcol hardness impressor (Barber Colman Company, GYZJ-935).

Swelling measurements were carried out on the glass fiber forced-cured DAPON resins employed for the measurement of Barcol hardness (hot). The specimen was refluxed in 500 ml of chloroform for 2 hr in a 1000-ml flask and the swelling weight ratio was determined as follows:

$$\text{swelling weight ratio} = \frac{\text{weight of swollen resin}}{\text{weight of original cured resin}} \quad (6)$$

RESULTS AND DISCUSSION

Justification of α

Tables II and III show the values of α , α_{992} , and $\alpha_{I.V.}$ measured for the diallyl phthalate prepolymers with different degrees of cyclization or molecular weight. Good coincidence of these values supports the justifications of the proposal of eq. (5).

Application of α to the Estimation of the Degree of Crosslinking of Prepolymers

The crosslinking reaction of the diallyl phthalate resin system is greatly affected by the type of composite, curing agents, additives, and curing conditions as well. The degree of cure of the prepolymers was examined by measuring the values of α as a function of curing time and temperature. In considering the significance of the practice of molding, the influence of metal molds upon the cure of prepolymers was also examined from the measured α values.

Curing Time and Temperature. In view of practical molding conditions, the effect of curing time upon the α values was plotted at 150°C. As may be seen in Figure 5, the cure was found to progress very rapidly for 3 min from the beginning of cure and then to proceed very slowly. After 15 min of cure, ca. 20% of the initial unsaturation of the prepolymer remained.

In order to clarify the influence of temperature upon the cure of prepolymers, the α values were measured for films made by a 1-min cure. Figure 6 shows that the degree of cure of prepolymers is almost the same between 150°C and 180°C, becoming rapidly larger above 190°C.

Influence of Metal Molds. The influence of metal molds on the cure of prepolymers was observed for the resin films that were cured at 150°C

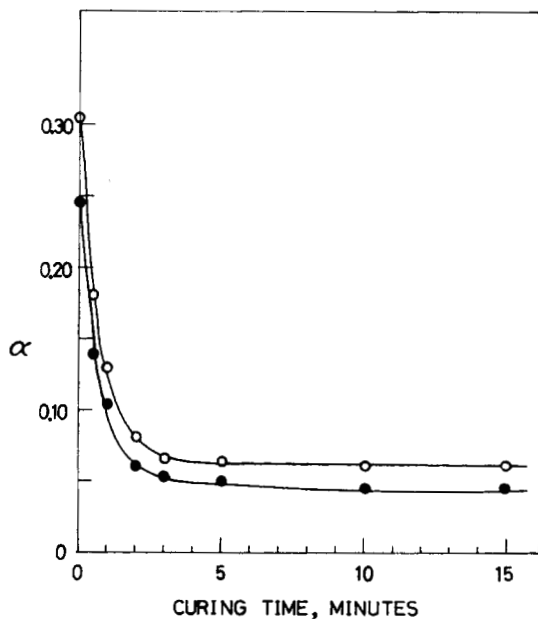


Fig. 5. Plot of α vs. curing time: (O) α ; (●) α^{*1645} .

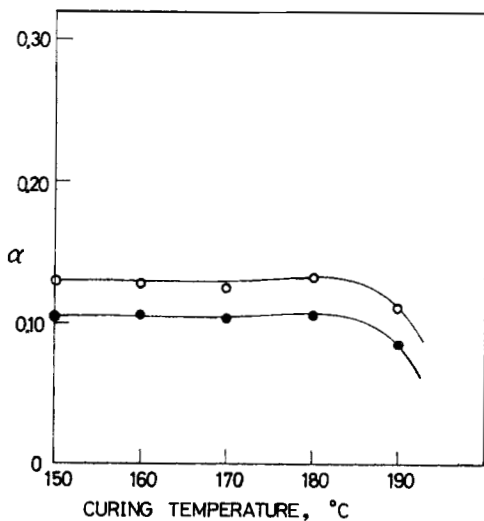


Fig. 6. Plot of α vs. curing temperature: (O) α ; (●) α^{*1645} .

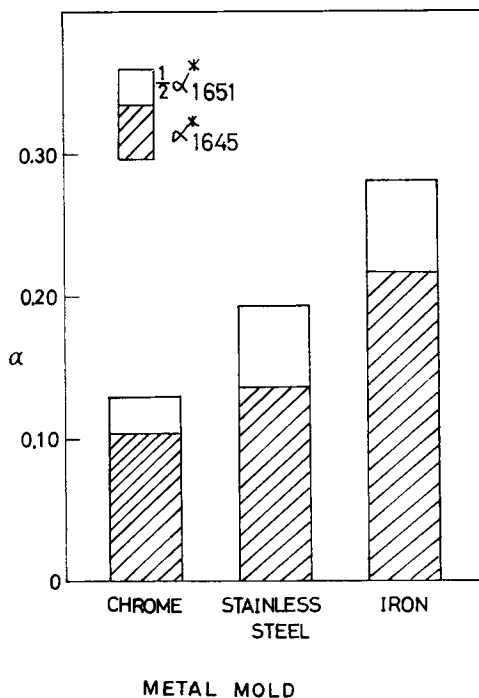


Fig. 7. Influence of metal molds upon α .

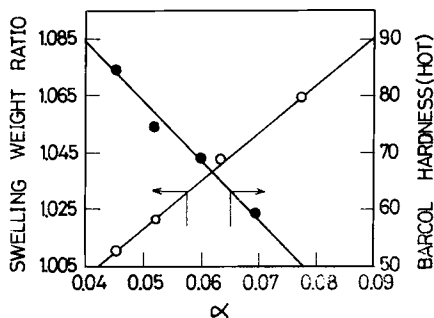


Fig. 8. Plot of α vs. swelling weight ratio and Barcol hardness (hot).

for 1 min. In the case of molds of iron, stainless steel, and chrome, clear, well-cured films were obtained, while in the case of copper molds, a clear film could not be made. Figure 7 shows that the α value decreases in the order of iron, stainless steel, and chrome. The influence of the metals upon the α values may be interpreted in terms of the interaction between the reactive electrons of the metals and the organic radicals generating and propagating in the course of prepolymer curing.

Relation of the α Values to Other Curing Test Methods. For practical reasons, the α value was compared with other parameters reflecting the de-

gree of crosslinking such as swelling weight ratio or Barcol hardness (hot) measured for glass fiber forced-cured DAPON resins. As may be seen in Figure 8, it is found that there is a good correlation between the α values and the swelling weight ratio or the Barcol hardness (hot), demonstrating that α can be a better parameter for the estimation of the degree of crosslinking of DAPON resins than troublesome testing.

References

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