Dynamic Mechanical Analysis of Tropical Wood–Polymer Composites

M. G. S. YAP,[1]* Y. T. QUE,[2] and L. H. L. CHIA[2]

Departments of [1]Chemical Engineering and [2]Chemistry, National University
of Singapore, 10 Kent Ridge Crescent, Singapore 0511

SYNOPSIS

Wood-polymer composites (WPC) of Geronggang (GE; *Cratoxylon arborescens*), a light tropical hardwood, impregnated with methyl methacrylate (MMA) and styrene-*co*-acrylonitrile (3 : 2; STAN), were prepared by *in situ* polymerization using γ radiation or catalyst–heat treatment. The dynamic flexural storage modulus, E', for oven-dried GE, moist GE, and GE–MMA and GE–STAN composites decreased with increasing temperature. The percentage decreases for GE with 10 and 16.5% moisture contents were 74.5 and 98.2%, respectively, which were higher than those for GE and GE composites, which ranged between 40 and 50%. The impregnated polymers were not as effective as water in acting as plasticizers, due to their nonpolar nature and much higher molecular weights. The α-transition peaks for moist GE and GE composites were more distinct and were shifted to lower temperatures than those for oven-dried GE. The values ranged between 75 and 150°C for moist GE and between 102 and 170°C for the GE composites. The α-transitions of the catalyst–heat-treated GE composites were lower than that of the radiation-induced counterparts. GE–STAN composites were also observed to have lower α-transition temperatures than those for GE–MMA for the respective treatment process, which seems to suggest that STAN interacted to a greater extent with cell wall components than did MMA.

INTRODUCTION

Wood has been considered as a unique composite material of semicrystalline cellulose in an amorphous matrix of lignin and hemicelluloses. It is regarded as a viscoelastic material, as wood has been shown to undergo a thermal transition from the glassy to rubbery state, namely, a glass transition. The presence of diluents such as water or ethylene glycol, the proportion of the individual wood components, and the frequency of oscillation were found to affect the temperature at which transition occurred.[1,2] Birkinshaw et al.[3] from their studies with softwoods and hardwoods showed that although there was considerable variation in the absolute values of storage and loss moduli, the general forms of the curves were similar for all species examined. He concluded that microstructural variations were not critical in determining dynamic mechanical behavior.

The impregnation of wood with polymers results in composite materials with enhanced strength properties, dimensional stability, and resistance to biodeterioration.[4-6] Studies of the dynamic properties of wood–polymer composites showed that the storage moduli were much higher than can be accounted for from the quantity of impregnated polymer present. Siau[7] and Moore[8] attributed the high modulus to the interaction between wood cell wall components and polymer. Handa et al.[9] observed that for beech composites prepared from polyethylene glycol monomethacrylate and unsaturated polyesters the dynamic moduli increased logarithmically as the polymer fraction increased.

In this study, methyl methacrylate (MMA) and styrene-*co*-acrylonitrile (3 : 2; STAN) Geronggang (GE) composites were prepared and their viscoelastic properties, determined as the dynamic storage modulus, E', and the loss tangent, tan δ, were compared with those of the wood. These studies also

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 43, 1999–2004 (1991)
CCC 0021-8995/91/111999-06$04.00

enabled the extent of interaction between the impregnated polymer and the wood cell wall components to be investigated.

EXPERIMENTAL

Preparation of Composites

The impregnation system for wood–polymer composites (WPC) preparation is shown in Figure 1. Oven-dried Geronggang specimens (6.5 × 3.0 × 40.0 mm) were evacuated in the impregnation chamber. The monomer or monomeric mixture was introduced at atmospheric pressure and the wood immersed for various periods of time to obtain a range of polymer loadings. In the γ radiation process, the samples were individually wrapped in foil and irradiated in a Co-60 source. In the catalyst–heat treatment, 0.25% by weight of the catalyst, azobisisobutyronitrile (AIBN), was included in the monomeric system. The samples were wrapped in foil and cured in a 60°C oven.

The GE composites prepared were GE–poly(methyl methacrylate) (GE–MMA) and GE–poly(styrene-*co*-acrylonitrile) (STAN; 3 : 2). The polymer loading for the composites was calculated as follows:

$$\%\ \text{Polymer loading} = \frac{100(W - W_0)}{W}$$

where W = weight of WPC and W_0 = weight of oven-dried wood.

Dynamic Mechanical Analysis

A Du Pont 983 Dynamic Mechanical Analyzer (DMA) interfaced to a 9900 programmer and data analyzer station was used to obtain the dynamic flexural storage modulus, E', and loss tangent, tan δ, of oven-dried and moist GE and GE composites. Test samples were clamped at a length between 18.0 and 19.0 mm and set into oscillation at a constant amplitude of 0.2 mm. E' and tan δ were scanned over the temperature range of −120 to 200°C, using a heating rate of 5°C per minute. Liquid nitrogen was used to cool the system to subambient temperatures. Duplicate determinations were made for each specimen to ensure reproducibility of results.

RESULTS AND DISCUSSION

Viscoelastic Behavior of Oven-Dried and Moist GE

The variations of the dynamic flexural storage modulus, E', and the loss tangent, tan δ, with temperature of oven-dried GE and GE containing 10 and 16.5% moisture content are shown in Figure 2. The temperature profiles show that E' decreased with increasing temperature and that the % decrease was

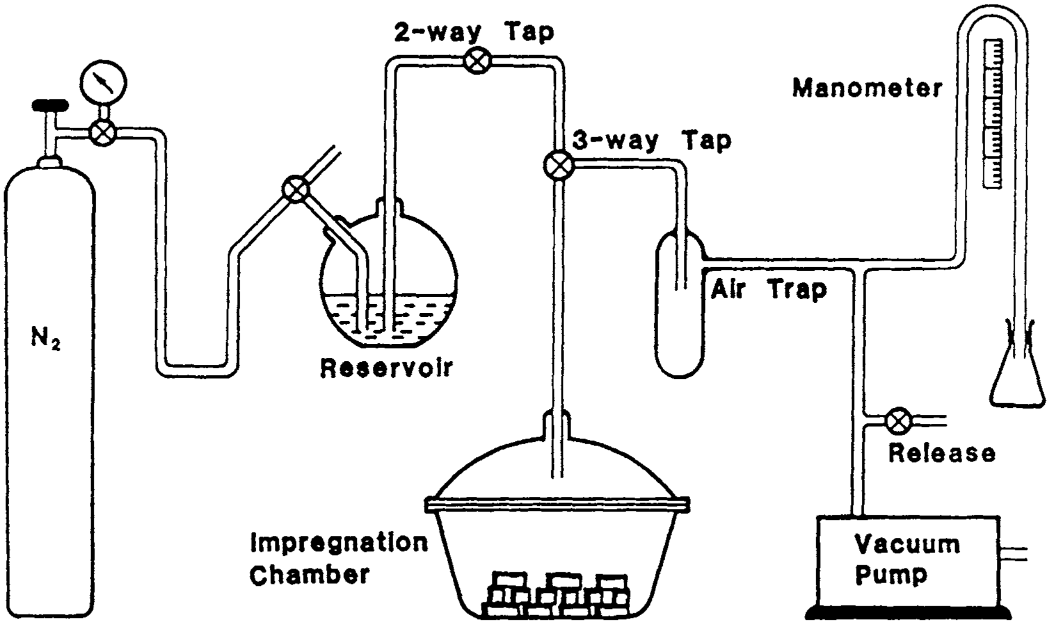

Figure 1 Setup for WPC preparation.

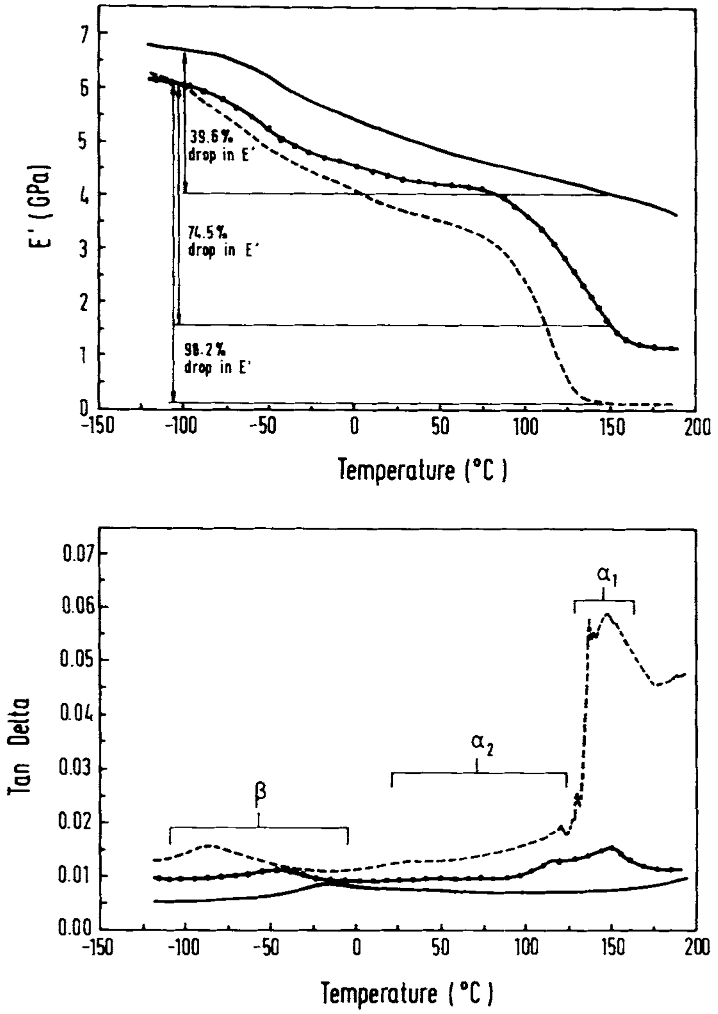

Figure 2 Comparison of E' and tan δ of oven-dried GE (——) with moist GE of moisture content 10% (●●●●) and 16.5% (– – –).

higher for the moist GE (74.5 and 98.2% for 10 and 16.5% moisture content, respectively) than for oven-dried GE (39.6%), determined between −100 and 150°C. These trends are typical of the viscoelastic behavior of wood in general.[1,2] The greater drop in E' for moist wood can be attributed to the plasticizing effect of water on cell wall components. The disruption of highly ordered hydrogen bonds in the wood structure, through formation of less ordered water–water hydrogen bonds, weakens the resistance of wood to applied stress and, hence, results in the loss of strength and stiffness as moisture content increases.[2,10]

That water affects the viscoelastic behavior of wood is also evident from the temperature scan of loss tangent, tan δ, for oven-dried and moist GE. It is noteworthy that α-transition peaks are observed only for the moist GE samples. These peaks, attributed to large-scale segmental motion, as indicated by the accompanying decrease in E', are characteristic of glass transitions, possibly of *in situ* hemicelluloses and lignin present in wood.[2] However, wood devoid of moisture appears not to exhibit glass transition changes. This latter observation is supported by the lack of a sharp decrease in E' and distinct α-transitions in the temperature scans of tan δ for 10 species of oven-dried wood studied by Birkinshaw et al.[3]

A summary of values of E' at −100 and 150°C and β-dispersions and α_1- and α_2-transitions for oven-dried and moist GE is tabulated in Table I. It is observed that moisture lowered the β-dispersion and α-transition temperatures, which can be explained by the fact that plasticizers are known to lower the activation energy required for chain motion.[11] The β-dispersion and α-transition tempera-

Table I Dynamic Storage Moduli, E', and β-, α_1-, and α_2-Peaks for GE

Specimens	PL (%)	Average E' (GPa) at −100°C	Average E' (GPa) at 150°C	Average E' (GPa) at %$\Delta E'$	Transition Temperatures (°C) β	Transition Temperatures (°C) α_1	Transition Temperatures (°C) α_2
GE (oven dried)	-	6.71	4.05	39.6	−16.7	—	—
GE (10% moisture)	-	6.07	1.55	74.5	−41.7	150.0	112.0
GE (16.5% moisture)	-	6.07	0.11	98.2	−75.0	141.7	75.0

tures of moist GE that were determined appear high compared to values reported by Kelly et al.[2] for spruce and maple, of comparable moisture contents, where the α-transitions were well below 100°C and the β-transitions below −100°C. The data were more similar to those obtained for rubberwood by Chan et al.[12]

Viscoelastic Behavior of WPC

The temperature profiles of E' and tan δ for GE–MMA and GE–STAN composites, for both radiation-induced and catalyst–heat-treated composites, together with that for untreated GE, are shown in Figures 3 and 4, respectively. E' values for −100 and

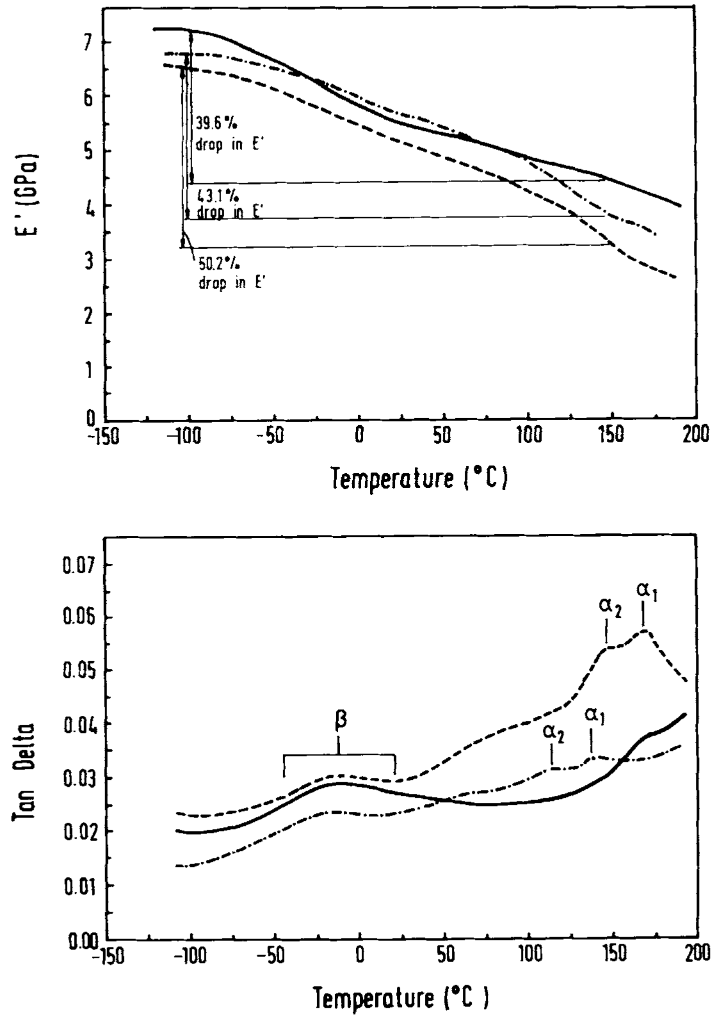

Figure 3 Comparison of E' and tan δ of oven-dried GE (——) with radiation-induced GE–MMA (– – –) and catalyst heat-treated GE–MMA (– • – • –) composites.

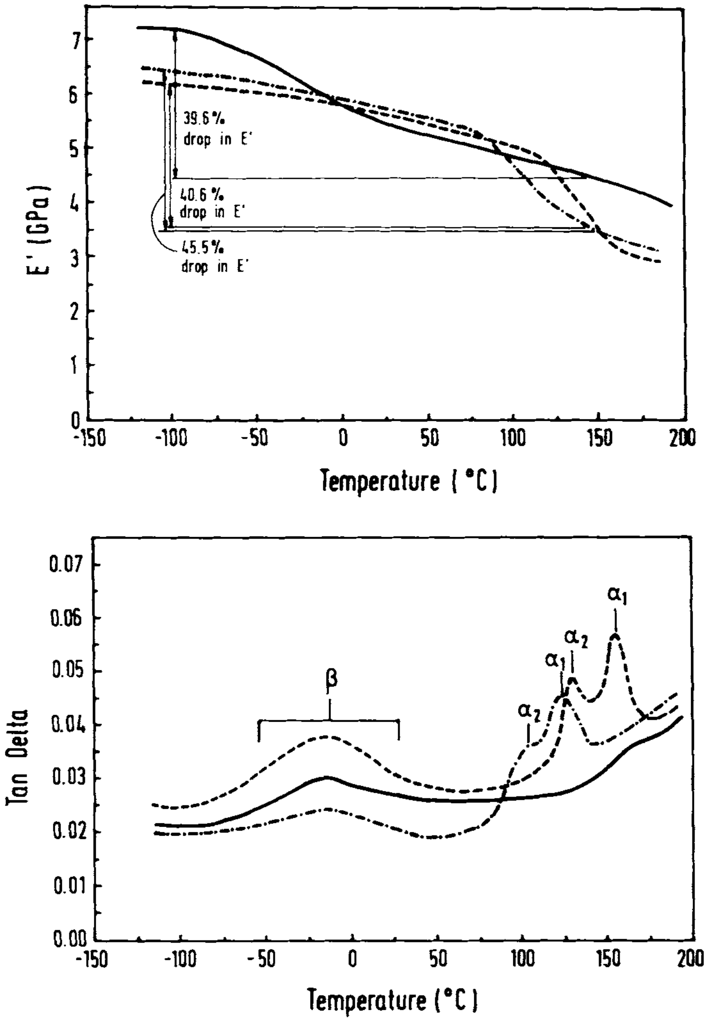

Figure 4 Comparison of E' and tan δ of oven-dried GE (——) with radiation-induced GE–STAN (– – –) and catalyst heat-treated GE–STAN (– • – • –) composites.

150°C and β-dispersions and α-transition temperatures for these samples are summarized in Table II.

As in the case for GE, the E' of GE–MMA and GE–STAN composites decreased with increasing temperature. Above about 100°C, E' decreased more sharply for the composites and, concomitantly, the α-transitions were more prominent in the tan δ temperature scans. The overall % decrease in E' over the temperature range between −100 and 150°C for

Table II Dynamic Storage Moduli, E', and β-, α_1-, and α_2-Peaks for GE–MMA and GE–STAN

		Average E' (GPa) at			Transition Temperatures (°C)		
Specimens	PL (%)	−100°C	150°C	%$\Delta E'$	β	α_1	α_2
GE-MMA	60	6.50	3.24	50.2	−15.8	170.0	145.8
GE-MMA[a]	60	6.71	3.82	43.1	−17.5	111.7	139.2
GE-STAN	81	6.11	3.63	40.6	−21.7	130.8	155.0
GE-STAN[a]	82	6.42	3.50	45.5	−21.7	101.7	123.3

[a] Catalyst–heat-treated GE composites.

the GE composites were only marginally different from that of GE and were much less than that caused by the presence of water. This observation suggests that the impregnated polymers were not as effective as water in acting as plasticizers, mainly due to their nonpolar nature and much higher molecular weights. GPC studies of *in situ* polymers indicated that their average molecular weight was about 10^5–10^6.[13]

The β-dispersions and α_1- and α_2-transition peaks for the GE composites were very distinct. The β-dispersions were very similar in value to that of GE, around −16 to −21°C, and the α-transitions were rather high, ranging between 100°C and 170°C, but were comparable to that for GE with 10% moisture. The α-transitions for rubberwood composites were between 80 and 130°C.[14]

The α-transitions of heat-catalyzed GE–MMA and GE–STAN composites were lower than those of their radiation-induced counterparts, even though the polymer loadings were similar. This and GPC studies,[13] which showed differences in the molecular weight of the *in situ* polymers prepared by the two methods, are the only indications that the two processing methods resulted in impregnated polymers that differed. However, the bulk properties of catalyst–heat and radiation-induced composites have been shown by many researchers to be identical.[14,15]

The α-transitions for GE–STAN composites are lower when compared to those for GE–MMA composites for the respective treatment processes. Assuming that greater interactions with cell wall components result in the lowering of α-transition temperatures, as in the case of water, the present data therefore suggest that STAN interacted to a greater extent with cell wall components than did MMA. This observation is reasonable as acrylonitrile is known to be slightly polar and swells wood.[16] Furthermore, FTIR and thermal characterization of the above composites have shown conclusively that the extent of wood–polymer interaction was highest in GE–STAN.[17,18]

REFERENCES

1. L. Salmen, *J. Mater. Sci.,* **19,** 3090 (1984).
2. S. S. Kelly, T. G. Rials, and W. G. Glasser, *J. Mater. Sci.,* **22,** 617 (1987).
3. C. Birkinshaw, M. Buggy, and G. G. Henn, *J. Mater. Sci. Lett.,* **5,** 898 (1986).
4. J. F. Siau, J. A. Meyer, and C. Skaar, *Forest Prod. J.,* **14**(4), 161 (1965).
5. J. E. Langwig, J. A. Meyer, and R. W. Davidson, *Forest Prod. J.,* **18**(7), 33 (1968).
6. R. L. Calleton, E. T. Chong, and R. C. McIlhenny, *Wood Sci. Technol.,* **4,** 216 (1970).
7. J. F. Siau, PhD Dissertation, Syracuse University, New York, 1968.
8. G. R. Moore, PhD Dissertation, Pennsylvania State University, 1981.
9. T. Handa, S. Yoshizawa, M. Suzuki, and T. Kanamoto, *Kobunshi Ronbunshu,* **35,** 117; *Chem. Abstr.,* **88,** 172107y (1978).
10. W. B. Banks and E. J. Gibbons, *Chem. Br.,* **24**(6), 569 (1988).
11. W. M. Bala and R. V. Subramaniam, *Polym. Eng. Sci.,* **26**(8), 576 (1986).
12. K. Y. Chan, M. G. S. Yap, L. H. L. Chia, and S. H. Teo, *Radiat. Phys. Chem.,* **33**(3), 205 (1989).
13. K. Y. Chan, MSc Thesis, National University of Singapore, 1988.
14. J. F. Siau and J. A. Meyer, *Forest Prod. J.,* **16**(8), 47 (1966).
15. Y. T. Que, MSc Thesis, National University of Singapore (1990).
16. W. E. Loos and G. L. Robinson, *Forest Prod. J.,* **18**(9), 109 (1968).
17. M. G. S. Yap, Y. T. Que, L. H. L. Chia, and H. S. O. Chan, *J. Appl. Polym. Sci.,* to appear.
18. M. G. S. Yap, Y. T. Que, and L. H. L. Chia, *J. Appl. Polym. Sci.,* to appear.

Received November 18, 1990
Accepted January 23, 1991