X-Ray Diffraction Studies in Resins: Effect of Entanglements and Chain Structure

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Synopsis

X-ray diffraction halo of alkyd, amino, and epoxy resins were recorded. The effective d obtained from them was used to estimate certain physical parameters like cross-sectional area, number of carbon atoms per chain, and stiffness parameters from the empirical curves of Boyer and Miller. Amino resin was found to behave differently than the rest of the resins which have a benzene ring in their backbone. These ideas find a confirmation from the ultrasonic and dielectric measurements performed on these very samples.

INTRODUCTION

Resins are polymers with binding power presently being used in paints and plastics. The structure of the polymers decides not only their chemical properties but also the physical parameters associated with them. Recently, we have studied the ultrasonic and dielectric measurements for alkyd, amino, and epoxy resins.[1-4] Amino resin shows parameters that differ from the rest. The reason is that its chain structure unlike alkyd and epoxy resins does not have any benzene ring. For this reason it was planned to study the X-ray diffraction analysis of these resins and see how the behavior of amino resin differs from the rest. Moreover, a detailed study of epoxy resins, which are different in their epoxide equivalent was also undertaken.

The different resin samples were obtained from the standard manufacturers and their structure was checked by UV and IR spectra. The X-ray diffraction patterns of these resins were recorded on a flat film using a $CuK\alpha$ X-ray source.

The next section describes the theory used to study these resins, the third section describes the experimental setup, the fourth section presents the results and discussion, and the fifth section gives the conclusions.

THEORY

The X-ray diffraction pattern of alkyd, amino, and epoxy resin samples consist of two halos, which confirms that these are amorphous. Traditionally, one specifies amorphous structure by the radial distribution function (RDF), which is determined from a Fourier inversion of the (reduced) scattering pattern.[5] The above method yields mainly the structure and electron density distribution along the chain molecule. The other parameters, viz., the cross-sectional area per chain molecule, N_c, the number of carbon atoms per entanglement, and σ, the stiffness parameter, are scarcely taken into account.

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It is in this latter context that the empirical method of Boyer and Miller[6-9] finds an application and we have used it to study the resins.

Out of the two halos the application of Bragg equation to the peak position of the outer halo leads to an effective d value, giving the distance of the closest approach of the carbon atoms in the neighboring chains. This is called the van der Waal packing of the carbon atoms. The inner halo corresponds to a distance greater than the above van der Waal packing and indicates the existence of an order involving larger distances. Some important definitions related to present work are given below.

Cross-Sectional Area of Polymer Molecule

It is a precisely defined and known quantity for any crystalline polymer whose lattice parameters are known. The Boyer and Miller[10] calculation has been reported with comments about an application to amorphous polymers and copolymers. The area per chain is

$$A = V/(n \cdot c)$$

where $V = (a \times b) \cdot c$ is the volume of the cell calculated from the published literature.[11] a, b, and c are unit cell vectors. n is the number of chains per unit cell and c is the fiber repeat distance.

Chain Stiffness Parameter (σ)

σ is defined as

$$\sigma = \langle r^2 \rangle_0 / \langle r^2 \rangle_{0f}$$

where $\langle r^2 \rangle_0$ and $\langle r^2 \rangle_{0f}$ are respectively the mean square displacement lengths (end to end distances) of a polymer in the unperturbed state and in the freely rotating state with fixed valence angles.[12]

EXPERIMENTAL

The X-ray diffraction pattern was recorded using a CuKα radiation by a pin hole (Hull type) camera. X-rays collimated from two pin holes were incident normally on the sample kept pressed between two mylar sheets. The patterns were recorded on a flat film kept at a distance 2.5 cm from the sample. The patterns consisted of two halos and were scanned on a Carl Zeiss microphotometer model G_1B_1 and G_1T_1 at an amplification of 6. A typical scan of the halo is shown in Figure 1 and corresponds to amino resin. This enabled an accurate measurement of the peak position and thus the radius of the halo. The latter was used to calculate the θ for use with the Bragg equation:

$$2d_{\text{eff}} \sin \theta = n\lambda$$

The $d_{\text{effective}}$ values in nm thus determined were used to estimate the cross section of the polymer molecule.
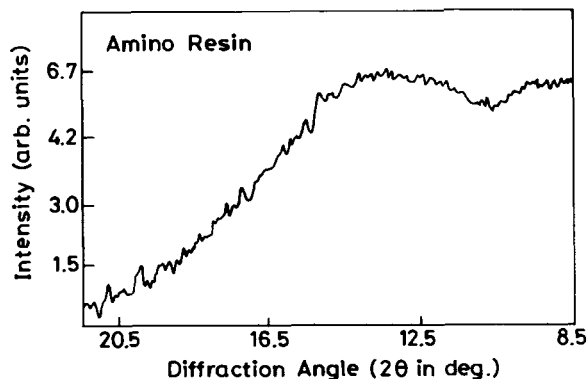
Fig. 1.

RESULTS AND DISCUSSIONS

The equivalent Bragg size of the electron density fluctuation is given by $d_{\text{effective}}$, which is of the correct order of magnitude. We have used the outer halo corresponding to the van der Waal distance in a specimen. Boyer and Miller have reported the relation of $d_{\text{effective}}$ values of about 47 polymers to the cross-sectional area[6] in their graph. The graph consists of three lines, viz. A, B, and C. Points for crystallizable polymers on line B correspond to the distance larger than van der Waal contacts and to van der Waal contacts for amorphous polymers.* The $d_{\text{effective}}$ values of resins studied in the present work fall on line B. With the help of this, one can easily calculate the cross-sectional area. With the help of this cross-sectional area, the other parameters N_c and σ can be calculated using the Boyer–Miller correlation.[7,8] Table I collects our results.

It is clear from Table I that amino resin has the lowest value of area of cross section, N_c, and σ, while all those resins containing benzene group in their backbone have larger values of the above-mentioned physical parameters. The above point of view is further supported by our dielectric measurements as shown in Table II. This table indicates that amino resin shows a large value of dielectric constant and dielectric loss than alkyd and epoxy resins, which supports our point of view, i.e., the larger values of dielectric constant and dielectric loss in amino resin is due to the absence of benzene rings.

Table III shows the ultrasonic measurements carried out on these resins. It is clear from this table that the backbone of amino resin consists of linear aliphatic groups and hence the amino resin shows a decrease in ultrasonic velocity at lower concentration. However, in case of alkyd and epoxy resin 230, a decrease in ultrasonic velocity with concentration appears at almost double the concentration.

Hence from the ultrasonic measurements it is clear that the amino resin solutions show the existence of entanglements at lower concentrations while

*This point has been clarified by Miller and Boyer on p. 2046 of their cited paper.[6]

TABLE I

$d_{\text{effective}}$ Values Determined from X-Ray Diffraction Halo, the Corresponding Cross-Sectional Area N_c, the Number of Carbon Atoms per Entanglement, and the Stiffness Parameter[a] σ

Resin	$d_{\text{effective}}$ (nm)	Area of cross section (nm^2)	N_c	σ
(i) Alkyd resin	0.59	0.34	440	1.91
(ii) Amino resin	0.55	0.30	387	1.84
(iii) Epoxy resin[b]				
Code no.				
(a) 220	0.65	0.39	500	1.96
(b) 230	0.67	0.41	516	2.00
(c) 250	0.68	0.44	533	2.25

[a] As read from Refs. 6–8.
[b] Epoxy resin 220 has epoxide equivalent 180, while epoxy resins 230 and 250 have epoxide equivalent 220 and 250, respectively.

TABLE II

Dielectric Properties of Alkyd, Amino, and Epoxy Resin at Room Temperature at 1 kHz[a]

Resin	Dielectric constant	Dielectric loss
Alkyd resin	1.23	0.2186
Amino resin	962	603.20
Epoxy resin (230)	1.67	2.2

[a] A 20% solution of alkyd resin in xylene, amino resin in n-butanol, and epoxy resin in xylene was taken.

TABLE III

Table Showing the Measured Value of Ultrasonic Velocity in Alkyd, Amino, and Epoxy Resins at 4 MHz at Room Temperature

Resin solvent	Concentration	Ultrasonic velocity $C \times 10^{-3}$ (m/S)
Alkyd resin xylene	10	1.35
	20	1.35
	30	1.29
Amino resin n-butanol	10	1.24
	20	1.15
	30	1.11
Epoxy resin Acetone	10	1.08
(230)	20	1.08
	30	1.01

alkyd and epoxy resins containing benzene ring in their backbones show the formation of entanglements at almost double the concentration.

As it is clear from Table I that epoxy resin 250 has largest values of area of cross section, N_c, and σ than other epoxy resin 220 and 230 samples. This is due to the largest epoxide equivalent of epoxy resin 250 than other studied epoxy resin samples. This point of view is supported by our dielectric measurements as shown in Table IV. It is clear from this table that the dielectric

TABLE IV
Dielectric Measurements of 20% Solution of Each Epoxy Resin in Xylene at 1 kHz and at 30°C

Epoxy resin	Dielectric constant	Dielectric loss
220	1.19	0.0382
230	1.67	2.2
250	2.22	7.56

constant and dielectric loss both increase with increasing expoxide equivalent, which confirms that these properties are highly epoxide-equivalent-dependent.

CONCLUSIONS

From the above results and discussions it was thus concluded that amino resin shows a different behavior in all of its physical properties (dielectric and ultrasonic measurements) than alkyd and epoxy resins. A successful interpretation in terms of benzene ring is given, i.e., in amino resin there is no benzene ring (which is present in alkyd and epoxy resins), and hence it behaves differently. Moreover, a successful interpretation of epoxide equivalent dependence on physical properties is given.

Both the conclusions were checked by ultrasonic and dielectric measurements, which confirms that our X-ray diffraction analysis about these resins using Boyer and Miller correlating curves are correct.

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