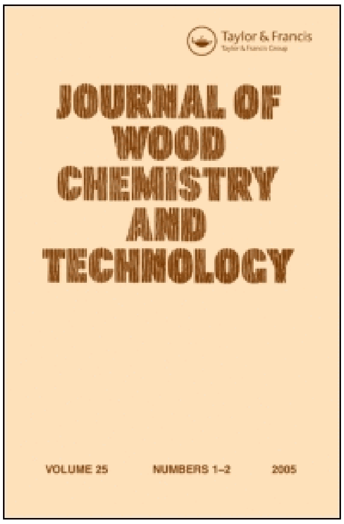

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Wood-Polymer Composites from Tropical Hardwoods I. WPC Properties

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WOOD-POLYMER COMPOSITES FROM TROPICAL HARDWOODS
I. WPC PROPERTIES

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ABSTRACT

Wood-polymer composites (WPC) of 13 different Malaysian tropical hardwoods and 10 vinyl monomers and mixtures of monomers were prepared by *in situ* polymerisation using gamma radiation or the catalyst-heat treatment.

The polymer loading achievable was found to be dependent on the wood species and the nature of the impregnated monomer. Low loadings were observed for the heavy hardwoods and for vinylidene chloride monomer. WPC showed improvement in termite and fungal resistance, dimensional stability and mechanical properties such as hardness, compression and static bending strengths. Thermal conductivities of WPC were found to be lower than the respective wood. From crib tests and oxygen indices, vinylidene chloride, bis(2-chloroethyl) vinyl phosphanate and bis (chloropropyl)-2-propene phosphonate were found to impart flame retarding properties to the WPC prepared. The dielectric constants of most of the WPC were marginally lower than that for the untreated wood.

INTRODUCTION

Wood has always been, and continues to be, a very important and versatile material with many uses because of its many excellent properties, albeit inherent deficiencies do exist. Since wood is porous, it has been treated with various chemicals such as tar, paints, creosote, resins and salts to improve wood properties such as dimensional stability and resistance to biodeterioration. When plastics became available, this material was used to impregnate wood to form wood-polymer composites (WPC), which were found to exhibit lower moisture sorption and greater dimensional stability[1-3]. Moreover, the impregnated polymer imparted additional hardness to the wood, resulting in enhanced compression and bending strengths and impact resistance[4-6]. In general, the improvement in property can be attributed to the polymer content, which is dependent on the type of wood, the polymer and processing applied.

WPC preparation involves the free-radical in situ polymerisation of the impregnated monomer, using either catalyst-heat treatment or gamma radiation. Review articles indicate that the majority of studies has been on temperate wood-polymer composites from softwoods, such as pine and spruce and hardwoods like maple, alder, beech and poplar[7-9]. Monomers that are commonly used are methylmethacrylate, styrene, acrylonitrile, vinyl acetate and mixtures of these and other vinyl monomers. Modifiers such as solvents, plasticizers and resins have also been added to the monomer[10], as well as dyes, antioxidants or salts to modify the final properties[11].

Research in WPC prepared from Malaysian tropical hardwoods, which has been done and is currently being undertaken, is reviewed in two parts. A total of 13 different hardwoods and 10 vinyl monomers and mixtures of these monomers have been studied. In this first part, the properties of WPC investigated and compared to those of untreated wood included fungal and termite resistance, dimensional stability and mechanical, thermal and dielectric properties[12-17]. Polymer loadings were determined and scanning electron micrographs showed the locations of the impregnated polymer in the wood. Part two, involves the characterisation of the viscoelastic behaviour and combustion patterns of WPC[14,16,17].

RESULTS AND DISCUSSION

Wood

The Malaysian tropical hardwoods, classfied broadly as heavy, medium and light hardwoods according to density, strength and durability properties were selected for WPC studies based on availability. However, for commercial applications, WPC would be fabricated only from the light and a few of the medium hardwoods, to improve their lower strength and durability properties shown in Table 1. The dwindling supplies and rising costs of the heavy hardwoods, has created interest in the utilization of lower grade woods such as Ramin, Jelutong and Rubberwood, whose usage can be extended by converting into WPC.

Polymer Loading

An important parameter in the preparation and characterisation of WPC is the polymer loading achievable for each wood and monomer. Table 2 summarizes the average % polymer loadings of the 13 hardwoods and 10 polymeric systems studied. These results indicate that the amount of polymer that can be introduced into the wood is dependent on the wood species and on the nature of the impregnated monomer. WPC prepared from the heavy hardwoods, specifically Balau and Chengal, were observed to have much lower polymer contents than those from the medium and light hardwoods. In the case of Merbau, although classified as a heavy hardwood, because of its lower density, its impregnation pattern was similar to that of the medium hardwoods. The lower loadings for the heavy hardwoods were not

TABLE 1 Classification of Malaysian Hardwoods Used For WPC Preparation[18]

VERNACULAR NAME	SPECIES	DENSITY (Kg/m^3)	STRENGTH*	NATURAL DURABILITY CLASSIFICATION**
Heavy Hardwoods				
Balau (B)	*Shorea spp*	975	A	2
Chengal (C)	*Neobalanocarpus heimii*	945	A	2
Merbau (M)	*Intsia palembanica*	801	B	2
Medium Hardwoods				
Kapur (KP)	*Drobalanops spp.*	755	B	4
Kempas (KM)	*Koompassia malaccensis*	881	A	4
Keruing (KR)	*Dipterocarpus spp.*	801	B	4
Seraya (S)	*Shorea spp.*	545-673	B/C	4
Rubberwood (RW)	*Hevea braziliensis*	640	C	4
Light Hardwoods				
Light Red Meranti (LRM)	*Shorea spp.*	545	C	4
Jelutong (J)	*Dyera costulata*	465	D	4
Machang (MA)	*Mangifera spp.*	561	C	4
Ramin (R)	*Gonystylus bancanus*	625	C	4
Geronggang (G)	*Cratoxylon arborescens*	545	D	4

* Group A - extremely strong, Group B - very strong, Group C - strong, Group D - weak.

** Group 1 - very durable, Group 2 - durable, Group 3 - moderately durable, Group 4 - not durable

TABLE 2 Summary of Average Polymer Loading WPC[12-17]

Wood	Average Polymer Loading (%)									
	PMMA	PMD	PVDC	PAN	PSTAN	PVA	PMVDC	PMBP	PMPP	PMAN
Heavy Hardwoods										
Balau (B)	11	33	9	14	-	21				
Chengal (C)	6 (4*)	-	-	-	-	-				
Merbau (M)	41	39	17	34	47	55				
Medium Hardwoods										
Kapur (KP)	44	36	3	35	53	48				
Kempas (KM)	39	37	18	33	39	41				
Keruing (KR)	40	49	5	27	41	33				
Seraya (S)	49	42	20	22	40	28				
Rubberwood (RW)	60	-	-	18	64	-	15	39		
Light Hardwoods										
Light Red Meranti (LRM)	98	-	-	-	-	-				
Jelutong (J)	148	-	-	-	-	-				
Machang (MA)	72*	-	-	-	-	-				
Ramin (R)	81	61	40	55	73	79				
Geronggang (G)	70(70*)				80(79*)		70(66*)	90	85	60(30*)

* Catalyst-heat treatment
Refer to LEGEND for abbreviations used

unexpected, as the heavy hardwoods have been found to be impermeable to preservative treatments. A correlation study of the gas permeabilities of these tropical hardwoods with polymer loadings showed that the heavy hardwoods, which had low gas permeabilities, also had low monomer impregnation[19]. High permeability in hardwoods is a function of the vessel diameter, and the numbers present per unit area, and is related to the absence of vessel deposits[20]. Extractives inherently present in hardwoods, often in larger amounts in heavy hardwoods, can also affect polymer loadings as these compounds inhibit free-radical polymerizations. Very high extractive contents, between 17-31%, have been reported for the three heavy hardwoods studied[21].

It is noteworthy that the affinity of monomers for wood differed. The impregnation of the different woods with vinylidene chloride consistently gave the lowest loadings when compared with the other monomers. Low loading was also obtained for the PMVDC copolymer in Rubberwood, but loading was higher in Geronggang. High loadings were achieved with PSTAN copolymer, PMMA and PVA. In later studies, vinyl monomers with specific properties of flame retardancy, namely bis(2-chloroethyl) vinyl phosphonate and bis(chloropropyl)-2-propene phosphonate, were used as copolymers with methylmethacrylate in the ratio of 1:3. Further studies on impregnating higher proportions of these flame-retardant monomers are being pursued.

WPC were prepared by the catalyst-heat treatment, using 2,2'-azo-bisisobutyronitrile as catalyst as well as by gamma radiation. As shown in Table 2, except for the PMAN copolymer, polymer loadings for both were very similar. As reported by other researchers[22,23], preliminary characterization indicated no significant difference in the properties of WPC prepared by the two methods.

Scanning Electron Microscope

Scanning electron microscope studies of sections of WPC show that the impregnated polymers occupied the lumina of vessels, fibres, as well as parenchymatous cells. The polymer either completely filled the cavity of the cell following its outline (Figure 1a) or partially filled the vessel lumen, forming a ring (Figure 1b). Studies of fractured surfaces (Figure 1c) by Boey et al[24] suggested that the polymer formed strong interfaces with wood cell walls, accounting for the observed increase in mechanical strength. Laming[25], however, reported that the polymers might be in close contact with the cell walls, but do not form bonds with the cell wall.

WPC and Wood Properties

A summary of the differences in various properties between WPC and wood is tabulated in Table 3. Improvement in dimensional stability is one of the important advantages of WPC over natural wood. The anti-shrink efficiency (ASE) and anti-absorption efficiency (AAE) of WPC to wood, when exposed to high humidity or soaking in water, showed that the impregnated polymers stabilised the wood to different extents. PSTAN composites exhibited the highest ASE and AAE values of 68% and 81% respectively. Ellwood et al[26] reported that only PSTAN composites have ASE values comparable to water-soluble polymers such as polyethylene glycol and phenolic resins.

The dimensional stabilization of wood by impregnated polymer can only be satisfactorily explained by the presence of graft copolymer and not by the physical bulking of wood resulting from homopolymerisation. The formation of graft copolymer is dependent on the ability of the monomer to penetrate the cell wall to react with wood cell wall constituents. As vinyl monomers are non-polar or slightly polar, a swelling agent may be necessary to facilitate

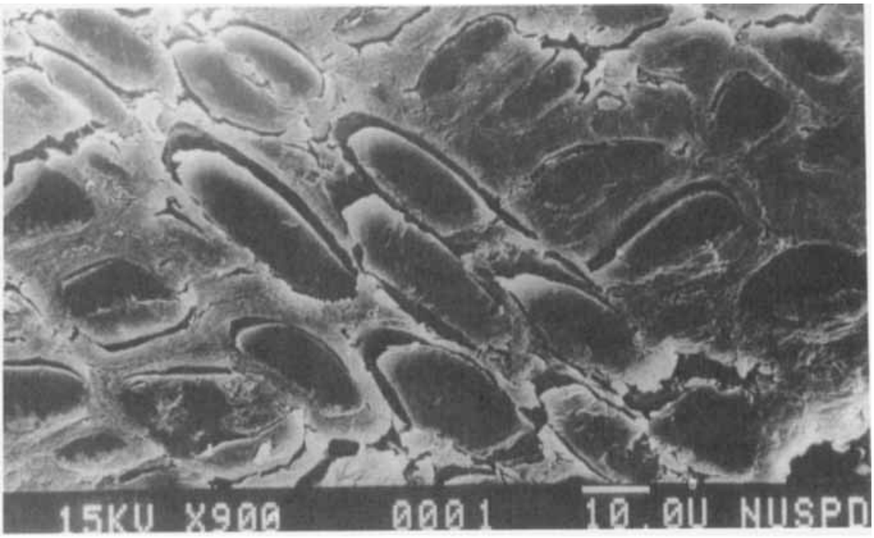

FIGURE 1(a). Transverse Section Of Rubberwood-PMMA Showing Presence Of Homopolymer In Ray Cells And Fibres

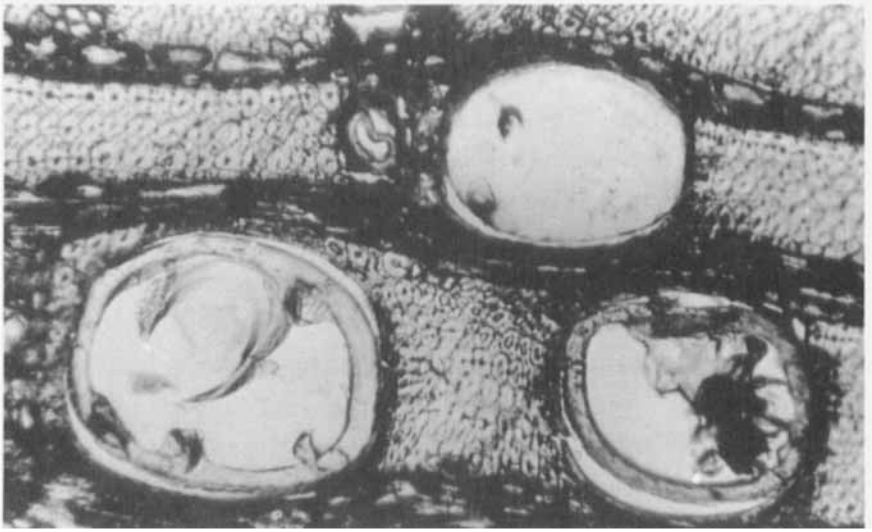

FIGURE 1(b). Transverse Section Of Kapur-PMMA Showing "Ring" Of Polymer In Vessels

FIGURE 1(c). Fractured Surfaces Of Kapur-PMMA Composites

grafting. However, Loos and Robinson[27], found that so-called "non-swelling" vinyl monomers did swell wood of low moisture content. The extent of swelling varied from 6.8% for AN to 0.05% for ST. A 3:1 ST:AN mixture was found to have a high swelling rate and equilibrium swelling value. In the present studies, Chan[16] found that MMA and STAN caused Rubberwood to swell by 1.12% and 9.2% respectively. Therefore, the superior improvement in dimensional stability of PSTAN composites can be attributed to the higher probability of grafting as a result of the swelling capacity of the monomer mixture. In the thermal characterisation of WPC[28], there was also evidence to substantiate the presence of grafted copolymer in RW-PSTAN composite.

The biological resistance of WPC compared to wood to termite[29] and white-rot fungal[30] decay, in terms of weight losses resulting from exposure to these populations, is found in

TABLE 3. Comparison of WPC to Wood Properties[12,13,29,30,32,33,]

Dimensional Stability	%
Anti-shrink efficiency	10 (KR-PMD) to 68 (KM-PSTAN)
Anti-absorption efficiency	27 (KP-PAN) to 81 (RW-PSTAN)

Biological Resistance	% Wt loss ratio of WPC : Wood
Termite resistance	0.23 (S-PMMA) to 0.85 (KP-PMMA)
Fungal resistance	0.38 (R-PMMA) to 0.55 (RW-PMMA)

Mechanical Properties	Ratio of WPC : Wood
Hardness - side	1.0 (B-PMD) to 5.9 (R-PSTAN)
- end	0.9 (S-PVA) to 3.9 (KM-PSTAN)
Max compression strength	0.9 (KP-PVA) to 2.3 (KM-PSTAN)

Static bending tests for Kapur and Rubberwood:

KP-PMMA

$\text{UTS} = 100 + 0.52x$

$\text{MOE} = 14 + 0.06x$

RW-PMMA

$\text{UTS} = 128 + 0.91x$

$\text{MOE} = 12 + 0.036x$

where UTS = ultimate tensile strength
MOE = modulus of elasticity
x = polymer loading (%)

Thermal Properties	Ratio of WPC : Wood
Thermal conductivity	0.72 (KR-PAN) to 0.98 (KM-PSTAN)
Crib test - weight loss	0.47 (KM-PVDC) to 1.25 (M-PMD)
flaming time	0.38 (M-PVDC) to 2.62 (R-PMD)
Oxygen index	1 (RW-PMMA) to 1.3 (RW-PMBP)
Dielectric constant	0.87 (KP-PAN) to 1.1 (KP-PMMA)

Table 3. The presence of polymer in wood reduced significantly the number of surviving termites and weight losses due to degradation. From SEM studies, fungal decay of WPC was observed to be limited to areas where the polymer was absent or where the wood cavities were not completely filled.

From the hardness tests[12,13], the impregnation of polymers into wood increased the side and end hardness of the majority of WPC studied. The degree of improvement depended to a large extent on the % of polymer loading. Comparisons of the different woods and polymeric systems, taking this factor into account, showed that, PSTAN imparted the highest increase, with PMD and PVA showing the lowest. The ultimate hardness values of the WPC prepared were dependent on the intrinsic hardness of the individual woods as well as the polymer content. Overall, Kempas composites, which had high intrinsic hardness and fairly high polymer loadings, and Ramin composites, which had lower intrinsic hardness but very high polymer loadings, showed the highest hardness strengths. In contrast, Balau and Merbau have high intrinsic hardness strength, but because of only limited loadings showed lower ultimate hardness values. The results for compression strengths parallel to the grain were similar to those obtained for the hardness tests.

The factors influencing the strength properties of wood are density, moisture content, direction of the grain, location of the wood sample in the tree, the type of tree and the physico-chemical composition of the cell wall of the sample. Clarke[31] observed that a high degree of lignification of the cell wall of fibres showed high strength properties.

The static bending tests performed for Kapur[14] and Rubberwood[32] composites showed improvements of ultimate tensile strength (UTS) and modulus of elasticity (MOE) over wood in a linear manner with % polymer loading expressed by the equations

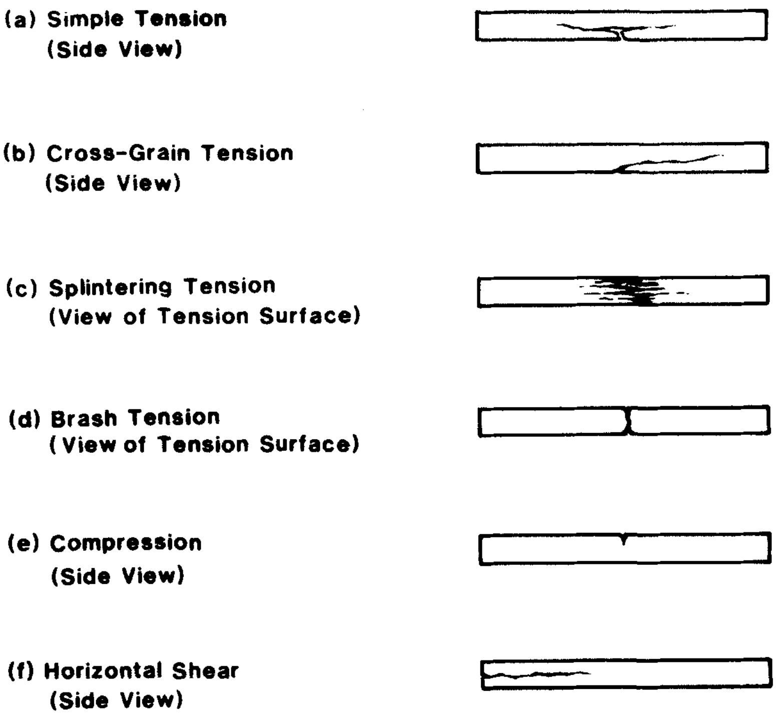

FIGURE 2. Types Of Failure In Static Bending Tests

in Table 3. However, because of the inherent variability of wood resulting in the inevitable scatter of data, the correlation coefficients obtained ranged from 0.6-0.9. The physical bulking of wood voids with polymer contributed to the observed improvements. Boey et al[24] suggested that further contribution to strength of composites could result from a strong interface between cell wood components and polymer, as such an interface would serve to transfer part of the stress of the wood to the polymer.

The static bending failure of Kapur and Rubberwood composites, assessed with about 20 specimens, were of the splintering tension mode, followed by the cross-grain and brash tension, illustrated in Figure 2. The untreated wood showed the same trend indicating that although the impregnated polymer increased the static bending strength, it did not alter the mode of failure.

Thermal conductivity measurements of WPC and wood showed that a reduction in thermal conductivity was exhibited by all the composites[33]. Since the filling of the voids with polymer should make WPC better thermal conductors, it was postulated that perhaps heat transfer was by a more complex mechanism than conduction or that the impregnated polymer entrapped pockets of air.

Crib tests showed that generally, the WPC became less or more flammable than the respective wood depending on the polymer loaded. However, Kempas and Ramin composites were less flammable than untreated wood irrespective of the polymer system. Of the polymers studied, PMMA and PMD imparted flammability, whereas PAN, PSTAN and PVDC caused the WPC to be more flame retardant to different extents. PVDC imparted the highest flame retardancy which can be attributed to the presence of chlorine. The flaming times were substantially lowered for PAN and PVDC impregnated woods, emphasising the flame-retarding property of these two polymers.

Oxygen index measurements showed that only PMBP and PMPP impregnated wood showed a large increase in oxygen index to wood[17,28]. The presence of chlorine and phosphorus in the polymers are contributory to the improved flame-retarding behaviour as demonstrated by Ahmed et al[34]. It was of interest that although the oxygen index of the PSTAN, PAN and PMMA were much lower in the range 17-19%, than that of wood around 26-27%, the composites had oxygen indexes similar to that of wood itself. PMVDC composites showed a slight increase in oxygen index, although PVDC known to possess flame-retarding property, has an oxygen index of 60%. This can be attributed to the low loadings achieved (< 15%) and the higher ratio of MMA to VDC in the preparation mixture.

Preliminary studies on the dielectric properties of composites showed that the dielectric constants were marginally lower than that for wood, except for Kapur and Keruing where they were slightly higher[35]. It was postulated that the presence of polymer led to a decrease in the number of polarisable units in the composites.

EXPERIMENTAL

Preparation of WPC

The impregnation system for WPC preparation is shown in Figure 3. Wood samples were evacuated in the impregnation chamber, followed by the introduction of the monomer at atmospheric pressure and immersion of the wood in the monomer for various periods of time. For the gamma radiation process, the samples were individually wrapped in aluminium foil and irradiated using a Co-60 source. In the catalyst-heat treatment[22], azo-bis-isobutyronitrile at 0.25% by weight based on monomers, was introduced with the monomer and subsequently cured in a 60^oC oven.

The polymer loading for the composites was calculated as follows :

$$\text{\% Polymer Loading} = \frac{100\,(W - W_o)}{W}$$

where W = weight of WPC
W_o = weight of oven-dried wood

Characterisation of WPC

1. Dimensional Stability

WPC and wood specimen of size 25 x 25 x 55 mm were soaked by immersion in distilled water. The weight and

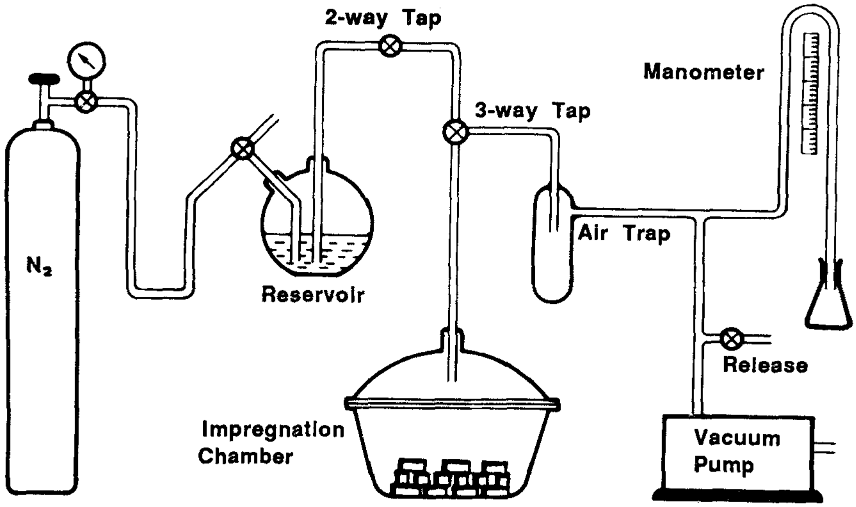

FIGURE 3. Impregnation System For WPC Preparation

dimensions of each block were recorded over a 40-day period. Anti-shrink efficiency (ASE) and anti-absorption efficiency (AAE) were calculated as follows :

$$\text{ASE (\%)} = \frac{100\,(S_w - S_c)}{S_w}$$

$$\text{AAE (\%)} = \frac{100\,(A_w - A_c)}{A_w}$$

where S is the fractional volumetric swell,

A is the fractional weight increase due to water absorption, and the subscripts w and c stand for untreated wood and WPC respectively.

2. Biological resistance. The details of these tests can be obtained from References 29 and 30.

3. Mechanical Properties. The hardness tests were done using a Monsanto-Houndsfield Tensometer according to ASTM D143-52,

with the ball diameter modified to 0.5 cm from the recommeded 1.13 cm, because of the smaller size of the specimen used. Compression strength was determined with a Shimadzu Universal testing machine and the static bending tests with an Instron Universal testing machine.

4. *Thermal Properties.* The following determinations, namely thermal conductivity, crib test and oxygen indices were performed according to Lee's Disk method[33], ASTM E160-50, Reapproved 1975 and ASTM D2863-77 respectively.
5. *Dielectric constant.* The details for this measurement can be found from Reference 35.

LEGEND

PMMA = polymethylmethacrylate
PMD = polymetylmethacrylate, using 5% dioxane as swelling agent
PVDC = polyvinylidene chloride
PAN = polyacrylonitrile
PSTAN = poly(styrene-co-acrylonitrile), 60:40 mixture ST: AN
PVA = polyvinyl acetate
PMVDC = poly(methylmethacrylate-co-vinylidene chloride), 3:1 mixture MMA:VDC
PMBP = poly(methylmethacrylate-co-bis(2-chloroethyl)vinyl phosphonate), 3:1 mixture MMA:BP
PMPP = poly(methylmethacrylate-co-bis(chloropropyl)-2-propene phosphonate, 3:1 mixture MMA:PP
PMAN = poly(methacrylate-co-acrylonitrile), 3:1 mixture MMA:AN

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