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X-Ray Diffraction Studies on Shellac/Melamine Resin Blends

INTRODUCTION

Several workers[1,2] have studied the x-ray diffraction patterns of shellac but have not mentioned which kind of shellac they used in their study. Shellac consists of hard resin, soft resin, and wax. Basu[3] obtained x-ray diffraction patterns from hard resin after repeated extraction of soft resin with ether. Two diffuse halos at 4.21 and 10 Å were reported. The 10 Å intense and diffuse ring was attributed to micellar aggregation of hard chain molecules, whereas the 4.21 Å sharper and less intense ring was attributed to the presence of a carbon chain of more than four carbon atoms as verified by Katz[4] for a number of organic compounds.

It has been reported that the extent to which phenolic resin is cured can be determined by observing the maximum intensity position in the x-ray diffraction pattern. Dow Corning's silicon resin DC 2106 has been found[5] to exhibit two halos at 9° and 20°. The angle of maximum intensity was found to decrease by 25′ with increasing cure. The shift amounted to 0.28 Å. The shift represents alterations in the molecular structure which takes place in the resin as the cure proceeds. This phenomenon may be explained on the basis of the crosslinking during cure process in the early stages of polymerization. Chain formation rather than the establishment of three-dimensional network is favored. The resin, at the beginning of cure, therefore, exhibits the characteristic intermolecular distance observed in models when linear chains are placed side by side. The curing proceeds with further crosslinking of the polymer. The average effective distance between the entities which were originally chains, therefore, increases with decrease in the Bragg angle.

In earlier papers,[6-8] it has been indicated that the study of shellac melamine resin blends were carried out in order to get an insight into the molecular mechanism involved in the reactions. It was further thought during the course of these studies that some prominent changes in the halo spacings may be observed with the extent of curing.

EXPERIMENTAL

Part of the x-ray diffraction work was carried out using CuK_α radiation. For determination of the crystalline phase, a Philips x-ray diffractometer working in transmission geometry was used. For photographic work, fine granules 1 mm thick were used, while for scanning, finely powdered specimens were used.

RESULTS AND DISCUSSION

Three halos at 2.48, 4.93 and 11.33 Å were observed in the x-ray diffractogram of shellac. The spacing of 2.48 Å, which is newly reported, may be due to scattering by packets of two carbon atom subunits in the same line in the chains of aleuritic acid molecules existing in the shellac structure to the extent of 40–50% of the weight of shellac.

As the amount of melamine resin in the blend increases, the spacing of the halo at 4.93 Å decreases, indicating that there is an alteration in the structure as the cure proceeds. The other halo at 11.33 Å shrinks toward the center of the diffractogram as the cure proceeds. Thus, the spacing of this halo for SMF 64 at the maximum of cure is 17.68 Å. Further increase of the melamine resin content in the blend broadens the halo; and thus for SMF 46, the spacing is 10.41 Å.

In Table I, values for d_1 (the spacing of the first halo), d_2 (the spacing of the second halo), $d_1 - d_2$, and for crystallinity of the specimen (as calculated) are given for comparison. The % crystallinity of the specimen was determined using Natta's method.[9] Crystallinity is equal to $(C/C + A) \times 100\%$, where C is the area of the crystalline phase and A is that of the amorphous phase. The halo at 11.33 Å corresponds to the crystalline phase of the substance and the other halo at 4.93 Å corresponds to the amorphous phase. For determining the area of the halos, the background scattering curves were drawn and the areas were then computed.

On this basis, the observed crystallinity of the SMF blend is found generally to increase with increase in the melamine resin content reaching somewhat a peak value of 35.6% at 30% melamine resin content. There is a decrease in the crystallinity for SMF 64 composition, and for SMF 55 there is an increase in crystallinity and then a gradual decrease. This shows that the curing reaction rate is not uniform.

TABLE I

Crystallinity Data of Shellac and Some SMF Compositions

Specimen	Melamine resin, wt-%	Shellac, wt-%	d_1, Å	d_2, Å	$d_1 - d_2$, Å	Crystallinity, %
Shellac	0	100	4.93	11.33	6.40	17.8
SMF 91	10	90	4.87	9.58	4.71	23.8
SMF 73	30	70	4.55	11.80	7.25	35.6
SMF 64	40	60	4.67	17.68	13.01	27.2
SMF 55	50	50	4.57	12.82	8.25	32.1
SMF 46	60	40	4.44	10.41	5.97	29.6

CONCLUSIONS

1. A shift in the spacings of the inner and outer halos in the diffraction patterns of SMF blends is observed with varying proportions of the melamine resin.
2. The angle of separation between the two halos increases with melamine resin content and reaches a maximum for SMF 64.
3. The second halo (d_2) shows a prominent change by moving toward the center of the diffractogram when the cure is complete.
4. The height of the amorphous peak (d_2) decreases with the increase in the amount of melamine resin in the blend up to SMF 64 and then practically remains constant, indicating that the amorphous portion is intact even after further curing.

In this connection, it is important to note that before any further conclusions can be reached, a detailed study is required of the x-ray diffractograms of the blends at different temperatures passing through their glass and melting transitions.

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