Catalyst–Accelerator Method for the Preparation of Wood–Polymer Composites at Ambient Temperature

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SYNOPSIS

Wood–polymer composites (WPC) are materials which may be prepared by impregnating wood with a variety of monomers which are subsequently polymerized by either gamma irradiation or by conventional radical initiators. The inclusion of the polymer into the wood matrix improves the physical properties of the composite compared to plain wood. The catalyst–accelerator method allows *in situ* polymerization of vinyl monomers at ambient conditions and thus reduces the loss of the volatile monomer during curing, which is a major disadvantage of the heat–catalyst method. The combination of peroxide initiators with an aromatic amine accelerator was optimized for the methyl methacrylate system. Polymer loadings and mechanical properties of WPC prepared from *Pinus radiata* using the catalyst–accelerator method were compared with those obtained using the gamma-radiation method. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Wood–polymer composites (WPC) prepared using either catalyst–heat treatment or gamma-radiation is well documented.[1-3] In this study, a catalyst–accelerator method was developed which allowed the preparation of WPC to be carried out at room temperature. This method is superior to the heat–catalyst method as the decomposition of most common initiators such as benzoyl peroxide or AIBN requires a temperature of around 70°C and there is a significant loss of monomer due to vaporization. This leads to a much lower polymer loading for these composites.

N,N-Dimethylaniline (DMA) was used as the accelerator in this work. The mechanism[4] for the reaction between an aromatic amine accelerator and the catalyst benzoyl peroxide (BPO) is
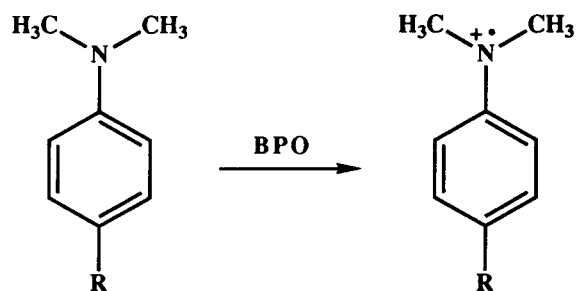
where R = H or CH₃   radical cation

The radical cation formed by the reaction has a much higher reactivity than that of BPO. The activation energy for this reaction is much lower than for the dissociation of BPO and the polymerization reaction may then occur at a lower temperature.

Paul et al.[5] monitored the exotherm generated by the polymerization of methyl methacrylate using accelerators to gain useful information about the effect of several factors on the polymerization rate and the degree of completion. Mixtures of BPO and dilauroyl peroxide (LPO) initiators were mixed with

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methyl methacrylate to which an amine accelerator (*N,N*-dimethyl-*p*-toluidine [DMPT]) had been added, and the rate of polymerization of the monomer was monitored. These polymerization reactions started at room temperature (24°C) using no external heating. The basic feature of the dual accelerator system was that the BPO began to decompose rapidly under the influence of DMPT and this served primarily to raise the temperature to a level where LPO could decompose readily. LPO does not react with the DMPT, but will continue to initiate polymerization when most of the BPO has reacted.

Okamoto[6] discussed the effect of the amine structure on the cure speed of methyl methacrylate. DMA was a slower accelerator than was DMPT. It took 4.5 h for the DMA reaction to reach the maximum exotherm temperature, while it only took 1.4 h for the DMPT-catalyzed reaction. The cure speed was increased for DMPT because the methyl group in the *para* position may donate electrons into the ring and thus increase the stability of the radical cation intermediate.

In this study, DMA rather than DMPT was chosen as the accelerator because it is easier to control the reaction and it was found to give longer impregnation times before the increase in viscosity due to that polymerization inhibited penetration of the monomer into the wood.

An Australian commercial timber, radiata pine (*Pinus radiata*), was used as the timber for our investigations. Radiata pine is by far the most commonly grown softwood in Australia. It is a plantation timber which is fast-growing and cheap to produce; however, it lacks the physical properties required in many building applications. WPC should allow different grades of timber to be manufactured from radiata pine and extend its range of applications in the building industry. Plantation-grown pines are relatively inexpensive when compared to hardwoods, so this along with the relatively low density of a softwood make radiata an ideal material for the preparation of WPC.

EXPERIMENTAL

Materials

Chemicals

Methyl methacrylate was purchased from ICI, BPO, and DMA were purchased from Ajax, and LPO was obtained from Interox. Methyl methacrylate was distilled to remove the inhibitor before use. The other reagents were used as received.

Radiata Pine

Test samples (free from decay and other defects) were cut from bulk materials to the dimensions (50 × 50 × 150 mm) required to conform to the standard adopted for testing samples: the Australian Methods for Mechanical Testing Small Clear Specimens of Timber.[7] These samples were oven-dried at 105°C for 24 h, cooled in a desiccator, and weighed before being used to prepare the composites.

Experimental Procedure

Catalyst–Accelerator Method

Dried wood samples were evacuated in a vacuum chamber (< 5 mmHg) for 30 min to remove air from the pores of the wood. A nitrogen-purged monomer/catalyst mixture was introduced into the vacuum chamber until the wood samples were covered. The concentration of the catalyst are 1% BPO, 0.5% LPO, and 0.5% DMA in distilled methyl methacrylate. These concentrations were found from several optimization experiments to give the best results. The samples were soaked in this reaction solution for approximately 90 min until the solution became viscous. The samples were removed, blotted dry with paper towel, and placed immediately into the oven to complete the curing process at 70°C for 5 h and then left in the oven overnight at 105°C to remove any excess monomer. These samples were subsequently cooled in a desiccator and then weighed.

Gamma-radiation Method

Dried wood samples were evacuated in a vacuum chamber as described in the method above. The nitrogen-purged monomer was then introduced into the vacuum chamber. The wood samples were left immersed in monomer for 24 h at room temperature. After the impregnation period, wood samples were removed from the chamber and individually wrapped, first in polyethylene film and then in aluminum foil. These two layers of wrapping were to prevent evaporation of the monomer. All the wrapped samples were then irradiated using gamma-radiation from a cobalt-60 source to give up to a total dosage of 5 Mrad. After irradiation, the samples were unwrapped and left in a fume hood overnight and then in an oven at 105°C for 24 h to remove any excess monomer.

Table I   Average Hardness of Radiata and Its WPC

Sample	Polymer Loading (%)	Hardness (kN)			
		Tangential	Radial	End	Average
Wood	0	3.70	2.83	3.83	3.45
WPC[a]	100.3	15.85	15.25	14.45	14.01
WPC[b]	100.1	12.5	N/A	N/A	—
PMMA		35			

Superscripts indicate method of polymerization: [a]composites prepared by the catalyst–accelerator method; [b]those prepared using gamma irradiation.

The amount of polymer in individual WPC samples was calculated in terms of polymer loading:

$$\% \text{ Polymer loading} = \frac{(C - W)}{W} \times 100$$

where C and W are the masses of oven-dried WPC and oven-dried wood, respectively.

ANALYSES

Mechanical Testing Methods

Mechanical tests on small clear samples of wood and WPC were used to characterize the effects of polymer incorporation on the physical properties of the materials. Most importantly, a detailed knowledge of all strength properties may be required to determine the suitability of composites for structural applications. The tests were performed according to "The Australian Methods for Testing Small Clear Specimens of Timber."[7]

Hardness (Janka) and compression tests were carried out using equipment at the Forestry Commission, Sydney. The equipment used in these tests consisted of a Maclow–Smith hydraulic universal testing machine together with a Schenck Trebel control station which incorporated an Ono Sokki DG-327 digital dial gauge which was used to measure the distance traveled for the compression test. The control station also consisted of an analog dial gauge from which the applied force could be observed within a range of 7–340 kN.

Hardness Test

The force (in kN) required to indent the specimen with the hemispherical end of a steel rod (diameter of curvature: 11.28 ± 0.05 mm) to a depth of 5.64

mm was measured. The settings for the rate of penetration of the test-head were determined by measurements on spare wood samples with approximately the same hardness characteristics as those of our samples.

Compression Perpendicular to the Grain

The specimen deformation was measured as the relative movement of the loading platforms, and the test was discontinued when the platforms had moved a distance equal to 5%[7] of the width of the test specimen, which in this case was equal to 2.5 mm. The rate of loading was accelerated at a predetermined rate to ensure that the value read off the dial gauge was a measure of force and not simply a load.

RESULTS AND DISCUSSION

Polymer Loading

Polymer loadings of the composites prepared using the two methods were similar: WPC prepared using the catalyst–accelerator method had an initial monomer loading of 104.0% and a final polymer loading of 100.3%. WPC prepared using radiation curing had an initial monomer loading of 108.0% and a final polymer loading of 100.1%. For gamma radiation curing, it has been found that polymer loading increases with the radiation dose.[8] A total dosage of 5 Mrad was chosen to ensure that polymer loadings were obtained which were similar to those from the catalyst–accelerator method.

Hardness Tests

In this study, the resistance to indentation was used as a measure for hardness. Indentation hardness of

the radial, tangential, and end surfaces were measured. Table I summarizes the average hardness of the radiata and its composites prepared using both methods of preparation. The values for wood and poly(methyl methacrylate) (PMMA) are included for comparison.

Results show that all the WPC samples exhibited greater hardness than did their corresponding untreated woods. However, due to the brittleness of the radiation-cured samples which cracked after the first indentation, readings of hardness for the all three faces of the samples (tangential, radial, and end faces) could not be measured for each of these samples. It is therefore inappropriate to compare the hardness of WPC prepared by the two different methods, although the average hardness on the tangential faces for the radiation-cured samples had a slightly lower value.

The brittleness of the radiation-cured samples could have been due to the degradation of the cellulose of radiata pine by gamma radiation. Raczkowski and Fabisiak[9] found that gamma radiation degraded the cellulose of dry pinewood when it was irradiated with 3 Mrad of the radiation, and this resulted in a decrease of the shear strength of the wood. However, WPC of hard wood prepared by the *in situ* polymerization using gamma radiation up to a total radiation dose of 5 Mrad had not shown apparent degradation of the cellulose.[10]

The composites have a weight fraction which is about 50% PMMA, though the hardness of both composites is less than half the hardness value of PMMA. There does not seem to be a synergistic interaction between the wood fibers and the PMMA, and the polymer simply fills the pore space in the wood.

Compression Tests

Compression tests give a measure of the ease by which a material undergoes deformation under stress. Since the polymer loadings of the WPC samples prepared using the two methods were very similar, it was expected that their compression test results would follow the same trend. The mean values of stress perpendicular to the grain at 5% compression and stress at the proportional limit for radiata pine and the composites are shown in Table II.

For the radiation-cured samples, no value could be obtained for the stress at 5% compression due to the brittleness of the samples which cracked when the loading platform moved a distance equal to only 2.4% of the width of the test specimens. There was

Table II Results of Compressive Tests of Radiata Pine and Its WPC

Sample	Polymer Loading (%)	Stress (MPa)	
		5% Compression	Proportional Limit
Wood	0	9.2	5.8
WPC[a]	100.3	50.9	33.7
WPC[b]	100.1	N/A (cracked)	36.9

Superscripts indicate method of polymerization: [a]composites prepared by the catalyst–accelerator method; [b]those prepared using gamma irradiation.

no significant difference in the values for stress at proportional limit for WPC prepared using both methods. Nevertheless, all WPC samples exhibited an increase in resistance to compression. This is due to the incorporation of polymer into the wood, which resulted in the reduction of the proportion of void spaces in the wood. Consequently, a greater force was required to deform the WPC than the wood alone. Comparison with PMMA was not possible because PMMA did not significantly deform using the test apparatus.

CONCLUSION

The catalyst–accelerator method developed in this study for the preparation of WPC has been shown to have advantages over the gamma-radiation curing method. This method is inexpensive to operate as no costly apparatus such as radiation source and radiation chamber are required as in the case of gamma-radiation method. The preparation time for WPC using the catalyst–accelerator method is shorter than is gamma-radiation curing.

The WPC prepared using the radiation method are more brittle than are those prepared by the catalyst–accelerator method, and this may be due to degradation of the cellulose fibers by the gamma radiation. The catalyst–accelerator method is superior to the catalyst–heat method as it allows the *in situ* polymerization of the monomer to be initiated at room temperature, resulting in virtually no loss of monomer during the initiation process since heating is not required to decompose the peroxide initiators.

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