

Use of Expanded-EPDM as Protecting Layer for Moderation of Photo-Degradation in Wood/NR Composite for Roofing Applications

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ABSTRACT: Changes in tensile properties, sample size, interfacial strength, and thermal conductivity of melt-laminating layers of wood/ebonite natural rubber (NR) and expanded ethylene-propylene diene rubber (EPDM) for polymeric roofing applications were monitored under a period of UV aging times for 60 days, the results being compared with single rubber layers of wood/NR and expanded-EPDM. The experimental results suggested that the tensile modulus of the wood/NR-EPDM melt-laminating layer increased with increasing aging time. The tensile strength of the wood/NR layer decreased after prolonged UV aging, and positioned between that of the wood/NR and expanded-EPDM layers. The sample size reduction of wood/NR layer with expanded-EPDM top coating layer was lower than that for wood/NR single layer. The peel

strength of the wood/NR-EPDM melt-laminating layer was found to decrease with increasing UV aging time as a result of delamination of the rubber layers. The thermal conductivity of the wood/NR-EPDM melt-laminating layer decreased from 0.085 to 0.070 W/m K with increasing aging times upto 40 days, but tended to increase to 0.080 W/m K at the aging time of 60 days. The experimental results in this work clearly suggested that expanded-EPDM could be used as protecting layer, not only for moderation of photo-oxidative degradations of wood/NR layer for roofing application, but also for minimization of dimension changes of the wood/NR-EPDM melt-laminating layer. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 335–342, 2010

Key words: coating; degradation; vulcanization; rubber

INTRODUCTION

Because of its unsaturated structures, natural rubber (NR) is likely to degrade under high temperatures and photo-oxidation, and these cause changes in molecular structures and mechanical performances. Rubber degradation is a process, in which the rupture of chemical bonds occurs in the rubber molecules. The degradation usually results in losses of mechanical properties and elasticity, and increases in set properties of the rubber products. Works by Santos et al.¹ examined the effect of UV radiation on the photo-oxidation of polyisoprene by varying the UV wavelengths of both synthetic rubber and NR using Fourier transform infrared and UV spectros-

copy. Their results showed that at 253 nm, the cross-linking reactions prevailed at the first stages of the photo-oxidation while chain scissions were dominant at the higher wavelengths. They also found that faster photodegradation process observed for NR was assigned to the presence of impurities such as OH and C=O moieties. Vinod et al.² focused on the effect of heat, ozone, and gamma radiation agings of aluminum powder filled NR composite by varying types of bonding agents. They suggested that aging of NR–aluminum powder composite at 70°C for 7 days caused an increase in tensile strength with lower elongation at break due to post-crosslinking process, the results being explained in terms of restrictions of the molecular mobility of polymer segments. Bauer et al.³ reported the effect of heat aging and fill gas accelerates of wedge and skim rubber from five different tires. They found that the oxidative aging of skim and wedge rubber inside the tire caused a loss of peel strength and tensile properties of these rubbers. Using N₂/O₂ as a fill gas could accelerate the oxidative aging by 30–40% relative to air. The degradation of the rubber can also be observed through the use of nuclear magnetic resonance.⁴

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To prevent NR products from thermal oxidations and photodegradations, a number of stabilizers, antioxidants,^{5–7} and protective coatings^{8–10} were recommended. Abad et al.⁵ studied the effect of various environmentally friendly antioxidants on degradation of vulcanized NR latex. The antioxidants used were cystine, tyrosine, asparagine, phenyl alanine, and alanine. It was observed that phenyl alanine exhibited the highest antioxidative performances. Ismail et al.⁶ considered the effect of arylphosphites antioxidants for NR and styrene-butadiene rubber vulcanizates and they suggested that Tri- β naphthyl phosphite was the satisfactory antioxidant. Bhowmick et al.⁷ investigated the effect of thermal stabilizers in photodegradation prevention for NR and polyethylene blend. The stabilizers used were isopropyl paraphenylene diamine, a high molecular weight phenolic antioxidant, and a commercially available blend of two high molecular weight hindered amine stabilizers. They recommended that isopropyl paraphenylene diamine was the most effective stabilizer in such blend.

Roofs made from polymeric materials have recently gained attentions due to readily processabilities, good mechanical properties, favorable environmental profiles, and cost savings. Ethylene-propylene diene rubbers (EPDM) are widely used for outdoor applications due to their saturated hydrocarbon backbone with a small amount of diene double bonds at the side chain. It has been desirable^{8–10} to produce a new energy saving roof, which has a combined function of roofing and insulation through uses of NR coated with EPDM. Recent work by Yamsaengsung and Sombatsompop^{8–10} developed a fully bonded ply roof from a hard surface NR roof through ebonite rubber system with incorporation of wood flour, the wood particles being used to increase the stiffness of the NR. The wood/NR roofs were coated by melt-laminating with expanded-EPDM layer. The work was initiated by improving the interfacial adhesion between the wood/NR and EPDM laminates by incorporating chemical coupling agents in the wood/NR layer.⁸ Molecular diffusion between the wood/NR and EPDM layers was observed, which was responsible for the increases in the adhesion strength at the interface. The thermal insulation properties of the wood/NR-EDPM laminating roofs were also improved by foaming the EPDM layer through the use of 4,4'-oxybis (benzenesulfonylhydrazide) (OBSh).^{9,10} They recommended that using the OBSh at 3.0 phr, wood/NR, and EPDM laminates with maximum peel strength (= 3 N/mm) with relatively low the thermal conductivity (= 0.08 W/m K) were achieved.

This article was formed as a part of ongoing investigations into development of wood/NR composite layers for polymeric roofing applications.^{8–10}

The main aim of this work focused on monitoring the changes in tensile properties, sample size, peel strength, and thermal conductivity of wood/NR composite layer coated with expanded-EPDM layer when experiencing artificial weathering conditions for 60 days. For comparison purposes, the properties of wood/NR composite and EPDM single layers under the same aging conditions were also conducted. Scanning Electron Micrographs (SEM) were used to support the experimental results obtained.

EXPERIMENTAL

Raw materials

Wood/natural rubber composite

- *NR and compounding ingredients.* To enhance the stiffness of the wood/NR composite, NR was formulated using an excessively high dosage of sulfur (20 phr) to produce an NR, whose compounding formulations with other reinforcing fillers are given in Table I. The NR (STR5L) used was supplied by Siam United Rubber. (Bangkok, Thailand).
- *Wood particles.* Wood particles were supplied by V.P. Wood. (Bangkok, Thailand). The average particle size was in the range of 100–300 μm . The moisture content in the wood particles was less than 1%, this being achieved by placing in an oven at 80°C for 24 h before use.¹¹ For comparison and continuation purposes to our previous works,^{9,10} the content of wood particles used was fixed at 40 phr.
- *Precipitated silica.* The amorphous white silica (Ultrasil VN3) with an average particle size of 27 nm, supplied by Siam United Rubber (Bangkok, Thailand), was used as reinforcing filler at 45 phr for the wood/NR composite. The moisture content of the precipitated silica was about 5%.
- *Chemical coupling agent.* To improve the interfacial adhesion between wood particles and NR, 0.5 wt % of N-(β - Bis-(3-triethoxylpropyl)

TABLE I
Vulcanization Recipes for Wood/Natural Rubber Composite

Chemicals	Content (phr)
Natural rubber	100.0
ZnO	33.4
Stearic acid	13.4
Mercaptobenzothiazole (MBT)	3.4
Diphenylguanidine (DPG)	1.4
Antioxidant	0.1
Sulfur	20.0
Wood sawdust particles	40.0

TABLE II
Vulcanization Recipes for Expanded-EPDM

Chemicals	Content (phr)
EPDM	100.0
ZnO	5.0
Stearic acid	1.5
Dibenzothiazole disulfide (MBTS)	0.6
Diphenylguanidine (DPG)	0.6
Sulfur	2.5
EPR-b-OBSH (varied)	0.0–11.0

tetrasulfan (Si69)) was used as chemical coupling agent,⁸ the Si69 coupling agent being supplied by Shin-Etsu Chemical. (Tokyo, Japan).

Ethylene-propylene diene monomer

- *EPDM rubber and compounding ingredients.* Ethylene-propylene diene monomer (EPDM-ESPRENE 505), based on 5-ethylidene-2-norbornene, with 49.8% ethylene and 10% diene contents was used, and the vulcanization recipes are given in Table II. The EPDM was supplied by Siam United Rubber. (Bangkok, Thailand).
- *Chemical blowing agents.* The modified 4,4' oxy-bis(benzenesulfonylhydrazide) or EPR-b-OBSH were used. The EPR-b-OBSH agents was supplied by A.F. Goodrich Chemical. (Bangkok Thailand), respectively. The decomposition temperature of the OBSH was 147°C.

Treatment of wood particles

N-(β - Bis-(3-triethoxypropyl) tetrasulfan) solution was prepared by mixing the Si69 coupling agent of 0.5 wt % of the wood content with ethanol¹² before sprayed onto the dried wood particles, and then mixed all together with a high speed mixer for 5min. After that, the mixtures were oven dried for 24 h at 80°C until a constant weight was achieved. The wood particles were used in the Si69-treated form throughout this work.

Preparations of wood/NR, expanded-EPDM, and wood/NR-EPDM melt-laminates

Unvulcanized wood/NR layer was prepared by masticating the NR on a laboratory two roll mill (Yong Fong Machinery. Samutsakorn, Thailand) for 5 min before compounding with the desired contents of the vulcanizing (ebonite) chemicals, precipitated silica and treated wood particles for further 25min, the detailed procedure being found elsewhere.⁸ Unvulcanized expanded-EPDM layer was prepared

by masticating the EPDM compound on a laboratory two roll mill (Yong Fong Machinery. Samutsakorn, Thailand) for 5 min before compounding with the vulcanizing chemicals and the OBSH agent for further 15 min. The vulcanized wood/NR and EPDM melt-laminating sheet of 5.0 mm thick was produced using a LAB TECH hydraulic press (Type LP-S-20) at a lamination pressure of 15 MPa, and lamination temperature of 140°C for 13 min, these lamination conditions being experimentally suggested by our previous work.⁸ It should be noted that these laminating conditions were given based on the optimum mechanical strength (maximum peel strength) obtained in our previous work.⁸ However, we felt that the conditions used were sufficient to decompose the blowing agent used and to result an expansion of the EPDM layer, although these conditions may not be the best for foaming of EPDM layer. The vulcanized wood/NR-EPDM laminating sheet was then kept at 25°C with 50% humidity before further use.

Artificial weathering test

The vulcanized wood/NR layer, expanded-EPDM layer, and wood/NR-EPDM melt-laminating layer were UV-aged under artificial weathering equipment for 60 days. The sample identifications for studying the effect of artificial weathering test are shown in Figure 1. The artificial weathering test was carried out in fluorescent UV/condensation weathering equipment (QUV, Q-PANEL, USA) according to ASTM G154-2004. The cycle consisted of 20 h of UVB ($\lambda = 310$ nm) radiation at 80°C and 4 h of condensation at 80°C. The irradiance intensity was 0.62 W m²/nm. The laminating samples were exposed for a period of 60 days; the aged samples were collected every 10 days and the properties were tested.

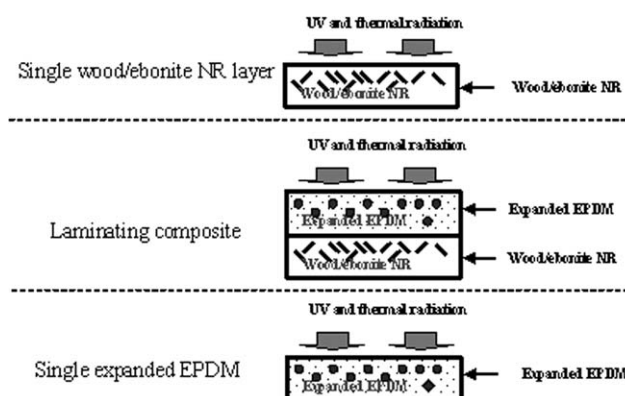


Figure 1 Sample identifications for studying the effect of aging time.

Characterizations

Foam morphology and mechanical properties of EPDM foam layer

- *Surface and foam morphology.* SEM was utilized to study the sample surface of wood/NR layer, and cell structure of expanded-EPDM layer. The SEM micrographs of surface and/or razor cut surfaces¹³ of composite layers were examined using a JEOL-JSM-6400 at 15 kV accelerating voltage.
- *Tensile properties.* The tensile properties of the wood/NR, expanded-EPDM, and melt-laminating layers were evaluated using ASTM D412-98(1998) with dumbbell-shaped samples using a universal testing machine (Model Autograph AG-I, Shimadzu, Japan) at the testing speed of 500 mm/min.
- *Relative sample size.* The changes in sample size before and after artificial weathering aging were monitored every 10 days. This was carried out by measuring the size of the test specimens using a digital micrometer with four decimal points. The relative sample size (RSS) of the samples before and after UV-aging can be obtained using eq. (1).

$$RSS = \frac{W_{\text{aged}}}{W_{\text{initial}}} \quad (1)$$

where W_{initial} and W_{aged} represent the sample sizes before and after UV-aging, respectively.

Peel strength and thermal conductivity of wood/NR composite-EPDM foam laminates

- *Peel strength.* An interfacial adhesion of wood/NR-EPDM melt-laminating layers before and after UV-aging was studied using rectangular laminate samples of 25 mm wide and 200 mm long. This was achieved by carefully cutting from the wood/NR-EPDM laminating sheet. A thin aluminum sheet was coated on the expanded-EPDM layer using a neoprene-rubber adhesive to avoid any elongating deformation of the expanded-EPDM layer during the peel test. A specially designed floating roller apparatus was utilized in accordance with ASTM D3167 (2004), the experimental procedure and conditions of the peel test being detailed in our previous work.⁸⁻¹⁰ The peel strength (P) was assessed using eq. (2).¹⁴ The reported results were obtained from at least five independent laminate samples.

$$P = \frac{F}{w} \quad (2)$$

where F is the peel force (N) and w is the sample width (mm).

- *Thermal conductivity.* In this work, the effect of weathering on the changes in heat flow across the wood/NR-EPDM laminate sheet was detected to determine the thermal conductivity. The test followed the ASTM-C 518-04 (2004) standard, Nepzsch test apparatus, which consists of a heat flow meter, hot and cold plates, and thickness measuring sensor. The temperature gradients were determined using thermocouples mounted on the hot and cold plates. The thermal conductivity of the wood/NR composite-EPDM laminates before and after UV aging were measured using eq. (3).¹⁵ An experimental error for thermal conductivity measurement was estimated to be about 1.0%.

$$k = \frac{Q \cdot s}{A \cdot \Delta T} \quad (3)$$

where k is the total thermal conductivity (W/m K), Q is the sample heat flow, (W) s is the sample thickness (m), A is the sample area (m²), ΔT is the temperature difference across the plates (K).

RESULTS AND DISCUSSION

Effect of UV-aging on tensile properties and sample size reduction

Figure 2 illustrates the effect of UV-aging time on tensile moduli of expanded-EPDM, wood/NR, and

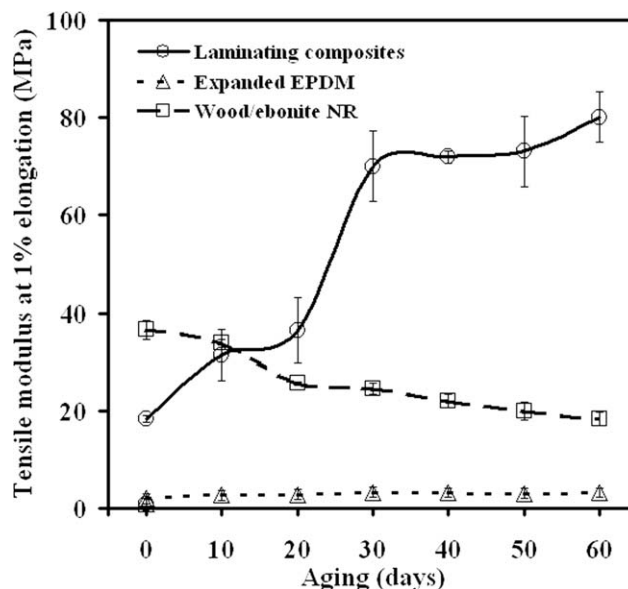


Figure 2 Effect of aging time on tensile modulus of expanded-EPDM, wood/NR, and wood/NR-EPDM melt-laminating layer.

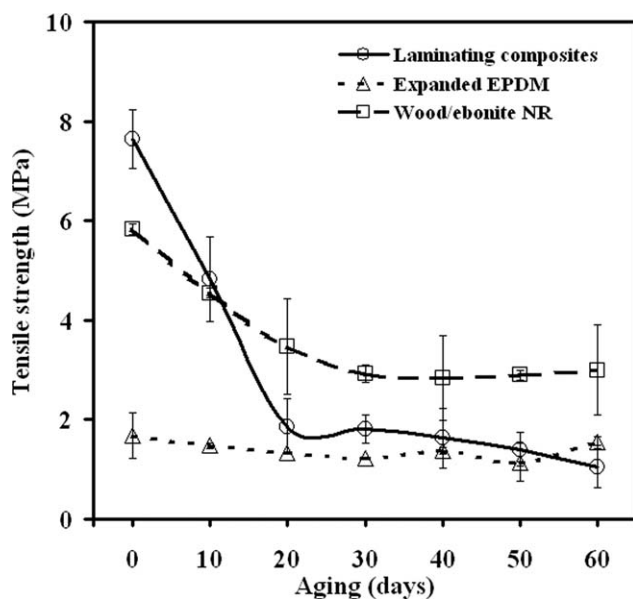


Figure 3 Effect of aging time on tensile strength for expanded-EPDM, wood/NR, and wood/NR-EPDM melt-laminating layer.

wood/NR-EPDM melt-laminating layers. For expanded-EPDM layer, the tensile modulus did not change with varying aging times. This was expected due to the high UV and thermal stability of EPDM.¹⁶ The tensile modulus of wood/NR layer slightly decreased with increasing aging time. The slight reduction in tensile modulus of wood/NR composite layer was caused by degradation of vulnerable unsaturated NR structures under a direct contact with UV and thermal radiation.¹⁷ It was interesting to observe that the tensile modulus for the wood/NR-EPDM melt-laminating layer sharply increased during the first 30 days of aging time and then leveled off at higher aging times. An explanation for this was that the wood/NR layer in the laminating form was protected by the EPDM topcoat, suggesting less UV-exposure and thermal radiations to the wood/NR layer. If this was the case, the degradation level of the NR was minimized, but instead, post-curing (post-crosslinking) and desulfuration processes were likely to occur. The post-curing or post-crosslinking reaction after prolonged aging could be supported by the works of Zhao et al.¹⁸ and Ha-Anh and Vu-Khanh,¹⁹ whereas the occurrence of the desulfuration reaction was previously found by Sombatsompop.²⁰ These post-curing and desulfuration processes proposed in this work would result in the increase in tensile modulus of wood/NR-EPDM melt-laminating layers. It should be noted that the desulfuration reaction was referred to as reduction of sulfur linkages from polysulfidic to mono- or di-sulfidic crosslinks, which caused increases in not only molecular rigidities or stiffness, but also

thermal resistance of the wood/NR-EPDM melt-laminating layer.²⁰

The results of tensile strength of expanded-EPDM, wood/NR, and wood/NR-EPDM melt-laminating layers as a function of UV-aging time are given in Figure 3. Similar to tensile modulus, the tensile strength of expanded-EPDM layer did not change with UV-aging time because of high thermal stability of the EPDM protecting layer. The tensile strength of wood/NR layer significantly decreased with increasing aging time, again because of the degradation of NR structures under the direct contact with UV and thermal radiation.¹⁷ In the case of wood/NR-EPDM melt-laminating layer, it was noticeable that the tensile strength of the wood/NR-EPDM melt-laminating layer decreased with increasing aging time, and positioned between that of the wood/NR and expanded-EPDM layers. The decrease in tensile strength of the wood/NR-EPDM melt-laminating layer was caused by the increased and desulfurated crosslinks as mentioned earlier, together with the extremely low tensile strength of the expanded-EPDM layer. It has been widely known that rubber vulcanizates with excessive crosslink densities and/or mono- and di-sulfuric crosslinks have lower tensile strength than those with polysulfuric crosslinks.^{20,21} The higher tensile strength of the wood/NR-EPDM melt-laminating layer confirmed the advantage of using expanded-EPDM top coat layer proposed in this work.

The effect of aging time on reduction in sample size for the expanded-EPDM, wood/NR, and wood/NR-EPDM melt-laminating layer was reported in Figure 4. It was found that the sample sizes for

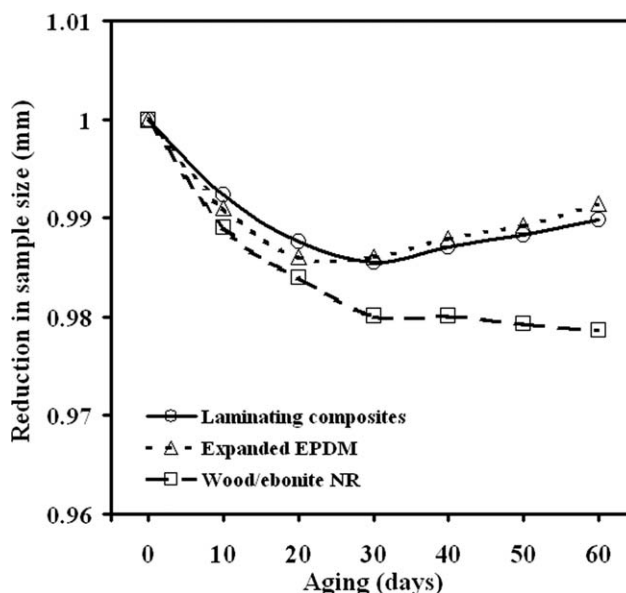


Figure 4 Effect of aging time on reduction in sample size for expanded-EPDM, wood/NR, and wood/NR-EPDM melt-laminating layer.

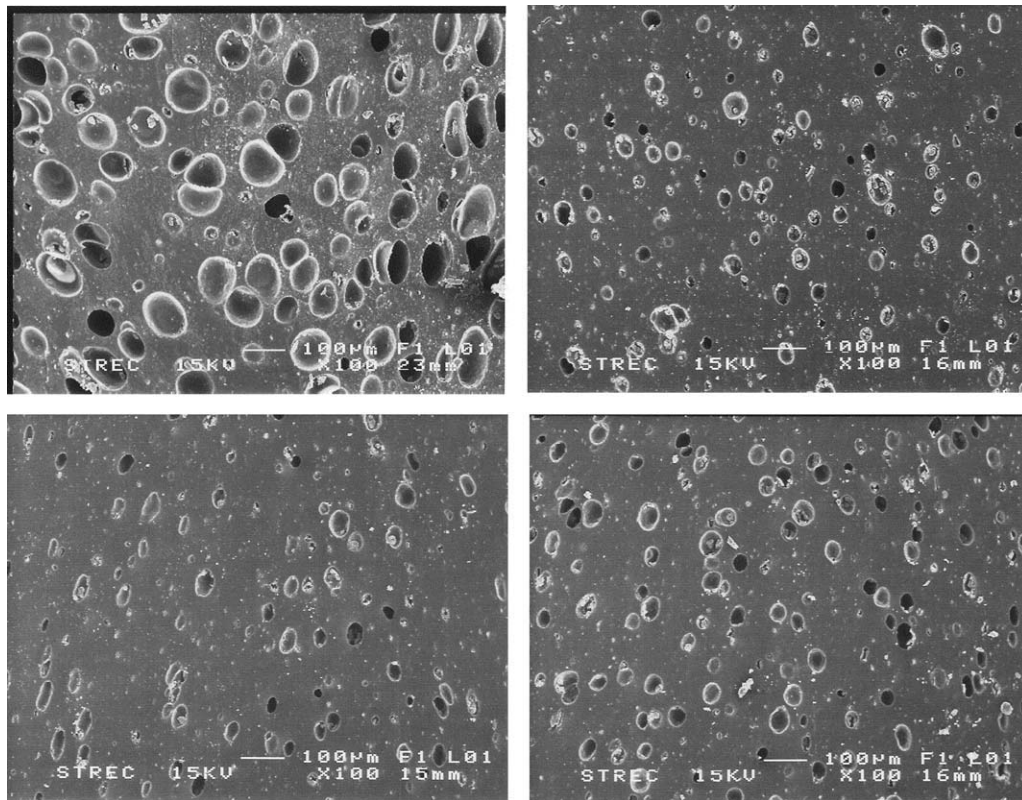


Figure 5 SEM micrographs at cross-sections of expanded-EPDM layer at different aging times.

expanded-EPDM and wood/NR-EPDM melt-laminating layers decreased with increasing UV-aging times up to 30 days and then started to increase at higher aging times. For the wood/NR layer, the sample size continued to decrease for a whole period of UV-aging. For a given aging time, the reduction in sample size for the wood/NR was greater than that for the expanded-EPDM and wood/NR-EPDM melt-laminating layers. This was unexpected as the wood/NR layer was solid, whereas the expanded-EPDM was cellular layer. It was postulated that the reduction in sample size of wood/NR layer was caused by migration of volatile and unreacted chemicals in the NR compound, whereas that of expanded-EPDM layer was mainly due to a diffusion of N_2 gas through the cell wall.^{22,23} The shrinkage of expanded-EPDM by gas diffusion was clearly observed by the SEM micrographs in Figure 5, suggesting that the size of EPDM foam cells decreased within the first 20 days, and then remained unchanged at higher aging times (40 and 60 days). It was also interesting to note that the size reduction in the wood/NR-EPDM melt-laminating layer was more dependent on that in the expanded-EPDM layer. This observation offers another advantage of using expanded-EPDM top coat as protecting layer to minimize the size reduction of the wood/NR layer.

Effect of UV-aging on peel strength and thermal conductivity

Figure 6 illustrates the effect of UV-aging time on peel strength for wood/NR-EPDM melt-laminating layer. It was observed that the peel strength for

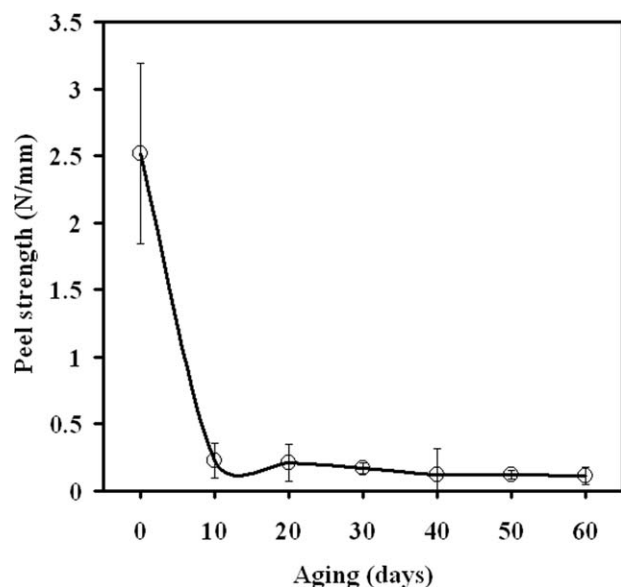


Figure 6 Effect of aging time on peel strength for wood/NR-EPDM melt-laminating layer.

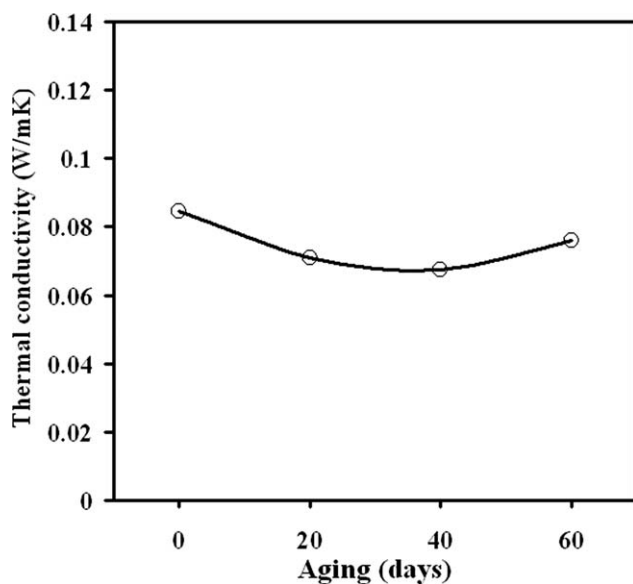


Figure 7 Thermal conductivities for wood/NR-EPDM melt-laminating layer as a function of aging time.

wood/NR-EPDM melt-laminating layer sharply decreased with increasing UV aging time. The significant decrease in peel strength of the aged wood/NR-EPDM melt-laminating layer was mainly caused by two reasons, one being differences in thermal expansions of wood/NR and EPDM layers as clearly evidenced by the results in Figure 4, and the other being changes in molecular structure changes (post-curing and desulfuration reactions) of wood/NR layer as mentioned earlier. If this was the case, the dimensions of wood/NR and EPDM layers would change at different magnitudes,²³ and thus led to delamination and air gap between these two rubber layers. The peel strength results and their explanations were in good agreement with the thermal conductivity results of the wood/NR-EPDM melt-laminating layer as shown in Figure 7. It can be seen that the thermal conductivity of the laminating composite decreased from 0.085 to 0.070 W/m K with increasing aging times up to 40 days, and then tended to increase to 0.080 W/m K at the aging times of 60 days. The decreased thermal conductivity at UV-aging times of 0–40 days probably resulted from the molecular degradation in wood/NR layer together with the delamination of the two rubber layers during UV aging. The former reason could be substantiated by the work of Somatsompop and Wood,²⁴ who stated that, polymers with degraded molecular chains would have lower thermal conductivity than those with longer chain molecules. The delamination of the aged wood/NR-EPDM melt-laminating layer was also the cause of lowering the thermal conductivity of the wood/NR-EPDM laminating layer. The delamination was referred to an existence of air gap between the

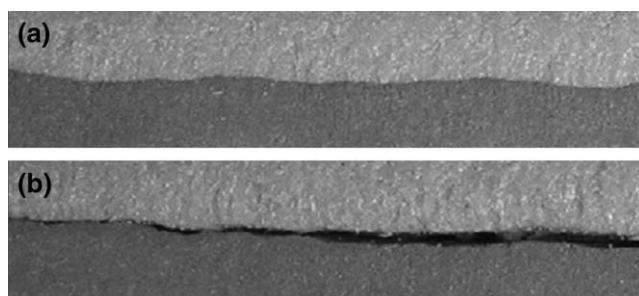


Figure 8 Cross-section of wood/NR-EPDM melt-laminating layer (a) before and (b) after aging.

wood/NR and expanded-EPDM layers and this can be seen in Figure 8. The effect of air gap from delamination process on heat transfer through the laminating composite layers is physically described in Figure 9. It can be seen that with the presence of air gap, the heat would transfer more difficultly from one rubber layer to another (Note: k of air = 0.026 W/m K and K of wood/NR-EPDM melt-laminating layer = 0.070–0.085 W/m K). The increase in thermal conductivity of the laminating composite layers at aging times of 40–60 days could be explained by the post-curing and desulfuration effects in the wood/NR layer. This claim could be verified by the tensile modulus results, which exhibited an increasing trend at the aging times of 40–60 days in Figure 2.

The experimental results in this work clearly suggest that expanded-EPDM could be used as protecting layer, not only for moderation of photo-oxidative degradations of wood/NR layer for roofing application, but also for minimization of dimension changes of the wood/NR-EPDM melt-laminating layer. However, to prevent permanent delaminations of the wood/NR and EPDM layers, some mechanical lamination techniques should be provided upon installations, such as screw-fastening and rivet-pinning techniques.

CONCLUSION

Melt-laminating sheets from wood/NR and expanded-EPDM layers were produced, and their

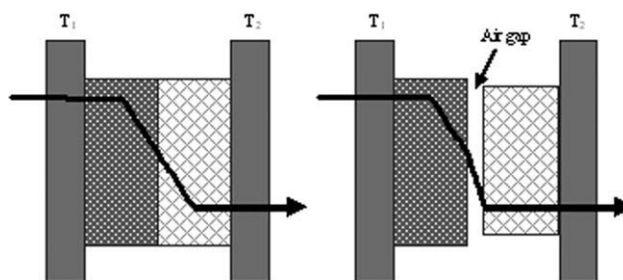


Figure 9 Temperature gradient model with and without delamination in wood/NR-EPDM melt-laminating layer.

tensile properties, sample size change, peel strength, and thermal conductivity were experimentally assessed before and after experiencing UV-aging conditions for a period of 60 days. It was found that under UV aging, the tensile modulus of the wood/NR layer laminated with expanded-EPDM protecting layer was greater than that of the wood/NR single layer, whereas the tensile strength of the melt-laminating layer was lower. The size reduction (shrinkage) of the wood/NR layer after UV-aging was minimized by the use of expanded-EPDM layer as top coating layer. The peel strength of wood/NR-EPDM laminating layers sharply decreased with increasing UV aging time because of layer delaminations, which also resulted in a decrease in thermal conductivity of the laminating composite. The thermal conductivity of the EPDM-wood/NR laminating composite observed in this work ranged from 0.070 to 0.085 W/m K.

References

1. Dos Santos, K. A. M.; Suarez, P. A. Z.; Rubim, J. C. *Polym Degrad Stab* 2005, 90, 34.
2. Vinod, V. S.; Varghese, S.; Kuriakose, B. *Polym Degrad Stab* 2001, 75, 405.
3. Bauer, D. R.; Baldwin, J. M.; Ellwood, K. R. *Polym Degrad Stab* 2006, 92, 110.
4. Somers, A. E.; Bastow, T. J.; Burgar, M. I.; Forsyth, M.; Hill, A. J. *Polym Degrad Stab* 2000, 70, 31.
5. Abad, L. V.; Relleve, L. S.; Aranilla, C. T.; Aliganga, A. K.; San Diego, C. M.; Dela Rosa, A. M. *Polym Degrad Stab* 2002, 76, 275.
6. Ismail, M. N.; Yehia, A. A.; Korium, A. A. *Polym Degrad Stab* 2001, 74, 247.
7. Bhowmick, A. K.; Heslop, J.; White, J. R. *Polym Degrad Stab* 2001, 74, 513.
8. Yamsaengsung, W.; Sombatsompop, N. *Polym Compos* 2009, 30, 248.
9. Yamsaengsung, W.; Sombatsompop, N. *J Macromol Sci Phys* 2008, 47, 967.
10. Yamsaengsung, W.; Sombatsompop, N. *Compos B*, to appear.
11. Sombatsompop, N.; Chaochanchaikul, K. *Polym Int* 2004, 53, 1210.
12. Thongsang, S.; Sombatsompop, N. *Polym Compos* 2006, 27, 30.
13. Yuan, X.; Jayaraman, K.; Bahattacharyya, D. *Compos A* 2004, 35, 1363.
14. Combellas, C.; Richardson, S.; Shanahan, M. E. R.; Thiebault, A. *Int J Adhes Adhes* 2001, 21, 59.
15. Wu, J. W.; Sung, W. F.; Chu, H. S. *Int J Heat Mass Transfer* 1999, 42, 2211.
16. Wang, W.; Qu, B. *Polym Degrad Stab* 2003, 81, 531.
17. Baldwin, J. M.; Bauer, D. R.; Ellwood, K. R. *Polym Degrad Stab* 2007, 92, 103.
18. Zhao, Q.; Li, X.; Gao, J. *Polym Degrad Stab* 2007, 92, 1841.
19. Ha-Anh, T.; Vu-Khanh, T. *Polym Test* 2005, 24, 775.
20. Sombatsompop, N. *Polym Plast Technol Eng* 1998, 37, 333.
21. Roberts, A. D. *Natural Rubber Science and Technology*; Oxford University Press: New York, 1990.
22. Sombatsompop, N.; Lertkamolsin, P. *J Elastom Plast* 2000, 32, 311.
23. Hsu, Y. T.; Chang-Liao, K. S.; Wang, T. K.; Kuo, C. T. *Polym Degrad Stab* 2006, 91, 2357.
24. Sombatsompop, M.; Wood, A. K. *Polym Test* 1997, 16, 203.