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Physical properties of polymer composite: Natural rubber glove waste/polystyrene foam waste/cellulose

Sa-Ad Riyajan\textsuperscript{a,*}, Isara Intharita, Pramuan Tangboriboonrat\textsuperscript{b}

\textsuperscript{a}Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Songkhla 90112, Thailand
\textsuperscript{b}Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand

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\section*{Abstract}

The polymer composite was prepared from the wastes of natural rubber glove (NRG) and polystyrene foam (PSF) blended with cellulose from sugar cane leaves via the laminate method. The NRG and PSF were firstly dispersed in toluene under continuous stirring. Then, maleic anhydride (MA) was added into the mixture. Effects of blend ratio and of MA content (0.5–15%, w/w) on physical properties of the polymer composite were investigated. The toluene resistance of the polymer blend was improved after adding MA and cellulose. The highest toluene resistance was achieved when using 12% cellulose. The chemical reactions of MA with polymer blend and with composite were confirmed by ATR-FTIR. The hardness of the polymer blend and composite increased as a function of PSF. In addition, their impact strength increased with increasing NRG and cellulose contents.

\section*{1. Introduction}

At present, the demand of natural rubber glove (NRG) exponentially increases due to the health awareness. After its use, NRG is generally left as garbage which is difficult to biodegrade since polyisoprene chains of NR are crosslinked either by sulphur (Riyajan et al., 2003; Hall et al., 2009) or peroxide system. The problem of NRG waste disposal is, therefore, growing as a direct result of rapid industrialization and population growth. Especially, the infectious waste from hospital and other toxic hazardous waste might cause serious environmental problem and great health risk to public. For example, the diseases like diarrhea, leptospirosis, typhoid and cholera can be transmitted through the mismanagement of waste. Moreover, the public increasingly concerns over the handling of medical waste because of the recent acquired immune deficiency syndrome (AIDS) dilemma, severe acute respiratory syndrome (SARS) epidemic, Avian influenza and those posed by other communicable diseases such as hepatitis B.

Susceptibility of NR products towards a microbial attack is a well known phenomenon (Hall et al., 2009). The environment authority agency such as The World Health Organization (WHO) recommends the landfilling or incineration (Johannessen et al., 2000) and pyrolysis process (Dong et al., 2001; Conrardy et al., 2010) to reduce the PS waste (Hall et al., 2009). The pyrolysis of the rubber waste by using Y-zeolite as catalyst gave mainly of limonene and oligomers of polyisoprene. The presence of the Y-zeolite catalyst in the pyrolysis of rubber caused an increase in the yield of hydrocarbon gases similar to the degradation of polystyrene (PS) (Berekaa et al., 2000). The destruction of NRG waste by molten salt oxidation produced CO\textsubscript{2}, N\textsubscript{2} and water (Hsu et al., 2000). In this case, the chemical composition of the degraded glove, analyzed by thermogravimetric analysis (TGA) under N\textsubscript{2}, played a fundamental role in pyrolytic behavior.

In parallel, the NRG waste can be reused in several applications such as mat and large tire as well as most of the constituent parts of both passenger and truck tire (Rajan et al., 2006). In addition, the rubber waste was blended with virgin synthetic rubber and NR to improve the polymer processing. However, the blend of NRG waste with polystyrene foam (PSF) waste was not found in literature. The reports concerned only about the use of PSF waste in polymeric flocculants (Wieslaw et al., 2005), ion adsorption (Long et al., 2010), polymer mortar panels and electrolyte (Bhutta et al., 2011). The polymeric flocculant, i.e., poly(styrene sulphonate) acid, was obtained from PSF waste and virgin PS during the sulphonation process using H\textsubscript{2}SO\textsubscript{4} as sulphonating agent and Ag\textsubscript{2}SO\textsubscript{4} as catalyst. The effectiveness of the flocculation depended on the number of sulphonic groups per monomer unit and its molecular weight. In addition, PSF waste blended with poly(methyl methacrylate) and reinforced with steel fiber was applied in polymer mortar panels (PMPs) (Bhutta et al., 2011). Due to their high ductile and load-bearing capacity, PMPs could...
replace a commercial polymer-impregnated mortar panel in practical applications.

In this present work, the NRG waste was blended with PSF waste by using maleic anhydride (MA) as a crosslinker. As reported in the previous work concerning NR/butadiene (BR)/ethylene propylene diene monomer (EPDM) blend, it was expected that the addition of MA would improve the properties of NRG/PSF blend (Zhang et al., 2010). The NRG waste was masticated by a two-roll mill and dispersed in toluene. The NRG dispersion was mixed with PSF and MA dissolved in toluene under continuous stirring. After drying at ambient temperature, the NRG/PSF blend was laminated with cellulose from sugar cane leaves by using a compression molding. Effects of polymer blend ratio, MA and cellulose contents on the properties, i.e., tensile strength, hardness and tear strength, of polymer composite were investigated. Their chemical structure and morphology were studied by using attenuated total reflection-Fourier transform infrared spectrophotometer (ATR-FTIR) and scanning electron microscope (SEM), respectively. Toluene resistance of the polymer composite was also determined.

2. Experimental

2.1. Materials

PSF waste was received from a local company in Songkhla province, Thailand. Poly(vinyl alcohol), MA and benzoyl peroxide (BPO) were purchased from Sonal Company (Songkhla, Thailand), Fluka (Schnelldorf, Germany) and Merck Schuchardt OHG (Seelze, Germany), respectively. Hydrogen peroxide and perchloric acid were purchased from Solvay Peroxythai Ltd. (Bangkok, Thailand and Guangdong, China) while sodium hydroxide was supplied from Lab Scan Analytical Science (Bangkok, Thailand).

In the preparation of cellulose fiber, sugar cane leaves were immersed in 10% NaOH solution for 24 h and then washed with water until reaching neutral pH. The wet cellulose was cast on a glass plate and dried at ambient temperature for 3 days and, subsequently, at 50 °C for 24 h. The diameter of dried cellulose fiber was determined under an optical microscopy (OM; Primo Star Company, Carl Zeiss).

2.2. Preparation of polymer composite

NRG waste from Sri Trang Company (Songkhla, Thailand) was masticated by using two-roll mill (Charoenchaikarnchange; Bangkok, Thailand) at 30–32 °C for 30 min. The masticated NRG was immersed in toluene for 2 days at ambient temperature and then stirred for 5 h. After stirring with a mechanical stirrer for 1 h, the size and size distribution of the NRG suspended in toluene were measured by a Laser Particle Size Analyzer (LPSA; Beckman Coulter LS 230).

The NRG suspension with various contents was blended with 10% (w/v) of PSF in toluene at room temperature by using a homogenizer (PL Trading International Co. Ltd.; Bangkok, Thailand). 0.5% BPO, 5% glycerol and different MA concentrations were added into the blend under stirring. In order to form a sheet of 0.45 mm in thickness, the mixture was poured into a glass plate (10 cm × 10 cm × 0.5 cm) at ambient temperature. The cellulose sheet was placed between two NRG/PSF sheets. After heating at 80 °C for 6 h, the dried polymer composite was compressed by compression molding (Charoenchaikarnchange; Bangkok, Thailand) at 150 °C for 10 h and was kept at ambient temperature overnight. Under a hot-press, the sample was preheated at 150 °C for 6 min and then compressed for 4 min before being cooled under 3 MPa at 30 °C for 4 min.

2.3. Characterizations and testing of polymer composite

The chemical structure of polymer composite was investigated by using ATR-FTIR (Equinox 55; Bruker) with 100 scans. Its gel content was determined by immersing a known weight of specimen (2.5 cm × 2.5 cm × 0.5 mm) in toluene at 32 °C for 5 days. The sample was then dried at 50 °C for 24 h and weighed until a constant weight was obtained. The degree of gel content was calculated from Eq. (1):

\[ \text{Gel content} = \frac{W_2 - W_1}{W_1} \]  

where \( W_1 \) is the original weight of the sample and \( W_2 \) is the weight of dried residual sample.

SEM (JMS-5800 LV, JEOL) was used for study of the morphology of cross-sectional sample at an accelerating voltage of 6 kV. After fracturing a specimen under liquid N2, its cross-sectional area was coated with platinum under a 12 Pa vacuum. The storage modulus and tan δ of the polymer composite were examined by dynamic mechanical thermal analysis (DMTA V) in tension mode at 10 Hz, 0.05% strain and different temperatures. The physical testing of polymer composite was analyzed by universal testing machine (LR10K, Lloyd Instruments) based on ASTM D 412 at 500 mm/min using 5 dumbbell test pieces. Its hardness was measured according to ASTM D 2240 while an Impacts-15 resilience test pendulum impact tester (Yasdus, No. 258-D) was applied for determination of impact resistance at 25–28 °C.

3. Results and discussion

3.1. Analysis of polymer composite

Before mixing the masticated NRG dispersed in toluene with PSF waste solution and MA, the size and size distribution of NRG suspension were measured by a particle size analyzer and the data are shown in Fig. 1. Fig. 1(a) shows the relationship between %cumulative particle and particle size while Fig. 1(b) represents the relationship between %volume and particle size.

Result indicated that 90% cumulative particle size of the dispersed NRG in toluene was less than 1000 μm (Fig. 5(a)). In addition, the median particle size of the dispersed NRG was about 500 μm as shown in Fig. 5(b).

ATR-FTIR was then used for analysis of the chemical structures of the 50/50 NRG/PSF blend in the presence of 10% MA and of the NRG/PSF blended with 10% MA and 5% cellulose or polymer composite. Fig. 2 shows the spectra of NRG/PSF blended with 10% MA (a) before and (b) after immersion in toluene and those of polymer composite having 50/50 NRG/PSF blended with 10% MA and 5% cellulose (c) before and (d) after immersion in toluene.

The characteristic peaks at 3025 cm\(^{-1}\) (C–H aromatic), 1610 cm\(^{-1}\) (C–C aromatic), 2920 and 2849 cm\(^{-1}\) (CH\(_2\)CH\(_2\)), 1490 and 1450 cm\(^{-1}\) (C=H\(_2\)), 905 and 697 cm\(^{-1}\) (C–H aromatic) of PS appeared in Fig. 2(a)–(d). The bands at 1076 and 1664 cm\(^{-1}\) attributed, respectively, to the symmetric C–S–C stretching vibrations and C=C of NRG were also noticed. The grafted MA and tear strength, of polymer composite were investigated. Their chemical structure and morphology were studied by using attenuated total reflection-Fourier transform infrared spectrophotometer (ATR-FTIR) and scanning electron microscope (SEM), respectively. Toluene resistance of the polymer composite was also determined.
addition, the increase of bands at 1745 and 1270 cm$^{-1}$ due to ester C=O and C–O–C of cellulose in polymer composite was detected. The peaks at 821, 896, 1046, 1382 and 2926 corresponding to the out of plane deformation of COOH, C–H deformation, C–O–C from β-1,4-glycosidic, OH bending and C–H stretching, respectively, also appeared.

3.2. Gel content

The influence of NRG/PSF ratio on the gel content of the polymer blend containing 10% MA without cellulose is presented in Fig. 3(a).

Results showed that the gel content of polymer blend having NRG/PSF of 30/70 was similar to that of 50/50 which was greatly lower than that of 70/30. It was believed that the high NRG content whose molecules were still partially crosslinked with sulphur was responsible for the high gel content. As expected, the gel contents of all NRG/PSF blends strongly increased by adding cellulose fiber as shown in Fig. 3(b). The gel contents of polymer composites containing 3, 5 and 12% were 58, 60 and 63%, respectively. It was possibly caused from the adsorption of macromolecular chains at the filler/matrix interface, filler/filler interactions and the chemical reaction between MA and polymer matrix as previously reported in the case of NR filled with cellulose (Bendahou et al., 2010).

The optical micrographs of PSF blended with 5% cellulose and various amounts of MA (0, 5, 10 and 15%) after immersion in toluene are displayed in Fig. 4.

The good dimensional stability of PSF/cellulose added with MA especially of 15% was observed in Fig. 4(d). This result indicated the occurrence of chemical interaction between PSF and MA or between cellulose and MA during blending process.

3.3. SEM morphology

The morphology affecting the physical properties of polymer composite was investigated. SEM micrographs in Fig. 5 show PSF blended with 5% cellulose in the presence of (a) 0, (b) 5, (c) 10, (d) 15% (w/w) of MA and those of polymer composite containing 50/50 NRG/PSF, 5% cellulose and (e) 0, (f) 10% (w/w) of MA.

In Fig. 5(a), it seemed that the polar cellulose fibers were hard to disperse in non-polar PSF and NRG/PSF matrix due to the difference in the surface energy of each component (Zhang et al., 2008). The strong adhesion between PSF and cellulose was observed after
addition of MA in Fig. 5(b)–(d). The effect of MA content at 5, 10 and 15% (w/w) on adhesion property of the polymer composite was presented in Fig. 5(b), (c) and (d), respectively. When adding 5% (w/w) in polymer composite (Fig. 5(b)), the poor adhesion between cellulose and polymer matrix was observed. But when MA increased from 5 to 10 or 15% (w/w) (Fig. 5(c) and (d)), the strong adhesion bonding between the polymer matrix and the cellulose fiber appeared due to more occurrences in chemical reaction between polymer matrix and hydroxyl group from cellulose which may reduce the damage of fracture. This result suggested that the adhesion between the matrix and cellulose fiber was very good. Accordingly, the interfacial strength was improved when MA was over 5% (w/w).

A large number of voids were observed on the fracture surface of all PSF samples. When NRG was added in PSF/cellulose in the absence of MA in Fig. 5(e), the voids were also noticed due to poor interface interaction. After adding MA, the strong adhesion or chemical bond between cellulose fiber and polymer matrix occurred in Fig. 5(f) which would affect the mechanical strength of the polymer composite.

3.4. Mechanical strength

Fig. 6(a)–(d) shows the effects of cellulose contents (0, 3, 5 and 12%) on tensile strength of the polymer composites having NRG/PSF of 0/100, 30/70, 50/50 and 70/30.

It was observed that the tensile strength of PSF was 2 MPa and that of polymer blend without cellulose in Fig. 6(a) decreased from 3.4, 1.4 to 0.7 MPa when NRG/PSF were 30/70, 50/50 and 70/30, respectively. After addition of 3, 5 and 12% cellulose in the 30/70 NRG/PSF, the tensile strength of the polymer composites in Fig. 6(b)–(d) increased from 5.2, 5.8 to 6.2 MPa, respectively. The results agreed well with those of NR filled cellulose previously reported (Bras, 2010). The drop in the tensile properties of the polymer composites when increasing NRG content was reasonably due to poor interaction between cellulose and the NRG/PSF matrix. Moreover, the poor dispersion and/or agglomeration of the filler in the matrix led to the in-homogeneity of phase morphology which became the dominant process in the mixing. This effect was more pronounced with increasing filler content.

At low cellulose content of 3% (w/w), the polymer composite exhibited an elastic non-linear behavior which is typical for amorphous polymer at temperature greater than glass transition temperature ($T_g$). At high filler content of 12%, the mechanical behavior of NRG/PSF waste was high because a considerable amount of fibers allowed the transfer of the applied load between them. The higher compatibility between cellulose fiber and the hydrophobic polymer matrix by adding MA which ensued higher filler/matrix adhesion was also responsible for this difference (Bendahou et al., 2010).

The effect of MA content on the hardness of polymer composite containing 50/50 NRG/PSF and 5% cellulose is shown in Fig. 7.

The presence of 5% MA significantly increased the hardness of the polymer composites from 46 to 65 shore A. With 10 and 15% of MA, the hardness values were constant, i.e., 64 and 62 shore A, respectively. The change in hardness was possibly caused from the chemical reaction between MA and NRG/PSF matrix which efficiently facilitated energy transfer process and, hence, toughened the composite (Chong et al., 2010). The influence of the both cellulose and polymer blend ratio on the hardness of the polymer blend is presented in Fig. 8(I).

Results showed that the hardness of the polymer composites decreased from 54 to 62 shore A when varying NRG/PSF from 30/70 to 50/50. Further increase in NRG content, the hardness of the polymer composites having 50/50 and 70/30 NRG/PSF were constant.
Fig. 5. SEM micrographs of PSF blended with 5% cellulose in the presence of (a) 0, (b) 5, (c) 10, (d) 15% (w/w) of MA and those of polymer composite containing 50/50 NRG/PSF, 5% cellulose and (e) 0, (f) 10% (w/w) of MA.

Fig. 6. Effect of cellulose contents of (a) 0, (b) 3, (c) 5 and (d) 12% (w/w) on tensile strength of PSF and polymer composite containing NRG/PSF of 0/100, 30/70, 50/50 and 70/30.

Fig. 7. Hardness of 50/50 NRG/PSF blended with different MA contents.
Fig. 8. (I) Effects of cellulose contents of (a) 0, (b) 3, (c) 5 and (d) 12% on hardness of polymer composite containing 50/50 NRG/PSF and (II) effects of cellulose contents on impact strength of polymer composites having NRG/PSF of (a) 30/70, (b) 50/50 and (c) 70/30.

This was due to the fact that the cellulose fiber sheet was in the center of specimen. It was confirmed by the insignificantly change of hardness of the polymer composites when changing the cellulose contents.

The data of impact strength of the polymer composites containing 30/70, 50/50 and 70/30 NRG/PSF plotted with cellulose contents are presented in Fig. 8(II).

The increase in impact strength when increasing the amount of NRG was explained from the ductile fracture initiated by the shear yielding mechanism (Mathew and Thomas, 2001). Due to the low $T_g$ of NR (−78 °C), the NRG chains easily moved at room temperature and played the role of toughening agent. The dual phase continuity and phase interpenetration might also enhance the impact resistance. It was reported that the co-continuous interpenetrating polymer network (IPN) structure exhibited high impact strength of polymer composite because the uniform rubbery phase allowed the energy to be dissipated into the whole sample (Mathew et al., 2001). This effective dissipation of energy was the principal role of rubbery phase in impact resistant materials.

The effect of cellulose content on the impact strength of the polymer composites was also displayed in Fig. 8(II). At 50/50 NRG/PSF, the impact strength values of the polymer composites with 0, 3, 5 and 12% cellulose were 7, 12, 21 and 23.5 J/m², respectively. The reinforcement might be because a polymer chain could interact with several units of the fibers. If this chain breaks due to the impact energy, the load is transferred to many other chains providing the increase in impact strength of the material (Megiatto et al., 2010).

4. Conclusions

The polymer composite was developed from the blend of NRG and PSF wastes with addition of MA and cellulose from sugar cane leaves. Their mechanical properties were better than those of PSF due to the chemical reaction between PSF/cellulose and MA which were confirmed by gel content and ATR-FTIR. The highest tensile strength of sample was found in 30/70 NRG/PSF blended with 10% MA and 12% cellulose. This observation was supported by SEM, toluene resistance, impact strength and hardness. The polymer composite would potentially be used in artificial wood, artificial bone, pot and picture frame.

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References

Berekaa, M.M., Linos, A., Reichelt, R., Keller, U., Steinbüchel, A., 2000. Effect of pre-treatment of rubber material on its biodegradability by various rubber degrading bacteria FEMS. Microbiol. Lett. 184, 199–206.

Bendahou, A., Kaddami, H., Alain Dufresne, A., 2010. Investigation on the effect of cellulosic nanoparticles’ morphology on the properties of natural rubber based nanocomposites. Eur. Polym. J. 46, 609–620.

Bhutta, M.A.R., Ohama, Y., Tsuruta, K., 2011. Strength properties of polymer mortar panels using methyl methacrylate solution of waste expanded polystyrene as binder. Constr. Build. Mater. 25, 779–784.

Bras, J., Hassan, M.L., Bruzesse, C., Hassan, E.A., El-Wakil, N.A., Dufresne, A., 2010. Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. Indus. Crops Prod. 32 (3), 627–633.

Chong, E.I, Ahmad, I., Dahlan, H.M., Abdullah, I., 2010. Reinforcement of natural rubber/high density polyethylene blends with electron beam irradiated liquid natural rubber-coated rice husk. Radiat. Phys. Chem. 79, 906–911.

Conrardy, J., Hillanbrand, M., Myers, S., Nussbaum, G.F., 2010. Reducing medical waste. AORN 91, 711–721.

Dong, D., Tasaka, S., Inagaki, N., 2001. Thermal degradation of monodisperse polystyrene in bean oil. Polym. Degrad. Stabil. 72, 345–351.

Hall, W.J., Zakaria, N., Williams, P.T., 2009. Pyrolysis of latex gloves in the presence of Y-zeolite. Waste Manage. 29, 797–803.

Hsu, P.C., Foster, K.G., Ford, T.D., Wallman, P.H., Watkins, B.E., Pruneda, C.O., Adamsen, M.G., 2000. Treatment of solid waste with molten salt oxidation. Waste Manag. 20, 363–368.

Johannessen, L.M., Dijkstra, M., Bartone, C., Hanrahan, D., Boyer, M.G., Chandra, C., 2000. Health Care Waste Management Guidance Note. The International Bank for Reconstruction and Development/The World Bank, NW Washington.
Long, C., Li, Q., Li, Y., Liu, Y., Li, A., Zhang, Q., 2010. Adsorption characteristics of benzene–chlorobenzene vapor on hypercrosslinked polystyrene adsorbent and a pilot-scale application study. Chem. Eng. J. 160, 723–772.

Mathew, A.P., Packirisamy, S., Thomas, S., 2001a. Studies on the thermal stability of natural rubber/polystyrene interpenetrating polymer networks: thermogravimetric analysis. Polym. Degrad. Stabil. 72, 423–439.

Mathew, A.P., Packirisamy, S., Radusch, H.J., Thomas, S., 2001b. Effect of initiating system, blend ratio and crosslink density on the mechanical properties and failure topography of nano-structured full-interpenetrating polymer networks from natural rubber and polystyrene. Eur. Polym. J. 37, 1921–1934.

Mathew, A.P., Thomas, S., 2001. Izod impact behavior of natural rubber/polystyrene interpenetrating polymer networks. Mater. Lett. 5, 154–163.

Megiatto Jr., Jackson, D., Ramires, E.C., Frollini, E., 2010. Phenolic matrices and sisal fibers modified with hydroxy terminated. Polybutadiene rubber: impact strength, water absorption, and morphological aspects of thermosets and composites. Indus. Crops Prod. 31, 178–184.

Rajan, V.V., Dierkes, W.K., Joseph, R., Noordermeer, J.W.M., 2006. Science and technology of rubber reclamation with special attention to NR-based waste latex products. Prog. Polym. Sci. 31, 811–834.

Riyajan, S., Sakdapipanich, J.T., Yasuyuki, T., 2003. Controlled degradation of cured natural rubber by encapsulated benzophenone as a photosensitizer. J. Appl. Polym. Sci. 90, 207–205.

Wiesław, W., Agnieszka, S., Barbara, W., Wioletta, S., Bajdur, M., Sułkowska, A., 2005. Preparation and properties of flocculants derived from polystyrene waste. Pyrolysis of representative medical waste. Polym. Degrad. Stabil. 90, 272–280.

Zhang, H., Datta, R.N., Talma, A.G., Noordermeer, J.W.M., 2010. Maleic-anhydride grafted EPM as compatibilising agent in NR/BR/EPDM blends. Eur. Polym. J. 46, 754–766.

Zhang, W., Zhang, X., Liang, M., Lu, C., 2008. Mechanochemical preparation of surface-acetylated cellulose powder to enhance mechanical properties of cellulose-filler-reinforced NR vulcanizates. Compos. Sci. Technol. 68, 2479–2484.