Effect of Wood Sawdust on the Aqueous Polymerization of Methyl Methacrylate

M. M. EL-AWADY

Department of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt

SYNOPSIS

The effect of different woods such as water-treated Eucalypt Sawdust (ESD), alkali-treated ESD, and untreated white pine SD in the presence and absence of Cu^{2+} ions on the aqueous polymerization of methyl methacrylate (MMA) was studied. It was found that the percent conversion was considerably higher in the presence of treated ESD and white pine SD. The percent conversion was further increased upon copper-treated ESD. The highest conversion values (> 95%) were those obtained in the presence of copper leached from alkali-treated ESD and the least conversion values (< 16%) were those obtained in the absence of copper in the untreated ESD.

INTRODUCTION

In Egypt, only about 10% of local wood (Casuarina, Eucalypt, etc.) produced is used as industrial wood, while the remaining 90% serve as fuel wood. As a result of greater consumption of foreign currency in importing high-quality woods currently used, such woods are to be taken into consideration to cover the shortage in the supplies for pulp and for different solid wood industries. Two features of Eucalypt wood species' quality that can affect utilization are their lower dimensional stability[1] and their high content of wood extractives.[2] The latter can deleteriously affect the use of such woods in the two rapidly enlarging areas of consumption—fibre products[1] and particle board. Moreover, these extractives introduced a number of problems to the pulping industry, where the polyphenols that are the main constituents of extractives lower the yield of pulping, increasing chemical consumption, and some polyphenols can inhibit pulping reactions.[3] The extractives can also corrode the different equipments used in pulp[4] or in different solid wood industries. Also, it was proven that removal of extractives from woods with solvents improved to a large extent the strength of adhesive joints[5] and also improved the adherence of paint and varnish films and plastic overlays.[6]

The polyphenolic compounds (tannins) that do not include lignin are the most common components[7] in the Eucalypt extractives. There are also the tropolones, fats, resins, carbohydrates, terpene, etc. Having identified the tannins interference effect, a few suggestions can be advanced to improve the situation[8] or maybe eliminate the problems:

1. *Preleaching.* By placing the wood prior to use in water—possibly hot water—a considerable amount of tannins can be leached.
2. *Preleaching by solvents.* This would be expensive but also effective.
3. *Complexing the polyphenolic compounds by heavy metal ions.* Polyphenol tannins are well known to complex heavy metal ions. Easily and rapidly forming complexes of natural polyflavonoid tannins extracts with copper, arsenic, and chrome have been reported in the literature.[9] Copper, for instance, forms stable complexes by chelating with flavonoid molecules. The results are similar to cross-linking with formaldehyde—a complex with a very effective molecular weight is formed, too large to be soluble in conventional solvents. This is an advantage when the complex is within the wood since it is not prone to leaching out. This solution is indeed expensive if one considers the amount of copper washed in just "neutralizing" the tannin ef-

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fect. On the contrary, this chelating property is recently utilized[10] as a wood preservative against the decay caused by soft-rot fungi.

In this article, we describe the effect of the pretreated Eucalypt sawdust (SD) (alkali and water treatment) on the reaction rate of polymerization of methyl methacrylate (MMA) in the aqueous solution at different temperatures. The effect is extended to study the effect of addition of copper ions and the tannin–metal complex formed on the rate of conversion of MMA monomer. The combination of such a low grade of wood with plastic through the polymerization of MMA may be considered as one of the ways for upgrading Eucalypt wood species as a raw material. The obtained product (wood–polymer combination) can be molded into different forms and used in building and furniture industries.

EXPERIMENTAL

Materials

Local Eucalypt wood (*Eucalyptus camaldulensis*) and white pine wood (*Pinus strobus*) were used in this study. SD was prepared from a mixture of heartwood and sapwood of the wood blocks. The mixture was ground in a mill to possess a range between 35–45 mesh size.

MMA monomer was a product of Merck (Germany), stabilized with 100 ppm hydroquinone and used without purification. The sodium bisulphite ($NaHSO_3$ about 60% SO_2) used is a product of EL-Naser Pharmaceutical Chemical Co., ARE. The other chemicals used were analytical-grade reagents.

Treatment of Wood

Water Treatment (Water Leaching)

Eucalypt sawdust (ESD) was subjected to water treatment by soaking in distilled water for about 48 h at room temperature with occasional shaking by hand. The ESD after filtration was dried at 105°C.

Alkali Treatment

The ESD was treated with 6% NaOH solution for 1 h at 50°C using a liquor ratio of 20 : 1. The treated wood, after washing several times with distilled water, was air dried at 105°C until constant weight.

Treatment of ESD with $CuSO_4$ Solution

The ESD was soaked in excess solution of $CuSO_4 \cdot 5H_2O$ (0.05 mol/L) for about 1 week to assure complete reaction of copper with wood components. The copper-treated SD after filtration was washed several times with distilled water to remove the excess copper sulphate solution. The residue was dried at 105°C until constant weight.

Elution of Copper Ions from Cu-Treated ESD

The Cu-treated ESD (1 g) was transferred into 100-mL $NaHSO_3$ solution (0.05 mol/L). The quick-fitted conical flasks used were immersed in an automatically controlled ultrathermostate adjusted at 40 and 50°C and left for the desired time (30, 60, 90, 120, 150, 180, 210, and 240 min); during the time period, the flasks were shaken by hand. After shaking and filtering, the filterate was analysed for copper by the use of the atomic absorption spectrophotometer (Perkin-Elmer Model 370).

Polymerization of MMA

Polymerization of MMA monomer (4 g) in water (100 mL) was carried out in a 250-mL quick-fitted conical flask using 0.05 mol/L sodium bisulphite as initiator. The reaction was carried out in the presence or absence of wood SD (1 g). The conical flasks were immersed in an automatically controlled ultrathermostate adjusted at 40 and 50°C and left for selected polymerization time intervals; during the time period, the flasks were shaken by hand. The polymerization reaction was stopped at will by addition of 2% hydroquinone solution. The product (poly(MMA) + sawdust) was then filtered and washed with water and methanol and then dried in an oven at 105°C until constant weight.

The monomer conversion % to polymer was calculated from the following relation:

$$\text{Monomer conversion } \% = \frac{S_p - S}{M} \cdot 100,$$

where S_p, S, and M are the weights of sawdust–polymer mixture, sawdust, and monomer, respectively.

RESULTS AND DISCUSSION

Effect of Untreated Wood SD on the Polymerization of MMA

From Figure 1, it is observed that the polymerization reaction shows a considerable induction period in the absence and presence of the SD. While the untreated white pine SD samples were found to cata-

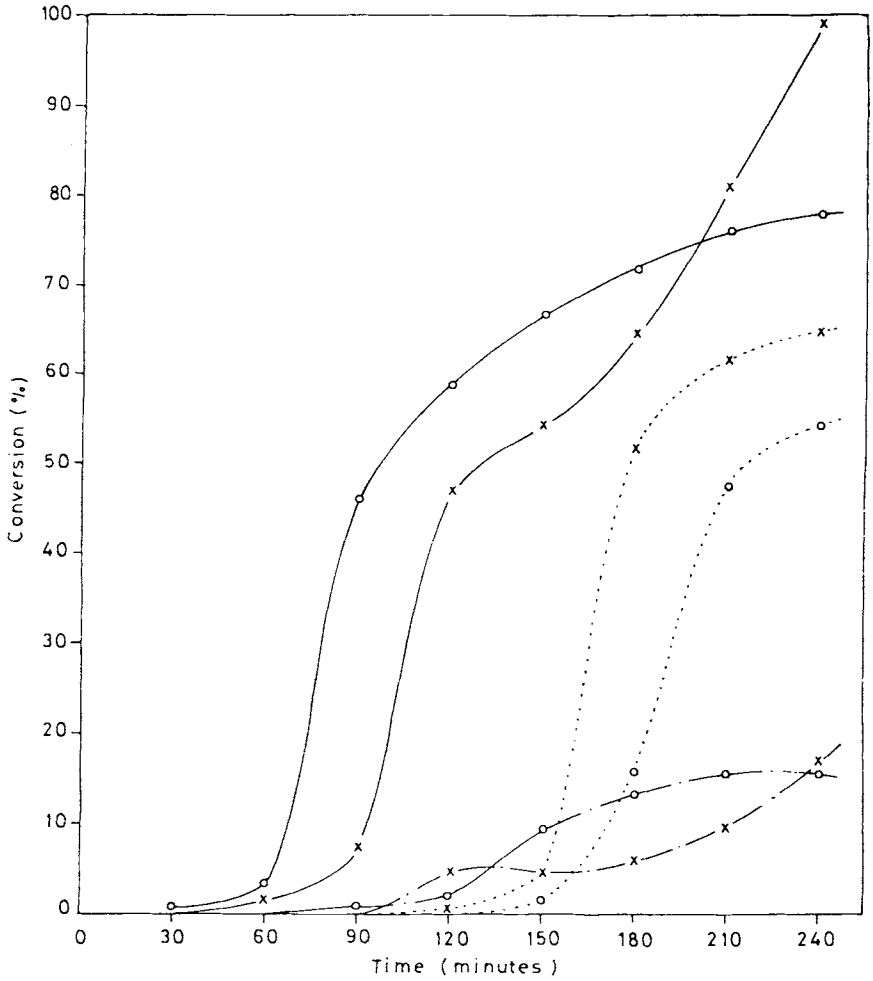

Figure 1 Effect of untreated wood SD on % conversion. (——), presence of untreated white pine SD; (- - - - -), absence of SD (blank); (— • —), presence of untreated ESD. (x), 50°C; (o), 40°C.

lyze to a large extent the polymerization reaction, the untreated ESD samples were found to inhibit or retard reaction. Both ESD curves are found to intersect each other; this may be attributed to the complex formation between the monomer and the tannin inhibitors leached in the aqueous solution. Accordingly, in the following experiments the ESD was subjected to alkali and water treatment to remove such inhibitors or subjected to reaction with copper ions to fix tannin substances.

Effect of Treated SD and Temperature on the Polymerization of MMA

The same conditions used in the presence of untreated SD are applied here. The effect of alkali-treated ESD, water-treated ESD, and untreated white pine SD for comparison on the polymerization reaction at 40°C has been investigated by means of conversion–time curves and the results are plotted in Figure 2. As can be noted from these plots, any experiment exhibits a characteristic sigmoid-shaped conversion–time curve, where the reaction rate is at its lowest state initially, increases steeply in the second state, and finally approaches steady state. From the figure and Table I, it is clear that alkali-treated ESD was found to have the highest catalytic effect on the conversion rate in comparison with that of water-treated ESD or with that of pine SD. In the case of untreated ESD, the conversion rate was very slow and the SD was found to have the highest inhibiting effect on the polymerization reaction.

From the curves, it is also visible that at the early stages of polymerization the untreated white pine SD has a somewhat higher effect than alkali-treated ESD, but at the later stages the catalytic effect for

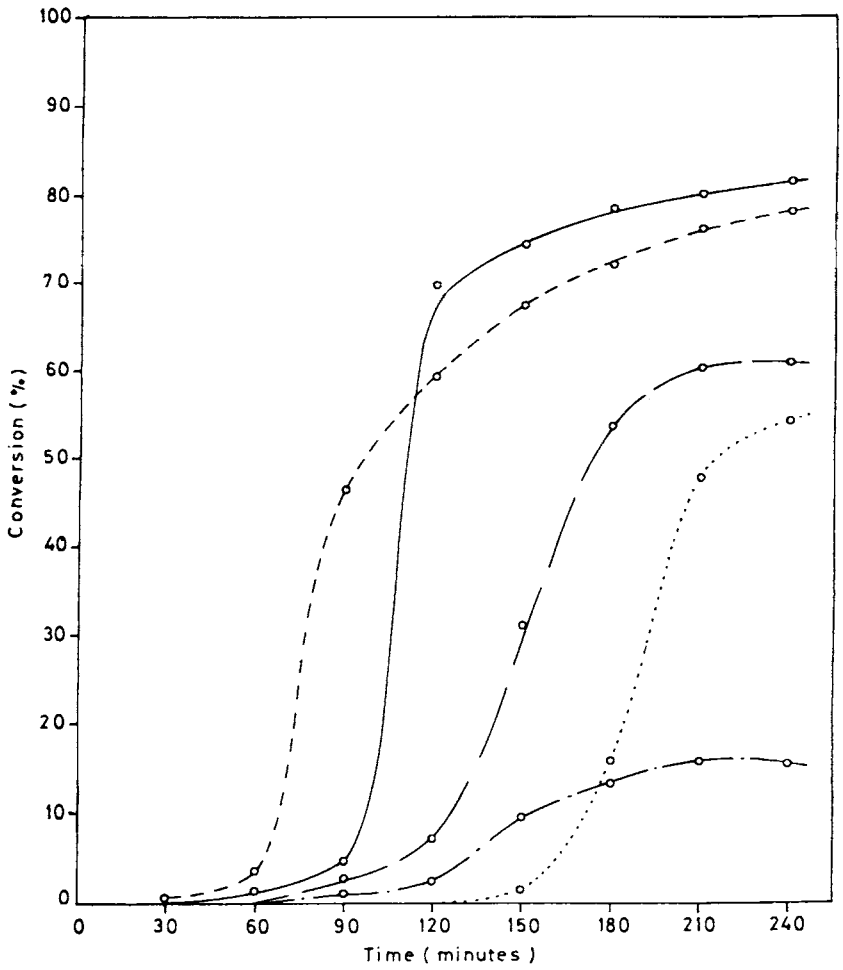

Figure 2 Effect of treated SD on % conversion at 40°C. (——), presence of alkali-treated ESD; (- - -), presence of white pine SD; (---·---), absence of SD (blank); (— —), presence of water-treated ESD; (— · —), presence of untreated ESD.

alkali-treated ESD exceeds that of white pine SD. This behaviour is attributed to the complete removal of extractives from ESD. In other words, alkali treatment of ESD removes mainly tannin components and some other chemical substances such as fats, waxes,[7] resins, etc. to different extents from the cell wall. The removal of some cell wall components creates new pores in the cell wall, resulting in a more open and assessible fine structure. As more surface area becomes available, the autocatalytic ef-

Table I Percent Conversion of MMA at 40°C

Type of Wood SD	Decrease in Treated ESD Weight	% Conversion Time (min)			Percentage of Extractive[a] in Untreated SD
		120	180	240	
Untreated ESD	—	2.5	10	15	11.2%
Water-treated ESD	7.1%	4	32	62	—
Untreated white pine SD	—	5	71	77	1.5%
Alkali-treated ESD	25.7%	70	79	82	—

[a] Analysis of extractives was carried out according to ASTM (1 : 1 methanol : benzene).

fect of the lignocellulosic material on the polymerization reaction is promoted. So, due to the small amounts of extractives present in white pine wood (1.2%), the values of conversion were found to be competitive with the values observed in the presence of alkali-treated ESD.

The effect of temperature on the percent conversion in the presence or absence of SD was observed at 40 and 50°C under the same previous conditions, and the data are represented in Figure 3. The explicit dependence of conversion upon temperature is evident from the succession of conversion–time curves. Increasing temperature from 40 to 50°C leads to a subsequent conversion increase. This behaviour is clearly shown in the absence of wood SD and presence of alkali-treated SD, while in the presence of water-treated ESD, untreated ESD, and untreated white pine SD a different trend is noted, where interference of conversion–time curves takes place. For example, in the presence of water-treated ESD, the conversion of MMA at 50°C is at its higher rate than that at 40°C until 2.5 h polymerization time; thereafter, the reverse case is obtained. These contradicting interferences can be attributed to the polyphenol substances leached out, which act as inhibitors to the reaction and may be, by time, dissolved or precipitated in the aqueous solution or extracted by MMA and consumed. Such interference completely disappeared in the case of using alkali-treated ESD because of the complete removal of extractive from the cell wall.

Effect of Copper-Treated SD on the Polymerization of MMA

The ability of Eucalypt tannins (polyphenolic substances) to complex with copper metal ions is pre-

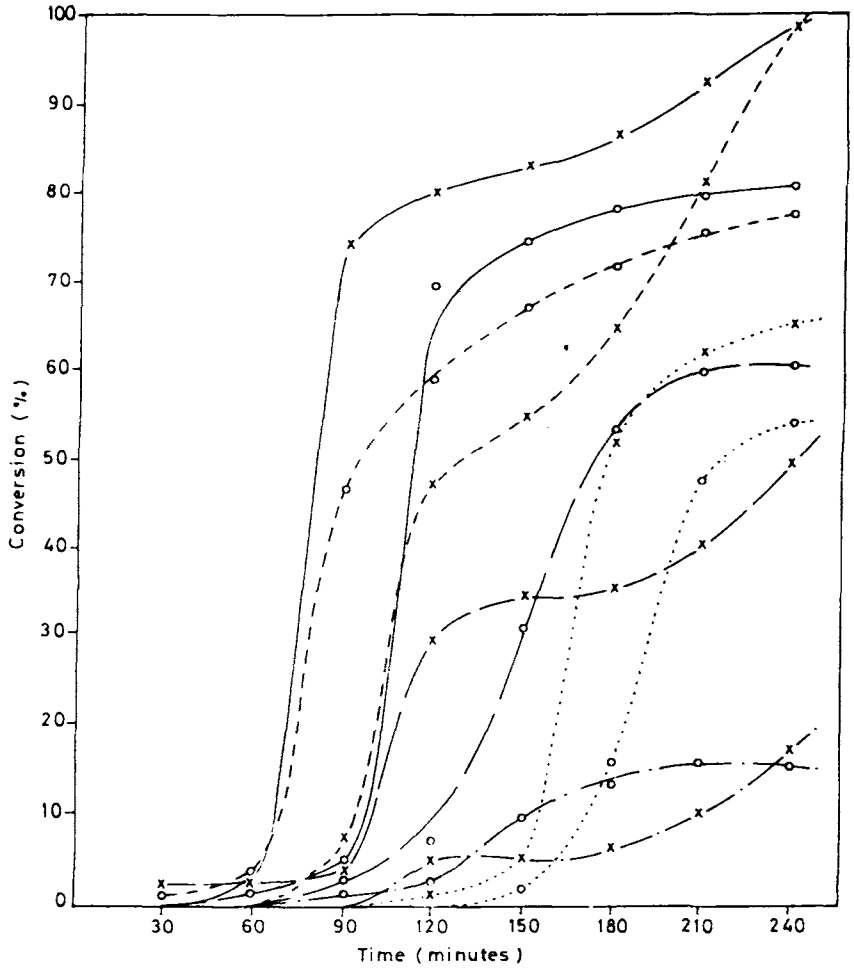

Figure 3 Effect of temperature on % conversion. (——), presence of alkali-treated ESD; (– – – –), presence of white pine SD; (·····), absence of SD (blank); (— —), presence of water-treated ESD; (— · —), presence of untreated ESD. (x), 50°C; (o), 40°C.

viously discussed, presumably given a chelated structure utilizing the catechol rings of phenolic substances. This chelating property is utilized in the work described here to eliminate the inhibition or retardation effect of the phenolic substances on the polymerization reaction. This is also an advantage when such an insoluble complex is within the wood texture since it is not prone to leaching out in the aqueous medium during the polymerization of MMA.

The polymerization of MMA was carried out at two different temperatures—40 and 50°C—using sodium bisulphite as initiator in the presence of copper-treated SD of Eucalypt and white pine wood. As can be noted from the conversion–time curves represented in Figure 4, any curve exhibits a characteristic parabolic-shaped conversion–time curve. This indicates that the reaction rate is at its fastest state initially and finally approaches steady state. In other words, this can be attributed to the nonexistence of any induction period. At 50°C, the conversion percentages observed for the copper-treated SD (Eucalypt types or white pine) reached values between 95 and 100%, while at 40°C the values varied between 90 and 95%; this means that the increase in temperature generally resulted in a narrow range of variation for the obtained conversion rates. Also, it could be deduced from Figure 4 that the increasingly higher rates are mostly due to the catalytic effect of the added copper ions to the SD, but only to very little extent due to the effect of temperature increase.

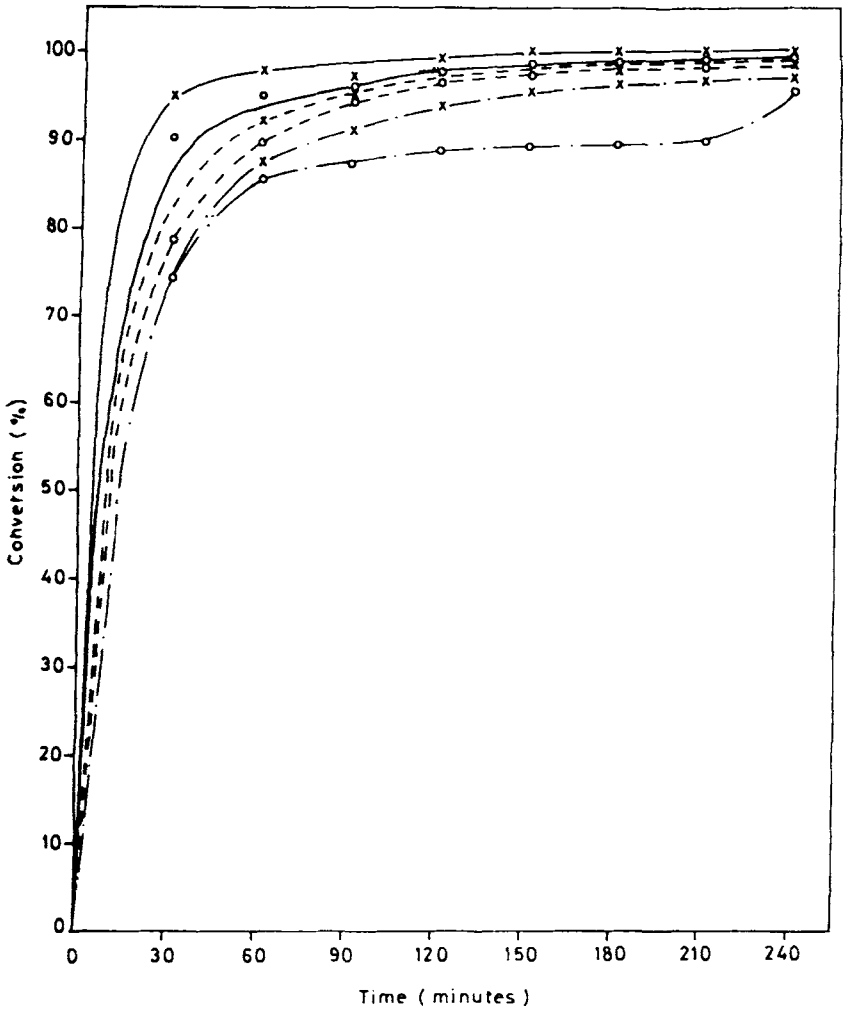

Figure 4 Effect of copper-treated SD on % conversion. (——), alkali-treated ESD + Cu; (— · —), untreated ESD + Cu; (- - - -), untreated white pine + Cu. (x), 50°C; (o), 40°C.

Such a coeffect can be explained as follows. It is proven experimentally[11,12] that Cu ions interact with Eucalypt wood in three different forms:

1. Cu^{2+} ions directly bound to carbohydrate (cellulose) and lignin guaiacyl units; the stable complexes formed by Cu^{2+} ions are in lignin rather than cellulose.
2. Cu^{2+} ions directly bound to lignin functional groups other than guaiacyl units; stable complex compounds are formed.
3. Cu^{2+} ions are physically adsorbed by various constituents of wood.

Although the Cu^{2+} in forms 1 and 2 is not likely to leach out extensively, the Cu^{2+} in 3 is leachable. The leachable copper in 3 and the loosely bounded copper in 1 and 2 can be obtained when the Cu-treated SD is subjected to interaction with $NaHSO_3$ initiation[10] solution; the increase of temperature can also accelerate the leaching of Cu ions from the SD.

The copper ions released in the aqueous medium were determined by atomic absorption and their concentrations are graphically represented in Figure 5. It is obvious from the figure that the values recorded at 50°C are considerably higher than those observed at 40°C. The maximum values were 13 and 7 ppm, recorded at 50°C (2 h) and 40°C (1.5 h), respectively. Moreover, the fluctuation observed indicates that the excessive amounts of Cu^{2+} leached

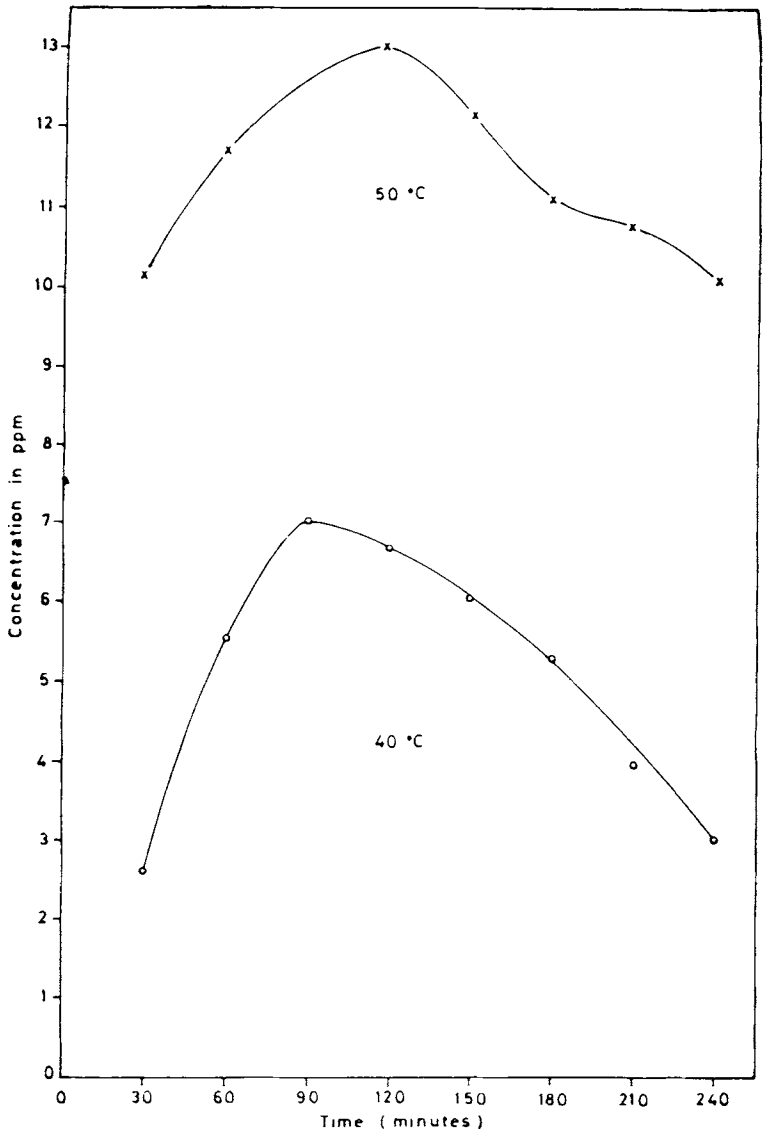

Figure 5 Leached Cu vs. time.

at the beginning of reaction would be subjected to reduction through the polymerization reaction steps to reach again the minimum at the end of reaction time. Under these conditions, additional radicals are produced and this is why the polymerization is catalyzed to a large extent. The following reactions are proposed:

$$NaHSO_3 \rightarrow Na^+ + HSO_3^- \text{ (ionization step)}$$

$$Cu^{2+} + HSO_3^- \rightarrow Cu^+ + HSO_3^{\cdot} \text{ (initiation step)}$$

$$HSO_3^{\cdot} + MMA \rightarrow M^{\cdot} - HSO_3 \text{ (monomer radical)}$$

$$nM + {}^{\cdot}M - HSO_3 \rightarrow M^{\cdot}M_n - HSO_3 \text{ (propagation)}$$

$$2M - M_n - HSO_3 \rightarrow \text{polymer (termination)}$$

To elucidate the effect of leached copper on the conversion rate, a set of experiments was carried out on the Cu-treated ESD:

1. A constant weight of air-dried sample (10 g) was soaked in 1 L initiation solution (0.05 mol/L $NaHSO_3$) at 40°C for 90 min. After filtration, the residue was dried at 105°C until constant weight. The copper ions were measured in the filtrate and it was found to be 7.2 ppm.
2. The polymerization of MMA was carried out in the presence of each of leached ESD (after dryness), nonleached ESD, and the filtrate using the same conditions applied before.

Examination of the results represented in Figure 6 indicates that when MMA is added to the initiator solution a relatively lower percent conversion is generally obtained, but when it is added to the filtrate the acceleration effect on the polymerization reaction reveals itself due to the presence of copper ions (7.2 ppm).

CONCLUSIONS

From the investigation reported here, the following conclusions may be drawn:

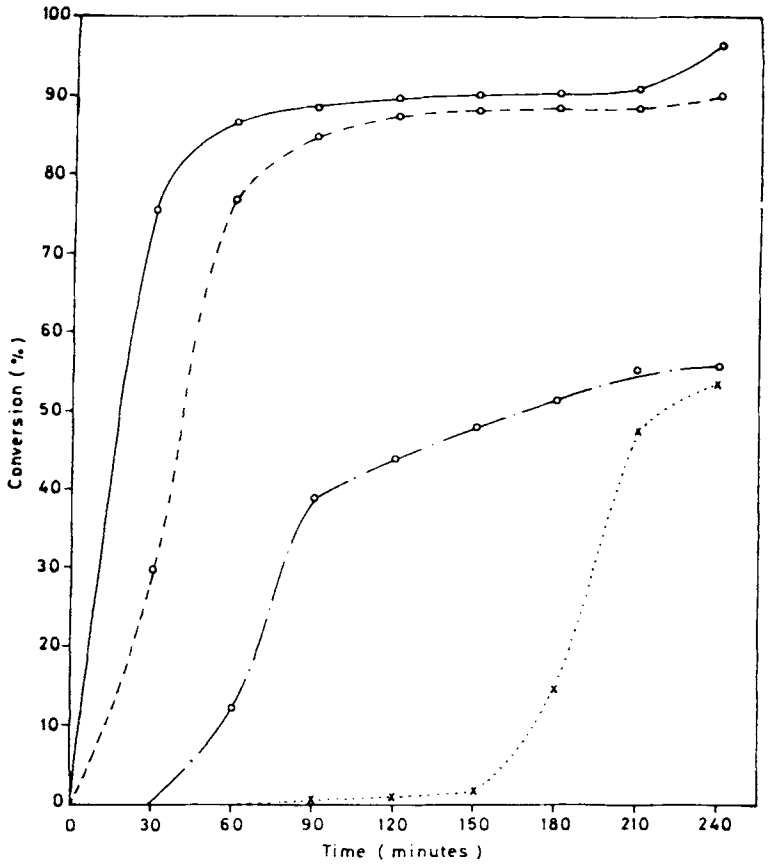

Figure 6 Effect of leached Cu on the percent conversion at 40°C. (——), presence of untreated ESD. (pretreated with Cu); (– – – –), presence of washed ESD. (pretreated with Cu); (—·—), filterate; (---·---), absence of SD (blank).

1. The untreated white pine SD was found to catalyze to a large extent the aqueous polymerization reaction of MMA, while the untreated ESD was found to inhibit or retard the reaction, and this was attributed to the presence of tannin inhibitors that can be leached in the aqueous solution.
2. The alkali-treated ESD was found to have the highest catalytic effect on the polymerization reaction in comparison with that of water-treated ESD or with that of pine SD. This is because of the complete removal of extractives from the ESD by alkali.
3. The catalytic effect of copper-treated SD on the percent conversion of MMA considerably predominates the effect of temperature and the effect of extractive removal by water or alkali from the ESD. The complexing of tannin compounds by copper ions is indeed a suitable solution to eliminate their inhibition effect and, on the other hand, to minimize their leaching in aqueous solution.

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