

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

The Effect of Lignin and Surface Activation on the Mechanical Properties of Rubberwood-Polypropylene Composites

H. D. Rozman^a; R. N. Kumar^a; M. R. M. Adlli^a; A. Abusamah^a; Z. Mohd Ishak^a

^a School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

To cite this Article Rozman, H. D. , Kumar, R. N. , Adlli, M. R. M. , Abusamah, A. and Ishak, Z. Mohd(1998) 'The Effect of Lignin and Surface Activation on the Mechanical Properties of Rubberwood-Polypropylene Composites', Journal of Wood Chemistry and Technology, 18: 4, 471 — 490

To link to this Article: DOI: 10.1080/02773819809349593

URL: <http://dx.doi.org/10.1080/02773819809349593>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE EFFECT OF LIGNIN AND SURFACE ACTIVATION ON THE MECHANICAL PROPERTIES OF RUBBERWOOD-POLYPROPYLENE COMPOSITES

H.D. Rozman, R.N. Kumar, M.R.M. Adli, A. Abusamah and Z.A. Mohd Ishak

School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia.

ABSTRACT

Lignin was employed in rubberwood-polypropylene (RW-PP) composites to serve as a bridging agent between polar wood filler and non-polar PP. Incorporation of lignin in the composites was able to improve the flexural and tensile properties of the composites. SEM showed evidence of improved adhesion as the result of the addition of lignin. Activation of the wood surface with sodium hydroxide (NaOH) improved the flexural and impact properties of the composites. The tensile modulus was improved, especially at 5% lignin loading. However, no improvement was detected in the tensile strength.

INTRODUCTION

The application of lignocellulosic material, especially wood, as a reinforcing component in polymer composites has received increased attention particularly for price driven/high volume applications. This development has been brought about since reinforcement by

lignocellulosic fillers offers several advantages over their inorganic counterparts, i.e., lower density, greater deformability, less abrasiveness to expensive moulds and mixing equipments, and of course lower cost. Moreover, lignocellulosic based fillers are derived from a renewable resource.

It is well known that compatibility between lignocellulosic material and polymer plays a crucial role in determining the properties of a composite. Lignocellulosic materials which have polar hydroxyl groups on the surface contributed predominantly by cellulose and lignin, have difficulty in forming well-bonded interface with non-polar polymer matrix such as polyethylene and polypropylene. Various chemical reagents have been employed to enhance the compatibility between the constituent materials. These include epolene E-43 (maleic anhydride modified-polypropylene),¹ poly[methylene (polyphenyl isocyanate)] (PMPPIC),² γ -methacryloxypropyltrimethoxysilane (A-174),³ vinyltri (2-methoxy ethoxy) silane (A-172),⁴ γ -aminopropyltriethoxysilane,⁵ poly(propylene-acrylic acid)⁶ and poly(propylene-ethylene acrylic acid).⁶

In this study, lignin is used to serve as a compatibilizer between rubberwood filler and PP matrix. Since, lignin contains polar hydroxyl groups and non-polar hydrocarbon and benzene rings, it is to be believed that it can play a role in enhancing the compatibility between both components. Thus, this phenomenon would improve the mechanical properties of a composite.

Surface modification of lignocellulosic material has been extensively studied either to improve dimensional stability towards moisture⁷ or to improve adhesion and bonding with the polymer matrix.⁸ In this study, attempts have also been made to study the effects of sodium hydroxide (NaOH) treatment on the mechanical properties of rubberwood-polypropylene (RW-PP) composites.

EXPERIMENTAL

Materials

Rubberwood (*Hevea brasiliensis*) powder was obtained from Malaysia Wood Industries Sdn. Bhd., Sungai Petani, Kedah, Malaysia. Rubberwood consists of 70% holocellulose, 40% alpha-cellulose, 22-29% lignin, 6-10% extractives (alcohol/benzene and hot water solubles), 20% pentosan and 0.8-2.3% of ash. The polypropylene (PP) used was purchased from Polypropylene Malaysia Sdn. Bhd., Malaysia with melt flow index and density of 12.0 g/10 min and 0.903 g/cm³, respectively. ALCELL[®] lignin was obtained from Repap Technologies Inc., USA.

Filler treatment

Rubberwood powder were ground to mesh size 35-60 (270-500 μm) using Endecotts test sieves. Four (4) levels of fillers were attempted, i.e. 10, 20, 40 and 60% of the overall weight of the composite. For each level of filler, three (3) levels of lignin were employed; 5, 10 and 15% (based on

the weight of the filler). Lignin powder was dissolved in ethanol (15% solution) before being mixed with the filler. The mixture was dried in an oven at 80°C for 6 hours to allow complete evaporation of ethanol.

For the surface activated filler, the filler was immersed in 10% NaOH solution for 1 hour at room temperature, followed by rinsing with distilled water. The treated filler was then oven-dried at 105°C for about 16-18 hours. The following process was the same as mentioned above. The treatment was carried out with composites with 40% RW filler loading.

Compounding and processing

The compounding of untreated and treated RW-PP was carried out using a Haake Rheocord System consisting of a Haake Rheodrive 5000 (drive unit) and Haake Rheomix 600 with roller blade (mixer). The mixing was carried out at 170°C for 20 minutes at a rotor speed of 25 rpm. The compound was then transferred to a mould with the dimensions of 160 X 160 X 3 mm. The compound was preheated for 10 minutes at 160°C followed by hot-pressing at the same temperature for another 10 minutes. Cooling was carried out for 5 minutes under pressure.

Testing

The sheet produced was cut into 3 types of test samples; i.e. flexural, tensile and impact tests. Tensile tests were carried out according to ASTM D618 on samples with the dimensions of 15 X 1.9 X 0.3 cm (length X width

X thickness), using Instron machine Model 1114 at a cross-head speed of 5 mm/min. Flexural test was conducted according to ASTM D790, i.e. a three-point bending system, using Universal Testing machine Model STM-10. The samples with dimensions of 15 X 1.5 X 0.3 cm, were tested at a cross-head speed of 2.0 mm/min. The Izod impact test was carried out according to ASTM D256 on unnotched samples with dimensions of 6.5 X 1.5 X 0.3 cm, using Zwick Impact Pendulum Tester Model 5101. A minimum of six samples were tested in each case. The calculations for flexural strength (modulus of rupture, MOR) and modulus (modulus of elasticity, MOE) are given below.

Modulus of Elasticity (MOE):

$$\text{MOE} = \frac{L^3 \Delta W}{4bd^3 \Delta S}$$

where;

L = the span between the centers of supports (m)

ΔW = the increment in load (N)

b = the mean width (tangential direction) of the sample (m)

d = the mean thickness (radial direction) of the sample (m)

ΔS = the increment in deflection (m)

Modulus of Rupture (MOR):

$$\text{MOR} = \frac{3WL}{2bd^2}$$

where;

W = the ultimate failure load (N)

L = the span between centres of support (m)

b = the mean width (tangential direction) of the sample (m)

d = the mean thickness (radial direction) of the sample (m)

Morphological Study

The fracture surface of the composites from the tensile test were investigated with a Leica Cambridge S-360 Scanning Electron Microscope. The objective is to get some information regarding fibre dispersion, bonding quality between fibre and matrix and to detect the presence of microdefects, if any. The fracture ends of the specimens were mounted on aluminum stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Effects of wood filler and lignin loading

Figure 1 shows the effect of wood filler and lignin loading on the flexural strength of RW-PP composites. It can be seen that the strength of the composite decreases as the percentage of filler is increased. Thus, the results show that the incorporation of filler in the PP matrix rendered the composite to have a lower ultimate flexural strength. The results would imply that more stress concentration sites would be created as more fillers

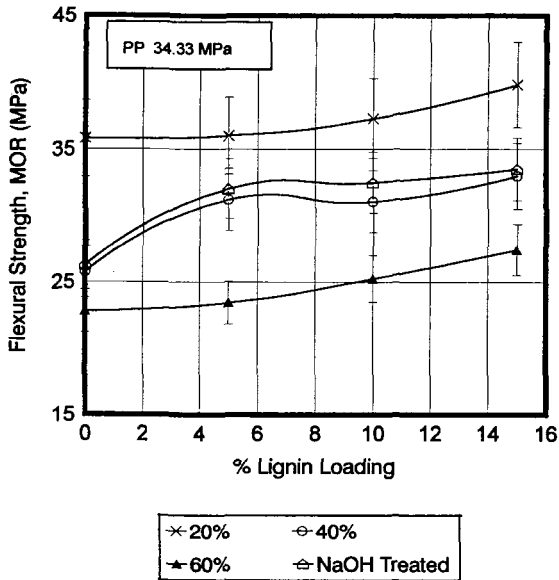


Figure 1. The effect of rubberwood (RW) level, alkaline treatment of the rubberwood (40% level), and lignin loading on the flexural strength of the composites.

are added. This would in turn encourage easy propagation of stress throughout the matrix. Similar observations have also been previously encountered for other lignocellulose filled thermoplastic composites.^{1,3}

The results also show the effect of lignin on the flexural strength of composites. There is an increasing trend in the strength as the amount of lignin is increased. The addition of lignin has resulted in the higher strength values of the rubberwood-lignin-filled polypropylene composites (RW-L-PP) as compared to the untreated counterpart. It is particularly interesting to note that the strength value for RW-L-PP composites with 20% RW is higher than that of PP. Thus, this provides a good indication that the

incorporation of lignin is able to improve the ultimate flexural strength of the sample. In fact, it can be seen that incorporation of lignin is able to outweigh the detrimental effect on the discontinuity in the polymer matrix posed by RW filler. This may reflect better adhesion at the RW-PP interface, which may be brought about by the lignin. Lignin is a polymeric material which consists of polar and non-polar substituents. The former is contributed by the phenylic hydroxyl groups and the latter is by the polymeric networks which consists of benzene rings, hydrocarbon linkages and so on. Thus, the amphiphatic nature of lignin may contribute to the better adhesion between wood and PP matrix.

The results also show that surface activation produces relatively similar ultimate flexural strength of the composites compared to the ones without activation.

Generally, RW-PP composites show an increasing flexural modulus (modulus of elasticity, MOE) as RW loading increases (Figure 2). The results show that the incorporation of RW filler is able to instill stiffness in a thermoplastic composite. Similar trend were observed by other studies.⁹⁻¹² Figure 2 also displays that the modulus of the composites are significantly increased as the lignin loading is increased. Thus, the results illustrate that both RW filler and lignin are able to interact synergistically and enhance the stiffness of composites. This may be attributed to the ability of lignin to improve the compatibility between RW and PP matrix, resulting in the increase in the strength as well as stiffness.

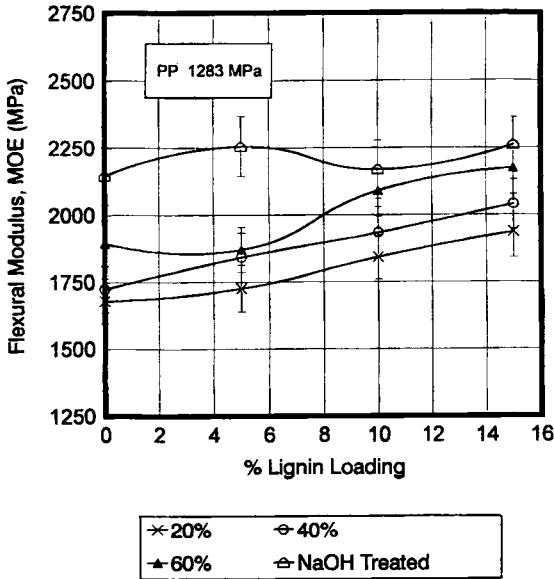


Figure 2. The effect of rubberwood (RW) level, alkaline treatment of the rubberwood (40% level), and lignin loading on the flexural modulus of the composites.

Activation with NaOH imparts significant changes in the flexural modulus of composites. The results indicate that the activation of the surface does improve the interaction of wood surface with the lignin. It is believed that the interaction produce rigid and relatively strong bonding which is sufficient to increase the stiffness and the strength of the composites, though the former is greatly enhanced than the later. This explanation is further supported by the results of tensile modulus and impact strength in Figures 3 and 5, respectively.

The impact strength of composites decrease as the filler content increases (Figure 3). This observation is quite expected for filled

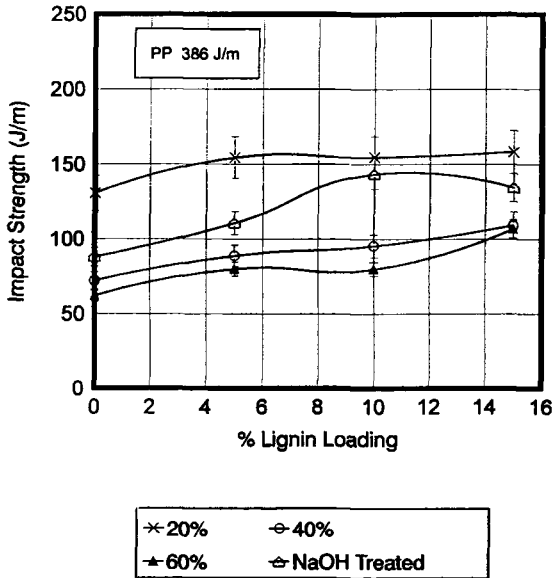


Figure 3. The effect of rubberwood (RW) level, alkaline treatment of the rubberwood (40% level), and lignin loading on the impact strength of the composites.

composites and has been commonly reported by various workers.¹³⁻¹⁵ As shown by flexural properties, addition of lignin has also resulted in the improvement of the impact strength. This may be as the result of an enhanced interaction between wood and PP as explained earlier. Samples activated with NaOH show significantly higher impact strength than its counterpart.

The results of tensile strength (Figure 4) show that the strength decreases with increasing RW loading. This is in agreement with the trend observed in other lignocellulosic filled composites.^{16,17} Unlike fibres which have uniform cross-section and relatively high aspect ratio (i.e. the length

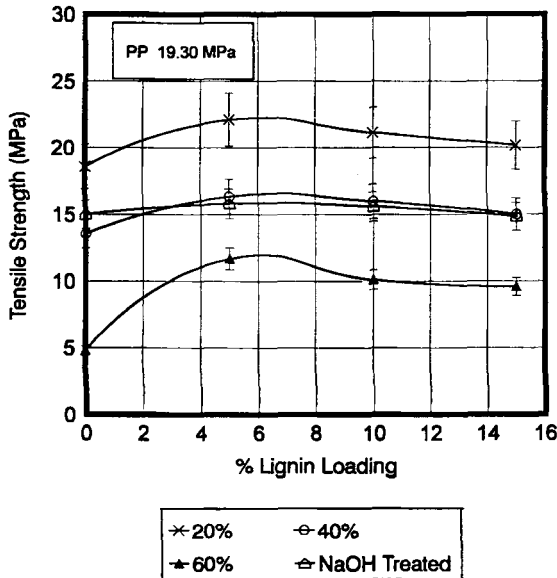


Figure 4. The effect of rubberwood (RW) level, alkaline treatment of the rubberwood (40% level), and lignin loading on the tensile strength of the composites.

to diameter ratio, l/d), for irregular-shaped fillers such as RW, their capability to support stress transmitted from the thermoplastic matrix is rather poor. Thus, the strength enhancement in the filled composite is in general much lower than that of fibre reinforced systems. Overall, the tensile strength of the composites is improved with the incorporation of lignin. It is interesting to note that, composites with 20% filler loading show greater tensile strength than PP. The results also show that the effect of the addition of lignin is becoming more obvious as the filler loading is increased. Composites with 60% filler shows the highest degree of enhancement in tensile strength compared to the lower filler loading. Thus,

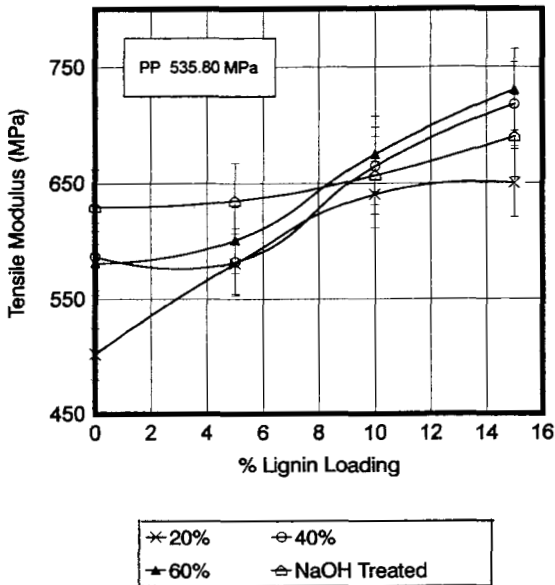


Figure 5. The effect of rubberwood (RW) level, alkaline treatment of the rubberwood (40% level), and lignin loading on the tensile strength of the composites.

the results indicate that lignin plays a positive role in improving the tensile strength of composite. Figure 4 also shows that the tensile strength of the activated composites does not show any improvement compared to the ones without activation.

The tensile modulus of composite shows an increasing as the filler loading increases (Figure 5). This clearly indicates the ability of RW fillers to impart greater stiffness to the PP composites. Similar observations have been reported by several workers for other lignocellulosic filled thermoplastics.^{16,17} It is interesting to note that the incorporation of lignin has increased the tensile modulus of RW-PP composites. This again

provides a strong evidence for better interaction between RW filler and lignin.

The tensile modulus of the NaOH activated sample is improved especially for the composites with 5% lignin loading. Further increase in lignin loading does not provide further improvement in the stiffness.

It is known that composite materials with satisfactory mechanical properties could only be achieved if there is a good dispersion and wetting of filler in the matrix that will give rise to strong interfacial adhesion. Thus, in this case it can be seen that lignin is able to improve the dispersion as well as the wetting of the filler and the polymer matrix. The enhancement in strength of the composites with lignin used as coupling agent may be due to the improvement in the interaction between the paramagnetic sites of the lignin and the PP. Kosikova et. al.¹⁹ measured the concentration of free radicals derived from lignin and PP and found that free radicals so produced from lignin and PP by the thermal oxidation promote the intra and inter molecular interaction between lignin and PP. An optimum level of lignin concentration is adequate for such an interaction and further increase in the radical concentration leads to oxidative degradation of PP and reduction in the strength. The present results on the effect of lignin concentration follows similar trend since beyond a certain lignin concentration, the strength either levels off or shows a decreasing trend.

The results of the performance of NaOH treated composites are in conformity with those reported by Kosikova et. al¹⁹ who observed that the

increased level of activity of lignin under alkaline conditions is due to the hindered phenolic hydroxyl groups which are potential radical scavengers and under alkaline conditions an increased free radical concentrations are formed through benzoquinone structures. Free radical concentrations of oxidized lignin has been reported to be $35\text{--}40 \times 10^{15}$ spins/g as compared to untreated lignin, $25\text{--}30 \times 10^{15}$ spins/g. The treatment of fine wood filler particles with a high surface area with alkali would therefore be expected to result in oxidized wood lignin with potential to produce high free radical concentrations under the conditions of interaction with PP during composite production. It has also been reported¹⁹ that the difference between the free radical concentration between the treated and untreated lignin increases as the temperature is increased. This is favourable since the composites are made at higher temperatures.

SEM micrographs of the fracture surfaces of RW-PP composites are shown in Figures 6(A) and (B) for 20% filler content and Figures 6(C) and (D) for 20% filler content with 20% lignin content. The micrographs show the random distribution of RW filler embedded in the PP matrix (Figure 6A). Figure 6B shows the presence of fibre pull-outs as the mode of failure. For the composites incorporated with 20% lignin (Figure 6C), the occurrence of fibre pull-out is still prevalent but relatively to a lower degree than the untreated composites. The occurrence of fibre breakage shown in Figure 6D indicates the improvement at the interface as the result of the addition of lignin.

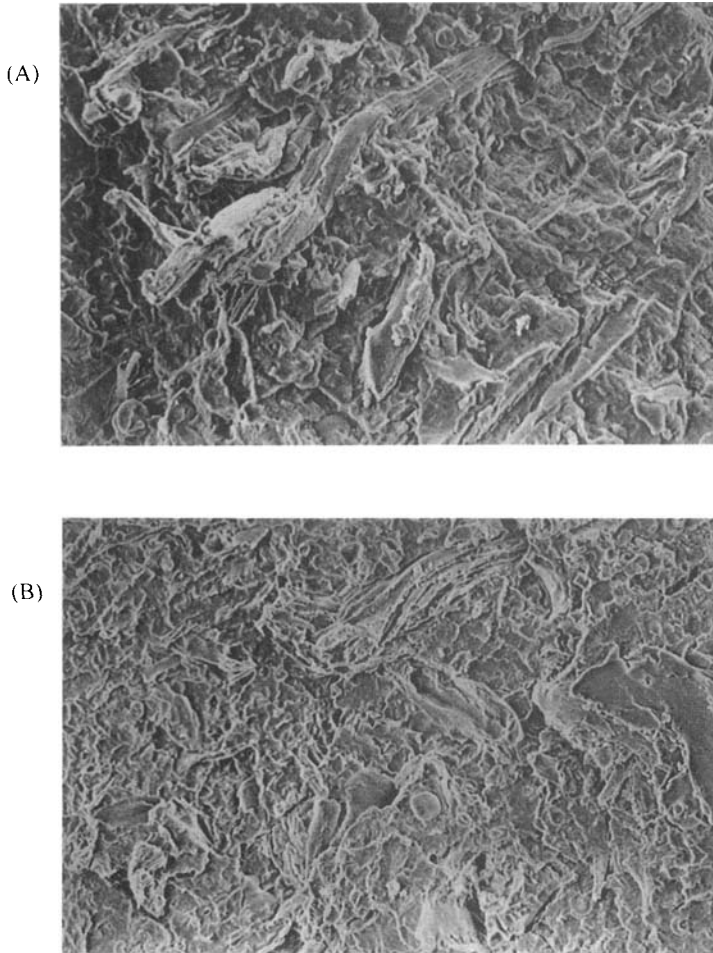
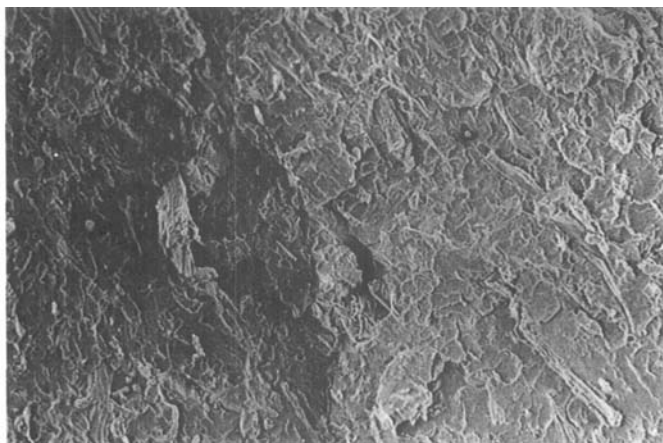


Figure 6. SEM Micrographs of composites with 20% rubber wood (RW) filler: (A) indicating the RW distribution; (B) indicating the fiber pull-outs; (C) with 20% lignin, indicating the occurrence of fiber pull-outs; and (D) with 20% lignin, indicating the occurrence of fiber breakage.

(C)



(D)

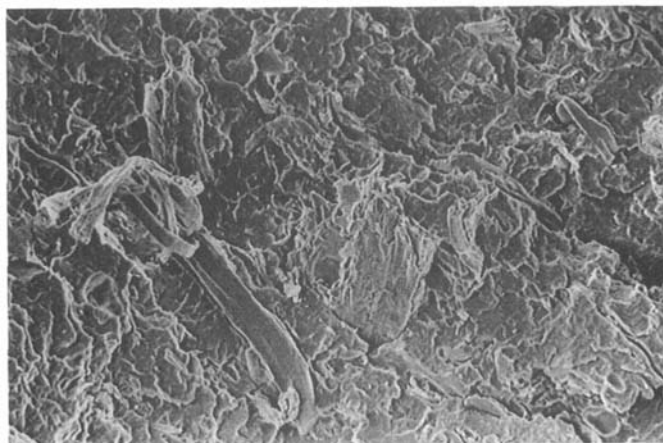


Figure 6. Continued.

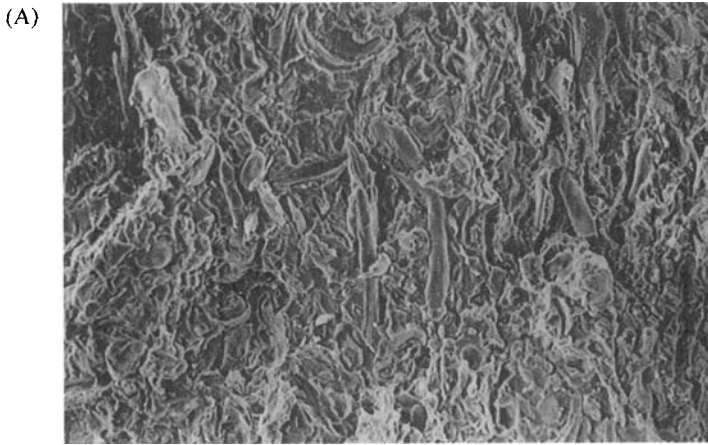


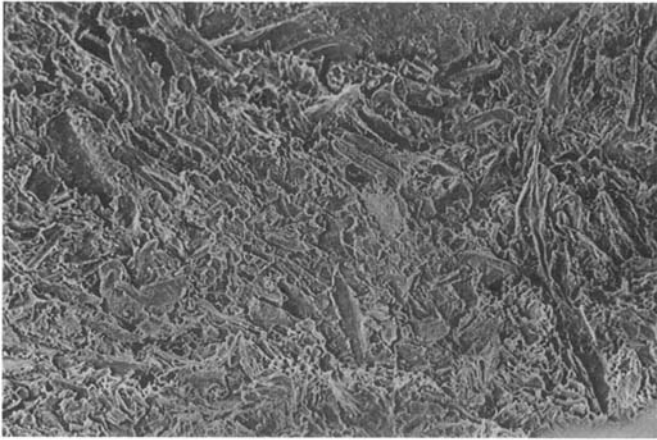
Figure 7. SEM Micrographs of composites with 40% rubber wood (RW) filler: (A) indicating the RW distribution; (B) with 20% lignin, indicating the RW distribution; and (C) with 20% lignin, indicating the interfacial region of RW filler and PP.

Figure 7(A) shows the micrograph of composites with 40% filler. The filler is seen to be distributed randomly in the polymer matrix. However, the incorporation of lignin has improved the distribution of filler in the matrix as shown in Figure 7(B). The addition of lignin is shown to improve the interfacial region between RW filler and PP matrix (Figure 7C). This provides a supportive evidence for the significant improvement in the strength and stiffness of the RW-L-PP composites as discussed earlier.

CONCLUSIONS

The study demonstrated that incorporation of lignin in the composites was able to improve the flexural and tensile properties of the composites.

(B)



(C)

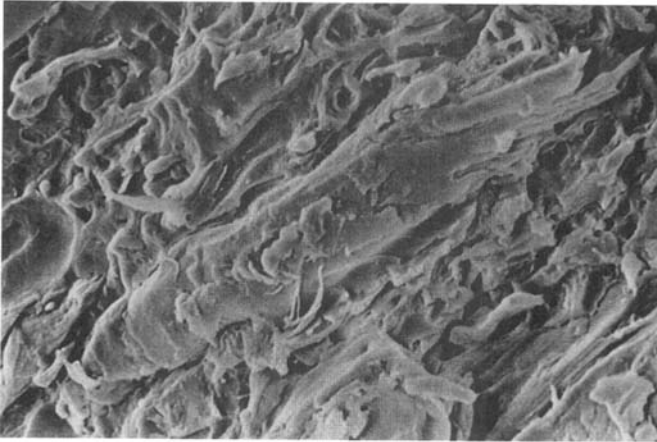


Figure 7. Continued.

SEM results showed the evidence of improved adhesion as the result of the addition of lignin. Activation of wood surface with NaOH improved the flexural and impact properties of the composites. Tensile modulus was improved especially at 5% lignin loading. However, no improvement was detected in the tensile strength.

ACKNOWLEDGMENTS

The authors would like to thank Universiti Sains Malaysia, Penang, for the research grant that has made this research work possible. Thanks are also due to Prof. M.H. Simatupang for the ALCELL[®] lignin and Malaysia Wood Industries Sdn. Bhd., for supplying the RW used in this study.

REFERENCES

1. G.E. Myers, I.S. Chahyadi, C.A. Coberly and D.S. Ermer. Intern. J. Polymeric Mater., 15, 21 (1991).
2. B.V. Kokta, R.G. Raj and C. Daneault. Polym. Plast. Technol. Eng., 28,(3), 247 (1989).
3. M. Xanthos. Plast. Rubber Processing and Appl., 3, 223 (1983).
4. R.G. Raj, B.V. Kokta, G. Groleau and C. Daneault. Polym. Plast. Technol. Eng., 29(4), 339 (1990).
5. D. Maldas, B.V. Kokta, R.G. Raj and C. Daneault. Polymer, 29, 1255 (1988).
6. Z.A. Mohd Ishak, A. Aminullah, H. Ismail and H.D. Rozman. J. App.

- Polym. Sc. (1997) (in press).
7. H.D. Rozman, R.N. Kumar, H.P.S. Abdul Khalil, A. Abusamah, R. Abu and H. Ismail. *Eur. Polym. J.*, 33, 1213 (1997).
 8. R.G. Raj, B.V. Kokta and C. Daneault. *Intern. J. Polymeric Mater.*, 14, 223 (1990).
 9. R.T. Woodhams, G. Thomas and D.K. Rodgers. *Polym. Eng. Sc.*, 24 (1984).
 10. G. Freischmidt and A.J. Mitchell. *Polym. Intern.*, 24, 241 (1991).
 11. G.E. Myers. *Intern. J. Polymeric Material*, 15, 171 (1991).
 12. K.L. Yam, B.K. Gogoi, C.C. Lai and S.E. Selke. *Polym. Eng. Sc.*, 30, 693 (1990).
 13. R.G. Raj, B.V. Kokta, G. Groleau and C. Daneault. *Plast. Rubber Processing Appl.*, 11, 215 (1989).
 14. D. Maldas and B.V. Kokta. *Intern. J. Polymeric Mater.*, 17, 1 (1992).
 15. C. Klason, J. Kubat and H.E. Stromvall. *Intern. J. Polymeric Mater.*, 10, 159 (1984).
 16. M.Y. Ahmad Fuad, R. Shukor, Z.A. Mohd. Ishak and A.K. Mohd. Omar. *Plast. Rubber Comp. Process Appl.*, 21, 225 (1994).
 17. R.G. Raj, B.V. Kokta and C. Daneault, *Intern. J. Polymeric Mater.*, 12, 239 (1989).
 18. D.M. Bigg. *Polym. Composites*, 8, 115 (1987).
 19. B. Kosikova, K. Miklesova and V. Dernianova. *Eur. Polym. J.*, 29, 11, 1495 (1993).