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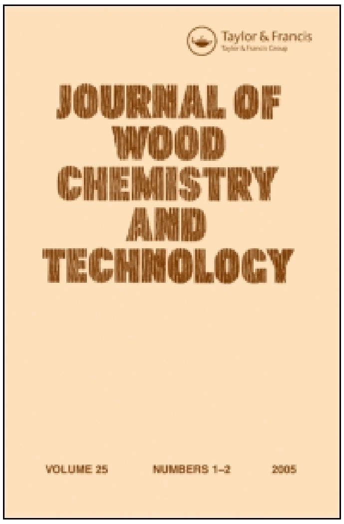

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AN INVESTIGATION OF THE REACTION OF EPOXIDES WITH WOOD

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ABSTRACT

The reaction of wood with two functionalised epoxides, allyl glycidyl ether (AGE) and glycidyl methacrylate (GMA), has been studied. For the reaction with whole wood samples of Scots Pine (*Pinus sylvestris*), maximum weight percent gains (WPG's) of 20% (GMA) and 7% (AGE) were obtained using pyridine as a solvent/catalyst. However, reaction of the epoxides with thermomechanically pulped Spruce fibre yielded WPG's of 15% (GMA) and 0% (AGE) under the same reaction conditions. In addition, the use of hydroquinone as an inhibitor of polymerisation yielded variable results. The observed WPG's obtained were found to be strongly influenced by the clean-up procedure used at the end of the reaction. The results suggest that, under the conditions used in this study, no reaction with the wood hydroxyl groups is occurring but that homopolymerisation of the epoxides is responsible for the observed data.

INTRODUCTION

Numerous wood modification reactions have been studied, of which the most useful are reactions with anhydrides, isocyanates or epoxides.[1-3] With anhydride reagents, an ester bond is formed which is susceptible to

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hydrolysis, thus resulting in gradual loss of adduct during service. In addition, reaction with any linear chain anhydride leads to formation of the corresponding carboxylic acid which must be removed from the modified wood before it can be used in a product. Modification with either isocyanates or epoxides does not lead to the above disadvantages.

The reaction of an epoxide reagent with wood is believed to lead to the formation of an ether linkage with the cell wall polymers, due to nucleophilic attack by the hydroxyl groups upon the highly strained three membered ring of the epoxide group. This reaction leads to the formation of a product to which is attached a new OH group, which may then be involved in reaction with another epoxide (Figure 1).[1,4] This can lead to the formation of oligomers attached to the original OH site. The majority of epoxide modifications of wood have been performed in the vapour phase using pressure.[5-10]

Much of the literature on chemical modification has been concerned with improving dimensional stability or biological resistance.[1-11] However, recently wood or fibre surfaces have been modified using di- or poly-functional reagents so that a chemically active group is covalently bonded to the surface of the lignocellulosic material to facilitate improved bonding with resins or to allow for graft polymerisation.[13-16]

The initial purpose of this study was to further investigate the potential of using surface activated fibres for graft copolymerisation, with the ultimate aim of producing high-performance composites. Two epoxides were selected for this study, GMA which has been the subject of previous investigations,[17-20] and AGE which was considered to have potential for surface activation. During the course of this study, it became clear that the results previously reported[17-20] could not be reproduced, and

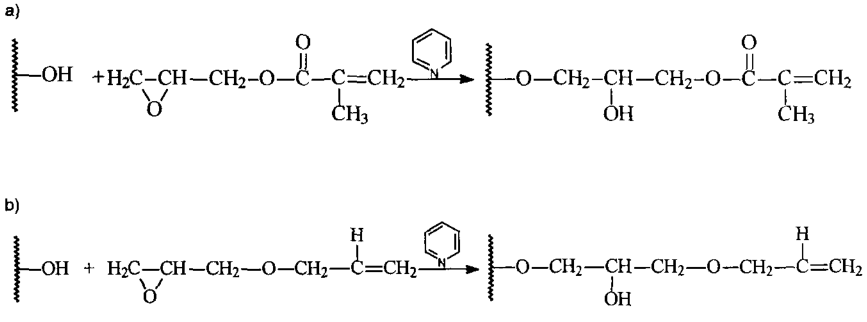

FIGURE 1. Reaction scheme for GMA (a) and AGE (b) with wood

furthermore that differences were observed between the behaviour of GMA and AGE. A more comprehensive study of the reaction of the two epoxides with whole wood and wood fibres was then undertaken, the results of which are reported herein.

RESULTS AND DISCUSSION

Proof of Bonding

In any chemical modification reaction of wood, it is necessary to prove that a chemical bond exists between the wood cell wall polymers and the reagent. In the case of reaction with certain anhydrides or isocyanates, where there is no possibility that homopolymerisation can occur, then there is justification for considering that a permanent weight gain with associated swelling of the substrate can be considered proof. Further support may be obtained by using FTIR where the existence of a carbonyl absorption can be assigned to the formation of an ester bond. With epoxide modification, the situation is complicated by the possibility that homopolymerisation may occur within the cell wall. If the

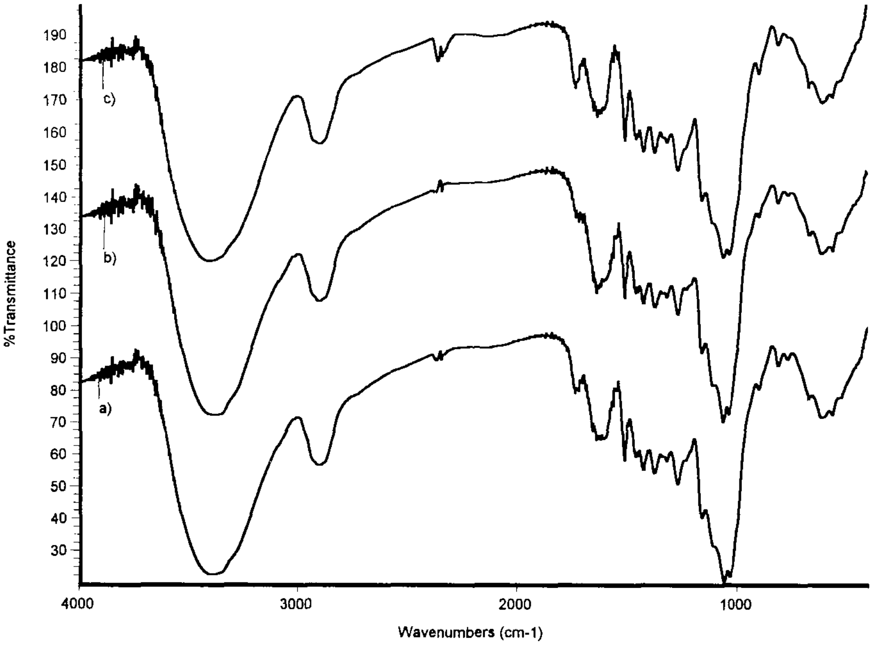

FIGURE 2. FTIR spectrum of GMA (a), AGE (b) and unmodified (c) TMP fibres.

homopolymer (or oligomer) is not solvent extractable because of inherent insolubility or entanglement within the cell wall matrix, a permanent weight gain will be obtained. This will also be accompanied by cell wall bulking. Thus a permanent weight gain is no proof of bonding. Similarly FTIR may show evidence of the formation of an ether linkage, but this may be attributed to the formation of homopolymer rather than reaction with the cell wall OH groups. Evidence for the reaction may be obtained by determining the OH absorption in the wood samples, but this region is strongly affected by hydrogen bonding interactions and by the presence of any residual water, and in addition reaction of the epoxide generates a new OH group in the product. Figure 2 shows the FTIR spectra of GMA

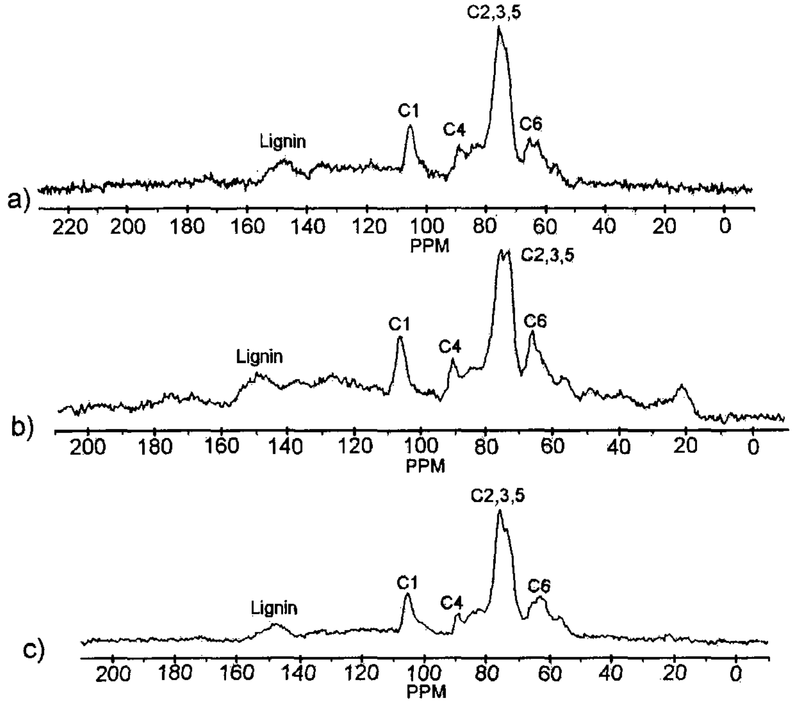

FIGURE 3. ^{13}C NMR spectrum of AGE (a), GMA (b) and unmodified (c) TMP fibres.

(15% WPG) (a), AGE (2% WPG) (b) modified and unmodified (c) TMP fibres. As can be seen from Figure 2, there is no spectral change observed between modified and unmodified samples. The same samples were also characterised by using ^{13}C NMR. The results are shown in Figure 3. The carbon atoms of the cellulose component are assigned to the relative peaks. (C_1 (anomeric C) 105 δ (ppm), C_4 88 δ (ppm), $C_{2,3,5}$ 71 δ (ppm), C_6 65 δ (ppm)). Lignin, due to its heterogeneous nature produces a broad peak at 150 δ (ppm).[26] The NMR spectra of AGE and GMA modified fibre display no significant difference from that the unmodified TMP fibre spectrum. It would be expected that some new peaks would be observed at 121-130 δ (ppm) region C=C (carbon double bond) for AGE and GMA modified, and 164-170 δ (ppm) (carbonyl) for GMA modified fibres. With Figure 3 (b) (GMA) there is a weak peak due to the terminal methyl of the methacrylic group at 20 δ (ppm).

Effect of Catalyst

Reactions were performed on whole wood using an epoxide and one of the following as catalyst: acetic acid, citric acid, triethylamine, tributylamine, or pyridine. Only with pyridine was a significant WPG recorded, 20% (GMA) and 7% (AGE). Poor results were obtained with acetic acid and butylamine, even though these solvents have swelling coefficients similar to pyridine.[2] Both acidic and basic conditions have been reported to facilitate reactions of epoxides with wood,[2,12] yet under the conditions used here, only pyridine catalysed the reaction. In other cases, a thick viscous deposit was often found at the bottom of the flask, suggesting that significant homopolymerisation had occurred.

Effect of Hydroquinone

In previous reports of the reaction of GMA with wood, hydroquinone (HQ) was used in order to inhibit homopolymerisation of the epoxide via the double bond of the methacrylate moiety.[19] In this previous report, it was stated that WPG decreased as the concentration of HQ was increased. This was thought to be due to HQ reacting with the GMA resulting in less of the epoxide being available to react with the wood OH groups. However, in the present study (Table 1) it can be seen that WPG showed random behaviour with both GMA and AGE as the concentration of inhibitor increased. The table shows the WPG's obtained for reaction with either of the two epoxides at three different concentrations, with different concentrations of HQ for 4 h reaction time at 90°C.

TABLE 1

The Effect of Hydroquinone Concentration on WPG

	GMA		
HQ conc. (M)	**(0.7 M)**	**(1.4 M)**	**(2.1 M)**
0	12.02	22.00	20.39
0.023	14.35	15.20	19.68
0.045	13.17	25.38	22.31
0.09	9.82	16.30	19.54
0.135	10.26	18.06	16.69
0.2	10.33	18.19	14.95
	AGE		
	(0.7 M)	**(1.4 M)**	**(2.1 M)**
0	6.87	8.28	9.68
0.023	7.04	7.71	19.64
0.045	8.03	7.04	18.16
0.09	6.99	6.67	9.06
0.135	7.09	7.91	19.28
0.2	6.44	6.49	17.87

Modification of Thermomechanically Pulped (TMP) Spruce Fibres

Exceptionally high WPG's were obtained for the reaction of GMA with TMP fibres. In four hours reaction at 90°C, WPG's of 85% and 109% were recorded in the absence and presence of HQ, respectively. With AGE, the corresponding WPG's were 6% and 21%, respectively. The very high values obtained with GMA may be related to the much higher accessibility of the reactive sites to the reagent in fibres compared to whole wood. The contrast with the results obtained with AGE suggests an alternative explanation. Since it has been proposed that the epoxide ring reacts with the cell wall OH groups, there is no obvious reason why such a dramatic difference between GMA and AGE should occur.

In addition, the inhibitor increased WPG in both cases, yet the presence of HQ should result in a lower WPG by preventing polymerisation via the

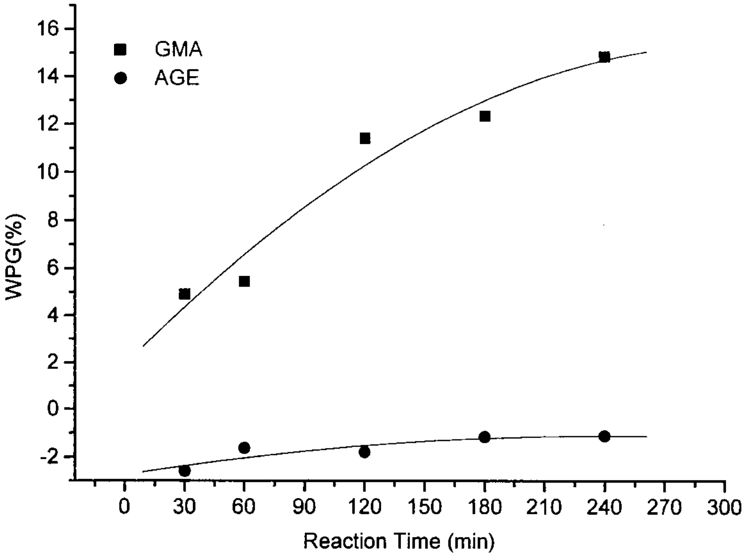

FIGURE 4. WPG(%) of GMA and AGE modified MDF fibres (Soxhlet extraction was used)

double bonds. Furthermore, if HQ reacts with the epoxides, then this should lead to an increase in homopolymerisation, leaving less epoxide available to react with the cell wall OH groups, resulting in a lower WPG (unless such homopolymerisation takes place within the cell wall). In order to determine whether homopolymerisation was the cause of the above observations, it was decided to perform a more rigorous extraction procedure than previously used with fibres.

Initially, extraction of modified fibres involved reflux in acetone/toluene (1/1, v/v) for six hours. This had previously proved sufficient to remove by products from reactions of other reagents with TMP fibres.[19] To improve upon the extraction procedure, fibres that had been subjected to solvent reflux were also extracted in a Soxhlet (using a

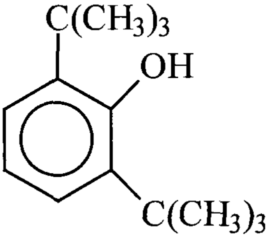

FIGURE 5. The molecular structure of 2,6-Di-tert-butyl phenol

solvent mixture of toluene/acetone/methanol; 4/1/1, v/v) for 6 h. In this case, with GMA WPG's in the region of 5-15% were now observed, and with AGE WPG's were generally 0% (Figure 4).

Since it was considered that reaction of the OH groups of the HQ with the epoxide rings was affecting the results, it was decided to use a sterically hindered radical scavenger (2,6-di-*tert*-butyl phenol (BP), Figure 5). With such an inhibitor, chemical reaction of the phenolic OH groups is prevented by the proximity of the bulky tertiary butyl groups, whilst the radical scavenging properties remain unaffected. In four hours reaction at 90°C with using BP as an inhibitor, WPG's of 15% and 0% were recorded with GMA and AGE, respectively.

Thus, it is apparent that AGE did not react with wood fibres, and that the method of extraction strongly influenced the apparent WPG's. Since the two epoxides are identical in reactivity they would have with the cell wall OH groups, it is very likely that GMA also does not react with the cell wall OH groups. The alternatives are that some polymerisation is occurring via the double bond of the methacrylic group, or that traces of water are leading to the formation of oligomers within the cell wall. Free-radical polymerisation should be prevented by the presence of inhibitor, whereas any oligomerisation mediated via the epoxide group would affect both GMA and AGE. To try to further understand the nature of the reaction, it was decided to study the effect of first removing the lignin and then the hemicellulose components of the fibre.

Reaction of AGE and GMA with Delignified Wood Fibres

It has been stated that the phenolic hydroxyls of lignin are more reactive to reagents than the alcoholic OH groups associated with the polysaccharide content.[21-24] In addition, hemicellulosic polysaccharides are more reactive than the cellulosic polymers due to the lower degree of supramolecular order and higher degree of branching of the former. It might therefore be expected that the effect of removing lignin from TMP fibres would be to lower the reactivity of such fibres in epoxide modification. With Acetylation, when the lignin is removed, the reactivity to cell wall modifying chemicals drops markedly with typical values of 22.6 to 14.5% WPG being observed after 4 h reaction at 90°C. With pure cellulose, no WPG was obtained. The results of reaction with virgin, delignified and pure cellulose obtained from TMP fibres are given in Table 2. Here it can be seen that the removal of lignin from the fibres does not affect the WPG's obtained to any significant extent, but with pure cellulose a significant WPG reduction was observed for GMA. The difference in reactivity between the two epoxides is again marked. The decrease in the WPG with α-cellulose compared to holocellulose with GMA suggests that a reaction with cell wall hydroxyl groups is indeed occurring. Yet if this is so, then it is difficult to explain why AGE exhibits such different behaviour, since the epoxide group is separated from the methacryl group by a methylene bridge. It is unlikely that any electronic explanation (resonance or inductive) would account for the difference in

TABLE 2

The WPG's of GMA and AGE Modified Different Components of TMP Fibres

	Acetic Anhy. WPG (%)	GMA WPG (%)	AGE WPG (%)
Original TMP Fibres	22.57	14.84	-0.8
De-lignified TMP Fibres	14.45	15.04	2.96
α-Cellulose of TMP Fibres	0	3.07	-0.07

The results are average of the five replicates, reaction time was 4 h and temperature was 90°C.

behaviour. A possible explanation may be connected with the morphology of the fibres. Fibres consisting of α-cellulose may be less susceptible to penetration by the reagent molecules.

Reaction of Epoxides with Pentanol

A further series of reaction was therefore carried out in order to understand the reaction mechanism between epoxides and alcohol groups. Pentanol was reacted with both GMA and AGE, both with and without HQ or BP. GMA formed a glassy insoluble polymer with pentanol. But, when HQ was present in the reaction environment, the product was a sticky, light brown honey-like material. In the presence of BP, the product was yellowish oily material. On the other hand, with no HQ present AGE formed an oily material. In the presence of HQ and BP, AGE produced a non-sticky yellowish product on the bottom of the reaction flask. The products were analysed by using FTIR spectroscopy. In GMA reactions (Figure 6), without HQ, the reaction was found to be taking place via the methacrylic group of GMA (disappearance of peak in the region of 1634 cm^{-1}, C=C bond). This strongly suggests that formation of homopolymer is taking place via the methacryl group. With HQ and BP, there is no

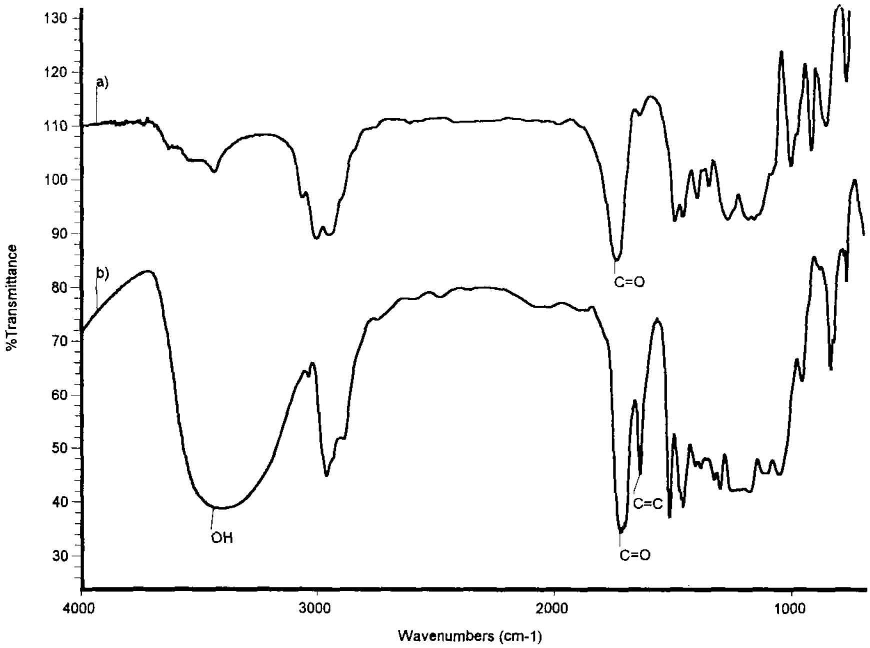

FIGURE 6. FTIR spectrum of the products of the reaction with GMA and pentanol (without HQ (a) and with HQ (b)).

change observed in the region of 1634 cm^{-1}. However, with HQ a new broad absorption appears around 3400 cm^{-1}, due to OH groups. On the other hand, with AGE, there was no change observed in the C=C absorption with and without HQ and BP. The behaviour of GMA is thus explained. There is no reaction with pentanol since no absorption appears in the OH region of the IR spectrum. However, in the presence of HQ, reaction of the epoxide group occurs with the phenolic OH groups of HQ.

Reaction of Epoxy Hexane with TMP Fibres

The results show that GMA is more reactive than AGE. The reason is probably that polymerisation occurred via the methacrylate group in GMA. For this reason, a series of reactions was performed with epoxy hexane (EH) which has no functionality except the epoxide ring. After four hours reaction at 90°C with EH, WPG's of -5.13% and -0.9% were recorded without and with HQ, respectively. Hence, under the conditions used here, there is no reaction between the epoxide group and wood. This behaviour mimics that observed with AGE.

CONCLUSION

In the light of these results, it is likely that no reaction takes place between AGE and the hydroxyl groups of fibres or wood. It is very likely that AGE reacts with itself to produce homopolymers within the cell wall. The evidence for the reaction of GMA with wood fibres is inconclusive. Polymerisation may occur via the epoxide or the double bond. There is no evidence that GMA is reacting with wood. Since the chemical reactivity of the epoxide ring is not affected by the ether linked group, it is concluded that the difference in behaviour between GMA and AGE is due to polymerisation occurring via the methacrylate group in GMA, and that reaction of the cell wall OH groups is unlikely.

EXPERIMENTAL

Whole Wood Modification

For wood modification, samples were prepared from Scots Pine (*Pinus sylvestris*) sapwood blocks of dimensions 20 x 20 x 5 mm (radial x tangential x longitudinal). Samples for experimentation were carefully selected so that the growth rings were parallel to the tangential direction. Before reaction, the samples were subjected to Soxhlet extraction with a mixture of toluene/acetone/methanol (4/1/1, v/v) for 6 h; then ovendried overnight at 105°C. After that, ovendried samples were allowed to cool in a desiccator.

The extracted ovendried samples were numbered and weighed to an accuracy of ±0.0001g. Dimensions were determined using a micrometer accurate to ±0.01 mm. Each reaction was carried out using five replicates. The samples were then transferred to a round bottom flask containing the desired amount of GMA or AGE, catalyst and HQ. The amount of GMA or AGE used was sufficient to provide a three-fold excess over total wood hydroxyl groups and calculated by the following equation.

$$AGE\ or\ GMA\ (mL) = \frac{3\ x\ N\ x\ Sw\ x\ AGE\ or\ GMA\ Molecular\ Weight}{Density\ of\ AGE\ or\ GMA}$$

N = 0.0149 (*The number of moles of hydroxyl groups per g dry wood. Calculation of the OH group concentration was reported in a previous paper*[25])
Sw = Sample weight

Reactions were performed under an inert (Argon) gas blanket. Each flask was sealed with a rubber septum, and a needle attached to a balloon filled with argon gas which was pierced through the rubber septum into the reaction flask to provide a slight positive pressure. All samples were placed in an oil bath set at the required temperature.

Following reaction, the wood blocks were immersed in acetone and refluxed for 30 min, then transferred to a Soxhlet extractor and extracted using the standard 4/1/1 solvent system for 6 h. After that, samples were ovendried overnight at 105°C. The products were stored in the desiccator until cool, then weighed and new dimensions determined. The weight percentage gain was calculated according to:

$$WPG\ (\%) = \frac{\textit{After Treatment Sample Weight} - \textit{Before Treatment Sample Weight}}{\textit{Before Treatment Sample Weight}}\ x\ 100$$

The percentage volume change was calculated according to:

$$VC\ (\%) = \frac{\textit{After Treatment Volume} - \textit{Orginal Volume}}{\textit{Orginal Volume}}\ x\ 100$$

TMP Fibre Modification

For fibre modifications, thermomechanically pulped TMP fibres were obtained from the BioComposites Centre. The fibres were extracted in a Soxhlet extractor, then extracted using the standard mixture for 6 h and dried overnight at 105°C. The extracted TMP fibres were allowed to cool in a desiccator over silica gel.

Approximately 1g of the extracted and oven-dry TMP fibres were transferred to a 100mL round bottom flask and weighed to an accuracy of ±0.0001g. After that the required amount of AGE or GMA was poured into the round bottom flask, and HQ added to some samples. The air in the reaction flasks was displaced by argon gas. Each flask was then sealed with a rubber septum, and a needle attached to a balloon filled with argon gas pierced through the rubber septum into the reaction flask. All samples were placed in an oil bath set at the required temperature.

The products were then cleaned by refluxing in acetone/toluene (1/1, v/v) for 2 h at 90°C. Subsequently, the acetone/toluene mixture was replaced by fresh acetone/toluene mixture and cleaning was continued for further 4 h. After that the products were filtered using sintered glass crucibles. Subsequently a modified extraction procedure was adopted whereby following acetone/toluene treatment, samples were then subjected to Soxhlet extraction with the standard mixture for six hours. After that all the products were dried overnight at 105°C and stored in a desiccator until cool then weighed. WPG(%) of modified TMP fibres were calculated.

Reaction of Epoxides with Pentanol

Reaction conditions were as follows:

a) 10mL GMA or AGE was mixed with 1mL pentanol in the presence of 50mL dry toluene.

b) 10mL GMA or AGE was mixed with 1mL pentanol and 0.2 M HQ or BP in the presence of 50mL dry toluene.

The reaction time was 6 h, the temperature was 90°C, and the reaction was carried out under an argon gas blanket. Following reaction, the solvent was removed on a rotary vacuum evaporator.

Reaction of Epoxy Hexane with TMP Fibres

Reaction conditions were identical with the AGE or GMA modifications, as described previously.

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