

Research Note

On the Dual Role of Starch, Cellulose and their Dialdehydes as Fillers and Accelerators in the Tertiary Amine Catalysed Curing of Epoxy Resin*

SUMMARY

Gel time studies of epoxy resins containing varying concentrations of water, starch, cellulose, or their dialdehydes were carried out at 120°C using the tertiary amines triethylamine (TEA) and hexamethylenetetramine (HEXA) as catalysts. In the 40 parts per 100 parts of resin (phr) polysaccharide-filled epoxy-HEXA system it was found that ~50% oxidised starch or cellulose produced unexpectedly high curing rate enhancements and gel times of 13 and 22 min, respectively, were obtained. With 100% oxidised starch the gel time increased to 37 min, while with 10% oxidised cellulose the gel time obtained was 91 min. The non-oxidised starch and cellulose gave even higher gel times. Thus, there seems to be some sort of a synergistic mechanism operating when the degree of oxidation of the polysaccharide is ~50% of the glucose monomer units. The difference in the effects of TEA and HEXA on the polysaccharide-filled epoxy curing reaction is explained on the basis of the decomposition of HEXA into its constituents (formaldehyde and ammonia/ammonia derivatives) under the reaction conditions employed, the formation of intermolecular and intramolecular hemiacetal and/or various hydrated aldehyde structures, and the difference in crystallinity and rigidity of the different polysaccharides affecting the availability of hydroxyl groups.

INTRODUCTION

Cellulosic materials and starches have been widely used as fillers for a variety of thermoset polymer systems (Wake, 1971; Menges & Mrotzek, 1981). The properties of the filled polymer systems depend greatly on the extent of the polymer-filler interaction; the greater the

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interaction, the less the possibility of phase separation with time or applied stress. In the case of tertiary amine catalysed curing of epoxy resin filled with cellulose and oxidised cellulose, Varma *et al.* (1984) not only found evidence for the role of celluloses as accelerators for the reaction (similar to other hydroxyl-group containing compounds) but also showed that they took part in the crosslinking reaction. In this investigation we have tried to study in more detail the 'accelerator effect' of starch, cellulose and their oxidation products in the curing reaction of epoxy resin catalysed by tertiary amines such as triethylamine (TEA) and hexamethylenetetramine (HEXA). Triethylamine was used since hexamethylenetetramine is known to decompose into formaldehyde and ammonia derivatives by a reversal of the reaction leading to its formation, causing different types of reactions to proceed simultaneously. Tertiary amines have been found to be quite suitable as sole curing agents in coating and adhesive formulations (Lee & Neville, 1967), and the presence of polar hydroxyl groups in the cured system helps to improve the adhesion. In this context, cellulose, starches and their modifications not only serve as fillers for cost dilution but also function as accelerators and contribute polar hydroxyl groups for improved adhesion.

EXPERIMENTAL

Materials

The epoxy resin Araldite GY 250 based on bisphenol A and epichlorhydrin of epoxy equivalent weight 192–196 and viscosity 225–275 P at 21°C was obtained from Ciba-Geigy, Bombay. Water soluble starch powder of 250-mesh fineness was supplied by Poona Chemical Laboratories, Poona, while hardwood cellulose powder of 150-mesh fineness and containing ~85% alpha-cellulose was obtained from Cellulose Products of India Ltd, Ahmedabad. All other chemicals were laboratory reagents and used without further purification.

Preparation of periodate oxidised starch

To 18.4 g (16.2 g, 0.1 mole, on dry basis) of soluble starch in 100 ml distilled water was added 3 g (0.014 moles) of sodium metaperiodate

dissolved in 200 ml water, and the mixture was stirred at room temperature for 30 h. Analysis (Scott, 1939) showed that all the metaperiodate had been consumed in the reaction, thus yielding a product in which 14% of the starch monomer units had been oxidised to the dialdehyde. The infrared spectrum did not show a prominent carbonyl peak since few of the carbonyl groups are free, but appear to be in hemiacetal linkage with primary alcohol groups and in hemialdal linkage by reaction with water (Mehltretter, 1967). In order to obtain 42% and 84% oxidised starches, the same procedure as above was followed, except that the sodium metaperiodate content was increased to 9 g and 18 g, respectively. One hundred per cent oxidised whole maize starch was also prepared in a similar manner.

Preparation of periodate oxidised cellulose

The same procedure was followed as reported before for obtaining 10% oxidised cellulose (Varma, 1984); 57% oxidised cellulose was also obtained by this method, except that the sodium metaperiodate content and the total volume of the reaction medium (water) were increased proportionately.

Gel point determination

Gel times were obtained with a Tecam Gelation Timer, Model GT 4, manufactured by Techne (Cambridge) Ltd, England.

Infrared spectra

A Perkin-Elmer 283B infrared spectrometer was used to obtain spectra of the oxidised starches as powder suspensions in nujol on sodium chloride plates.

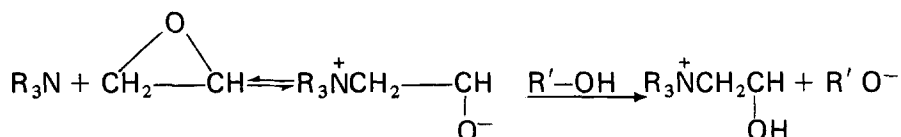
RESULTS AND DISCUSSION

The most common initiators for the curing of epoxy resins are active-hydrogen containing compounds such as primary and secondary amines. These reactions are exothermic and can proceed at room temperature. Tertiary amines, on the other hand, initiate the reaction only at elevated

temperatures (Narracott, 1953), and hydroxyl group containing compounds act as accelerators for this reaction (Schechter & Wynstra, 1956; Smith 1961; Varma *et al.*, 1984). The effect of hydroxyl concentration was seen in dramatic fashion when the concentration of cellulose and oxidised cellulose was varied from 5 parts per 100 parts of resin (phr) to 40 phr for the epoxy-HEXA system (Varma *et al.*, 1984). For example, in the latter study the gel time for 5 phr cellulose-filled epoxy was in excess of 600 min, while for 40 phr cellulose-filled epoxy it was only 91 min.

Water as accelerator

In the epoxy-HEXA system the gel times are not greatly affected when the hydroxyl functional groups are contributed either by water or by the polysaccharides (Table 1). Variation in the concentration of water from 5 to 40 phr did not cause any drastic decrease in the gel time (Table 1). On the other hand, with the epoxy-TEA system the gel time was observed to decrease from 280 min for 5 phr water to 22 min for 20 phr water. With tertiary amines of this kind, it has been reported by Schechter *et al.* (1956) that the reaction is strongly dependent on the hydroxyl group concentration. This was checked for one case by using 20 phr cellulose instead of the usual 40 phr (with TEA as the catalyst) when a three-fold increase in gel time, from 33 min to 100 min, was obtained (Table 1). Tertiary amines are believed to initiate epoxide polymerisation by their addition to epoxide, followed by reaction with hydroxyl groups (Schechter *et al.*, 1956)



This difference between TEA and HEXA can be explained by the fact that HEXA decomposes into its constituents (formaldehyde and ammonia) under the reaction conditions employed (see discussion later).

Polysaccharides as accelerators

For 40 phr polysaccharide-filled systems and with TEA as the catalyst, the gel times vary from a minimum of 30 min to a maximum of 65 min

TABLE 1

Gel Times for the Curing of Epoxy Resin Filled with Starch, Cellulose, and their Oxidation Products (reaction temperature was 120°C for all systems)

Type of filler/ accelerator	Quantity of filler (phr)	Gel time with hexamethylene tetramine catalyst (3 phr) (min)	Gel time with triethylamine catalyst (3 phr) (min)
Starch	40	75	65
14% Oxidised starch	40	62	63
42% Oxidised starch	40	13	—
84% Oxidised starch	40	35	—
100% Oxidised starch	40	37	40
Cellulose	40	91 ^a	33
Cellulose	20	225 ^a	100
10% Oxidised cellulose	40	61 ^a	30
57% Oxidised cellulose	40	22	53
Poly(vinyl alcohol)	20 ^b	43	39
Water	5	64	280
Water	20	48	22
Water	40 ^c	40	29
—	—	>600	>600

^a From Varma *et al.* (1984).

^b It was not possible to obtain a paste (slurry) with 40 phr poly(vinyl alcohol).

^c Uniform mixing was not possible, and the excess water separated and was evaporated off as the reaction progressed at 120°C.

(i.e. a two-fold variation), as seen in Table 1. This may be due to the fact that the so-called dialdehyde (i.e. periodate oxidised) starches and celluloses do not have free carbonyl groups. These carbonyl groups appear to be in hemiacetal linkages with primary alcohol groups and in hemialdal linkage by reaction with water. Thus, the number of hydroxyl groups available for the acceleration effect is more or less unaffected. The behaviour of poly(vinyl alcohol) is similar to the polysaccharides, though it is much more extensive. However, it must be remembered that the hemiacetal and hemialdal linkages are relatively weak and are easily cleaved so that the characteristic reactions of carbonyl groups are exhibited by the dialdehyde starches and celluloses. As will be shown presently, the latter fact helps in explaining the results when TEA is

replaced by HEXA, as with HEXA as the initiator the gel times for the starches, celluloses and their oxidation products vary from a minimum of 13 min to a maximum of 91 min for 40 phr filled systems. In other words, a seven-fold variation is seen here, in contrast to the two-fold variation with TEA. This is because, even though HEXA in its undecomposed form is a tertiary amine, it is known to decompose into its constituents (formaldehyde and ammonia/ammonia derivatives) in the presence of moisture and alcohols. Thus, we now have a complicated reaction mixture containing HEXA, formaldehyde, ammonia, polysaccharides and epoxy resin. The formaldehyde is capable of crosslinking the polysaccharides, ammonia can react with both the hydroxyl and the aldehyde groups of oxidised starches and celluloses in addition to the epoxy ring, and HEXA (undecomposed) can function in a manner similar to TEA. Thus, a large number of reactions proceed simultaneously. However, the formation of ammonia and its derivatives which can react with the carbonyl functions can explain, in large measure, why the oxidised polysaccharides have far lower gel times than the non-oxidised polysaccharides.

The most remarkable results were obtained with 42% oxidised starch and 57% oxidised cellulose (TEA as catalyst), where gel times of 13 min and 22 min, respectively, were noted. With 10% oxidised cellulose the gel time was 61 min and with 100% oxidised cellulose the gel time was 61 min and with 100% oxidised starch the gel time was 37 min. In other words, some sort of synergistic effect occurs when ~50% oxidised polysaccharide is used. From Figs 1 and 2 it is seen that *intermolecular* formation of hemiacetal and/or various hydrated aldehyde structures gives rise to four hydroxyl groups per glucose monomeric unit, whereas the *intramolecular* formation of such structures gives rise to three hydroxyl groups per glucose monomeric unit (as in the original starch or cellulose molecule) (Mehltretter, 1967). It can be speculated that the formation of hemiacetals and similar hydrated structures by intermolecular reactions occur much more easily when the degree of oxidation of the polysaccharides is about 50%, as opposed to when much higher or much lower degrees of oxidation are achieved. The resulting higher number of hydroxyl groups may be responsible for the greater acceleration effect observed. Recently, Laliberte *et al.* (1983) have also reported a synergistic effect in the curing of epoxy resin with dicyandiamine and *N'*-(4-chlorophenyl)-*N,N*-dimethylurea. Work is now in progress to explain the unique results obtained with ~50% oxidised

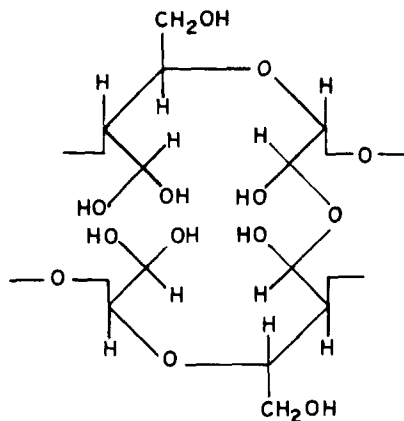


Fig. 1. A structural unit in hydrated dialdehyde (periodate oxidised) starch showing intermolecular dehydration between two hydrated aldehyde groups of adjacent molecules.

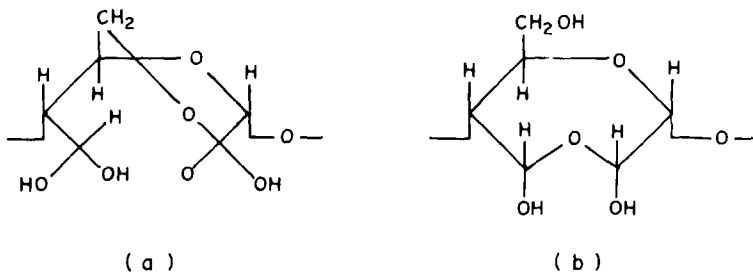


Fig. 2. Structural units in hydrated dialdehyde (periodate oxidised) starch showing: (a) intramolecular dehydration with primary alcohol group; and (b) intramolecular dehydration between two hydrated aldehyde groups.

cellulose and starch-filled epoxy resin initiator by HEXA. Also, it is not clear as to why the gel time for 40 phr cellulose with TEA is 33 min, while that for 40 phr starch is 65 min, and why the gel time for 57% oxidised cellulose increases to 53 min. The rigidities of the molecules, which affect the availability of the hydroxyl groups, may have a role to play in these phenomena. More detailed studies in this area are planned, and these may provide useful mechanistic information which

could be beneficially utilised in cellulose and starch-filled epoxy resin systems.

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