STUDY ON RHEOLOGICAL AND THERMAL PROPERTIES OF TREATED WASTE NATURAL RUBBER LATEX/POLYSTYRENE BLEND AS REDUCTANT

Orathai Boondamnoen[1], Rashid Azura[1], Masahiro Ohshima[2], Saowaroj Chuayjuljit[3], and Azlan Ariffin[1]*

[1] School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia

[2] Department of Chemical Engineering, Kyoto University, Kyoto, Japan

[3] Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok Thailand, e-mail: azlan@eng.usm.my*

Abstract

The waste natural rubber latex (WNRL) was treated by natural rubber latex (NRL) to improve the properties. The treatment was done prior to blending with polystyrene (PS). The preparation of treated waste natural rubber latex (TWNRL)/PS was conducted with ratio of 70/30 using internal Haake mixer at 140ºC with speed of 60 rpm. The WNRL/PS blend was prepared in a similar way for comparison purpose. The mixing torque was recorded during blending, while storage modulus and tan_delta were investigated using Rheometer. The thermal gravimetry (TG) and difference scanning calorimeter (DSC) were also studied. The results showed that TWNRL/PS blend gave lower mixing torque compared to WNRL/PS blend. Thus, it reveals that the treatment of WNRNL by NRL could improve the processibility. The storage modulus of TWNRL/PS blend showed lower value compared to WNRL/PS blend. This could be due to that the TWNRL/PS blend contains lower cross-linked molecules which have lower resistance to chains mobility. A study using DSC implied that TWNRL and PS are immiscible (two-phase system). This can be proven by the presence of two glass transition. In comparison, the T_g from DSC and tan_delta observed for TWNRL/PS and WNRL/PS blends showed no significant difference. However, the degradation temperature of TWNL/PS blend was slightly lower than that of WNRL/PS blend due to the requirement of energy for breaking the network molecule was lower.

Keywords: Blend, Recycled natural rubber latex, Rheology, Thermal analysis, Treated waste natural rubber latex

Introduction

In recent years, the recycled materials are growing in popularity due to the awareness of environment and economical issue. Waste natural rubber latex (WNRL) has a potential being reused because it contains high quality rubber hydrocarbon chains with lightly cross-linked molecules [1, 2]. Several reports have been done, Mathew [1] applied WNRL in epoxidised natural rubber compound, and the overall results showed the acceptable of using the WNRL as efficient economic filler. Another work reported that WNRL from textile cot industry showed the improved of impact properties of waste polypropylene (WPP) with acceptable result compared to virgin polypropylene (VPP) [3]. Due to the above reasons added with high strength and low cost of PS, it is beneficial to recycle WNRL by blending it with polystyrene (PS) for the present study. However, the processibility and thermal properties are important for polymer melt blending [4-7]. Hence, the aim of this work is to study the processibility, rheological and thermal properties of

WNRL/PS blend through treatment with NRL. The WNRL was treated with NRL prior to blending with PS. The NRL may break some cross-links in WNRL network, then more entanglement with PS which leads to the enhancing of adhesion between phases. This is similar with what has been reported by Zhang in his research, the presence of bitumen in waste rubber tyre/polypropylene (WRT/PP) blend increases the elongation due to the bitumen reduces the cross-links of WRT. It resulted as a good adhesion between WRT and PP phases. This study focuses on the composition of 70/30 TWNRL/PS blend due to our previous work [8] which showed drastic improvement of elongation and morphology at this composition with comparable strength to the untreated blend. Moreover, it is also because the purpose of recycling of WNRL, Hence, WNRL was used at high proposition. The mixing torque, storage modulus, differential scanning calorimetric (DSC) and thermogravimetry analysis (TGA) of 70/30 of TWNRL/PS blend were studied and compared with the untreated blend.

Experiment

Materials

The waste natural rubber latex (WNRL) was collected from a latex laboratory at School of Material and Mineral Resources Engineering, USM, Malaysia. Natural Rubber Latex (NRL) was obtained from ZRM Scientific & Supplies (Malaysia) Sdn. Bhd and the Polystyrene (PS) used was supplied by Total Petrochemical.

Treatment of Waste Natural Rubber Latex

The WNRL was treated with 20% by dry weight of NRL. It was heated up in the water bath at 50ºC and stirred using a mechanical stirrer for 5 minutes with speed of 300 rpm. After that, the NRL was added in WNRL and continued to be stirred for another 20 minutes. The treated waste natural rubber latex (TWNRL) was taken out from the water bath and kept in room temperature for a day before further process.

Preparing Sheet

The TWNRL was casted on a glass plate and dried at ambient temperature for 3 days. Then, it was hung for further drying. The TWNRL sheet was milled by a two-roll mill and cut into small pieces before blending them with PS. WNRL sheet was prepared in the similar way.

Preparation of Blending

The blend was conducted with the ratio of 70/30 of TWNRL/PS using Haake internal mixer at 140ºC. Firstly, PS was preheated in the hot chamber for 1 min and then was shear rotated for melting at a speed of 60 rpm for another 2 min. The TWNRL was then inserted and the mixing was continued for another 8 min. The blend was taken out and left at room temperature before molding. The WNRL/PS blend was conducted in the similar way. All blends were preheated for 6 min and compressed for 4 min at temperature of 140ºC. After that, the compressed sheets were cooled down under pressure for 3 min at room temperature. The samples were cut from the sheet before further test.

Characterization

All blends were prepared using the Haake internal mixer. The mixing was done at 140ºC with rotation speed of 60 rpm. The torque was recorded and plotted for each blending.

The rheological properties were performed using the rheomerter (ARES), the experiments were carried out using a rectangular type torsion testing with 40 mm length. The temperature scanned was from 35ºC to 150ºC for observing the dynamic mechanical properties from room temperature to higher temperature.

Thermal behavior was studied using Perkin Elmer DSC 8500. All samples were placed in aluminuim pans. The samples were studied from -70ºC to 200ºC with a heating rate of 10ºC/min under dry N_2 gas atmosphere for investigating the glass transition temperature (T_g) of the blends.

Thermal stability was studied using DTG-60H, Simultaneous DTA-TG Apparatus (Shimadzu). The sample of 10 mg was put in the aluminum pans and heated from 30 to 600ºC with a heating rate of 10ºC/min.

Results and Discussion

Rheological Properties

Figure 1 shows the plastogram of mixing of TWNRL/PS and WNRL/PS blends. Initially, PS was put in the hot chamber for 1 min preheating, then it was shear rotated. The torque was suddenly raised due to the incomplete melt of PS which resisted the rotation. After that, the shear rotation and temperature brought PS to be completely melted, so it resulted in the decrease of torque again at 3 min. However, the torque raised sharply after the TWNRL or WNRL was added into the chamber due to the unmelt TWNRL or WNRL. When the TWNRL or WNRL became soft and broke into small particles, the torque decreased gradually until it stabilized. It was also found that TWNRL/PS blend showed lower torque compared to WNRL/PS blend at all mixing time. This may be due to that the WNRL contains higher cross-linked molecules. The cross-linked molecule enhances the viscosity of mixing system and leads to higher resistance [9-11]. Similar observation was also reported that the rubber/poly(ethylene terephthalate) (PET) blend with cross-linking agent show higher torque compared to the uncross-linked blend [12]. This can be proved by storage modulus as shown in Figure 2. It implies that the treatment of WNRL by NRL could improve the processibility.
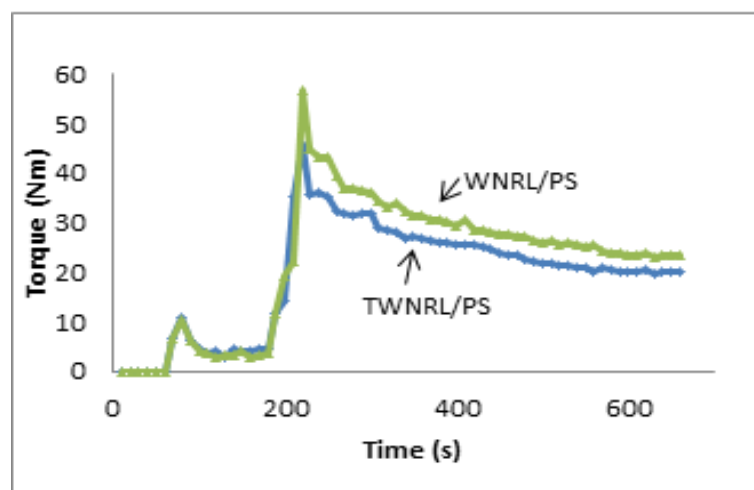

Figure 1. Torque development of WNRL/PS and TWNRL/PS blends

Figure 2 (a) shows Log storage modulus (Log G') at various temperatures of WNRL/PS and TWNRL/PS blends. It can be seen that the Log G' of both blends gradually decreased when the temperature increased until it drastically dropped around 100ºC and continuing

to decrease at molten state. This usually occurs due to the easier move of the molecules when they gain more energy from the heat. At molten state, the molecule chains can move freely, but the sample with high cross-linked molecules or entanglement shows high Log G' due to the molecule chains were tight together [13]. As a result, the WNRL/PS gave higher Log G' compared to TWNRL/PS at any temperature. Hence, it could be said that the WNRL/PS blend contained higher cross-linked molecule compared to TWNRL/PS blend. It was conjectured that the crosslinks was reduced through breaking sulfur linkages during treatment process which illustrated in Figure 3. Figure 2 (b) shows Log tan_delta at various temperatures from 30ºC to 200ºC. It shows that the T_g which corresponded to PS, the TWNRL/PS and WNRL/PS blends showed the similar glass transition temperature (T_g) even though the TWNRL was treated by NRL. It may be due to the original material of WNRL, TWNRL and NRL are similar, thus T_g were not significantly different. Moreover, it seems that lower amount of NRL could not affect the T_g.
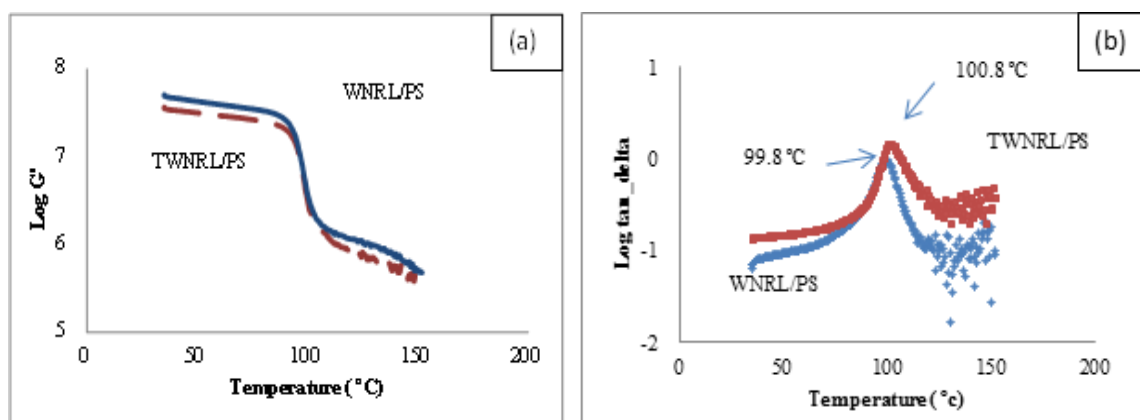

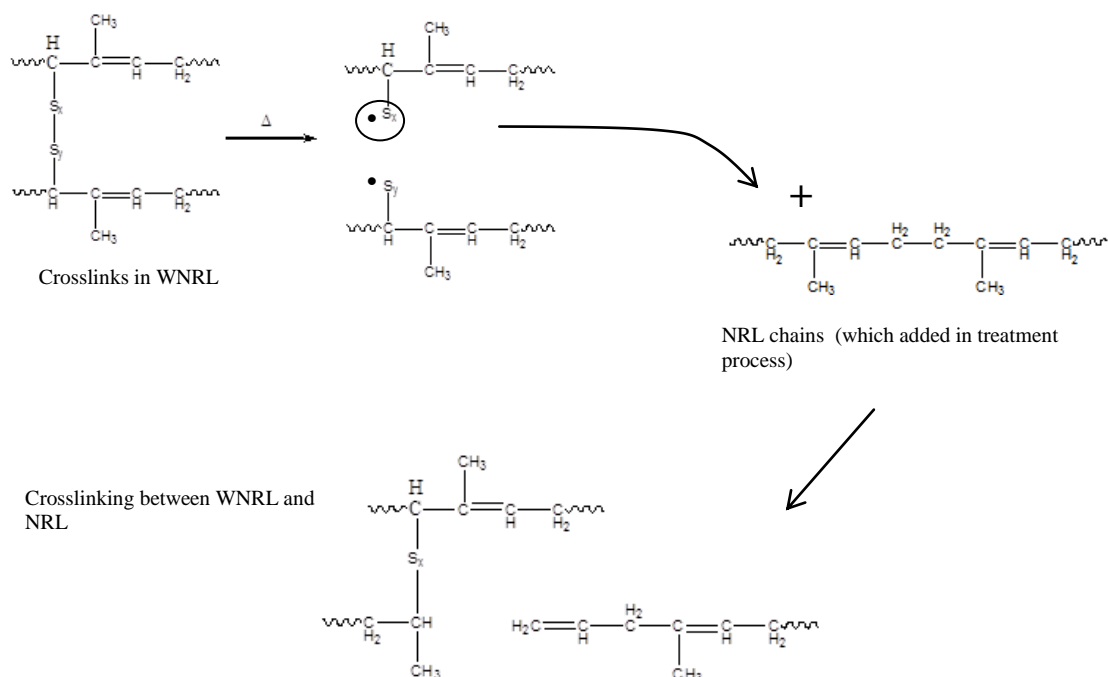Figure 2. (a) storage modulus and (b) tan_delta of WNRL/PS and TWNRL/PS blends.

Figure 3. Possible interaction between WNRL and NRL molecules
(adapted from [14, 15])

Thermal Properties

The thermal behaviors of WNRL/PS and TWNRL/PS blends were analyzed by DSC. Fig. 4 shows the glass transition temperature (T_g) where it was calculated as the half-height of the corresponding heat capacity. The T_g of pristine WNRL and pristine PS were -62.27 and 84.32ºC, respectively. Figure 4 (c) showed that the first peak was corresponding to T_g of rubber and the second peak was corresponding to T_g of PS. It can be clearly seen that all blends showed two T_g peaks. The peaks of WNRL/PS blend were showed at -61.87 and +99.87ºC and the peaks of TWNRL/PS blend were showed at -62.23 and +100.2ºC. It reveals that the rubber and PS in both of these blends are immiscible [13-15]. The T_g of PS which was examined using DSC and tan_delta were not significantly different. Furthermore, the T_g of the blends were shifted from the virgin material, which may be due to the interaction between boundaries of each particle of the components [16-18].
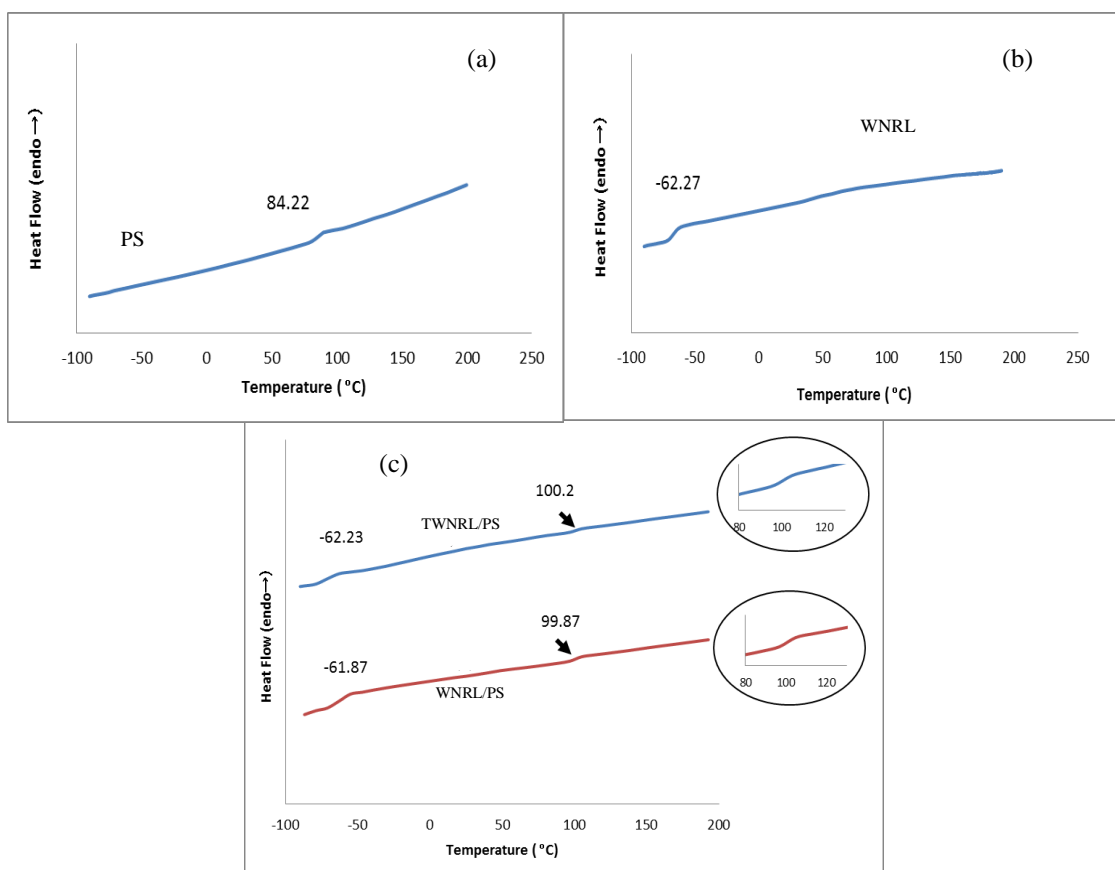

Figure 4. DSC curves of (a) PS, (b) WNRL and (c) blends.

Figure 5 shows TG and DTG curves of the blends. All the DTG curves showed two peaks which corresponded to each component. There were a major and a minor corresponding of rubber degradation (first peak) and PS degradation (second peak), respectively [5]. The major and minor peaks were also related to the quantities of rubber (70%) and PS (30%). It shows that the second peak of WNRL/PS and TWNRL/PS were not significantly different. Whereas, the TWNRL/PS gave lower temperature of rubber degradation (first peak) and the degradation temperature of blend at any percentage weight loss compared to WNRL/PS blend. It may due to the lower requirement of energy to break the cross-links in the network molecule [19]. Thus, larger difference was observed at low percentage weight loss (5% weight loss).
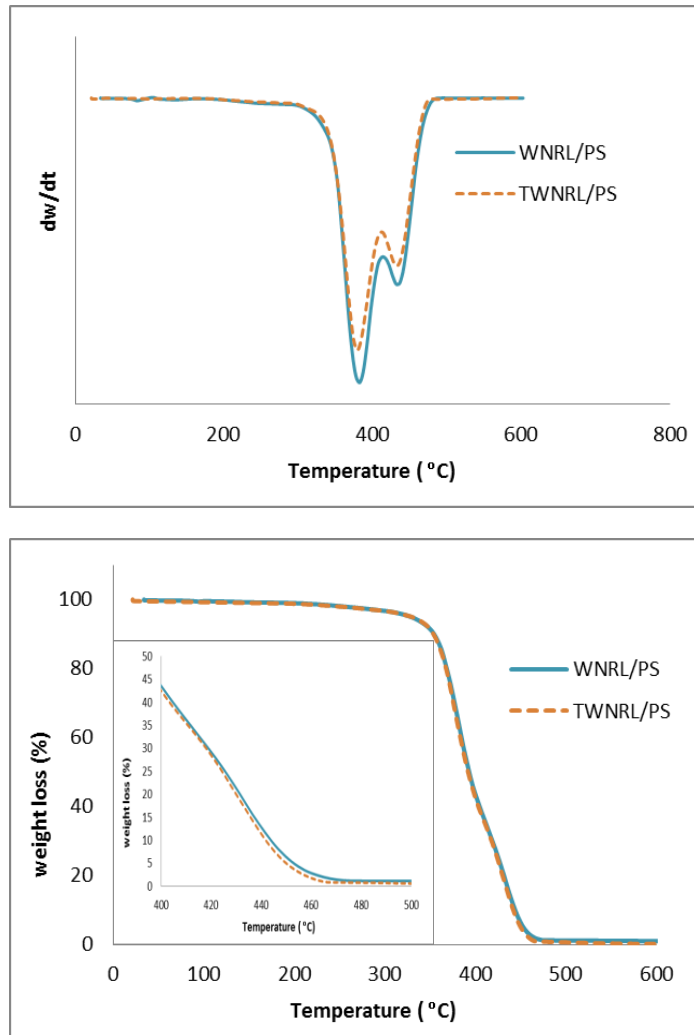
Figure 5. TG and DTG curves of (a) WNRL/PS and (b) TWNRL/PS blends Torque development of WNRL/PS and TWNRL/PS blends

Table 1. Degradation Temperature of WNRL/PS and TWNRL/PS Blends

Blends	DTG		Temperature at Weight Loss (º C)				
	1st Peak	2nd Peak	5% Wt Loss	25% Wt Loss	50% Wt Loss	75% Wt Loss	90% Wt Loss
WNRL/PS	382.42	433.37	335.17	373.04	393.33	425.58	444.10
TWNRL/PS	379.22	433.56	329.33	371.95	392.13	424.37	442.00

Conclusions

The treatment of WNRL by NRL could improve the processibility. A study using DSC implied that TWNRL and PS were incompatible. This is proven from the presence of two T_g. The T_g of TWNRL/PS and WNRL/PS blends which were observed from DSC and tan_delta were not significantly different. However, the degradation temperature at any percentage weight loss of TWNRL/PS blend showed slightly lower temperature. It may due to the lower requirement of energy to break the cross-links in the network molecule compared to WNRL/PS blend. The storage modulus of blend reveals that the TWNRL/PS

blend contains lower cross-linked molecules and agrees with the mixing torque during blending.

Acknowledgement

References

[1] G. Mathew, R.P. Singh, N.R. Nair, and S. Thomas, "Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber," *Polymer*, Vol. 42, No. 5, pp. 2137-2165, 2001.

[2] S. Rajalekshmi, and R. Joseph, "Studies on the rheology and the mechanical properties of thermoplastic elastomer from latex product waste and high density polyethylene," *Journal of Elastomers and Plastics*, Vol. 34, No. 4, pp. 314, 2002.

[3] J. Jose, S. Satapathy, A. Nag, and G.B. Nando, "Modification of waste polypropylene with waste rubber dust from textile cot industry and its characterization," *Process Safety and Environmental Protection,* Vol. 85, No. 4, pp. 318-326, 2007.

[4] H. Münstedt, and D. Auhl, "Rheological measuring techniques and their relevance for the molecular characterization of polymers," *Journal of Non-Newtonian Fluid Mechanics,* Vol.128, No. 1, pp. 62-69, 2005.

[5] R. Asaletha, M.G. Kumaran, and S. Thomas, "Thermal behaviour of natural rubber/polystyrene blends: Thermogravimetric and differential scanning calorimetric analysis," *Polymer Degradation and Stability*, Vol. 61, No. 3, pp. 431-439, 1998.

[6] J.T. Varkey, S. Augustine, and S. Thomas, "Thermal degradation of natural rubber/styrene butadiene rubber latex blends by thermogravimetric method," *Polymer-Plastics Technology and Engineering,* Vol. 39, No. 3, pp. 415-435, 2000.

[7] R. Stephen, S. Jose, K. Joseph, S. Thomas, and Z. Oommen, "Thermal stability and ageing properties of sulphur and gamma radiation vulcanized natural rubber (NR) and carboxylated styrene butadiene rubber (XSBR) latices and their blends*," Polyme*r *Degradation and Stability*, Vol. 91, No. 8, pp. 1717-1725, 2006.

[8] O. Boondamnoen, A.R. Azura, M. Ohshima, S. Chuayjuljit, and A.B. Ariffin, "Effect of latex treatment on properties of WNRL/PS blends," *Advanced Materials Research,* Vol. 488-489, pp. 478-482, 2012.

[9] A. Thitithammawong, C. Nakason, K. Sahakaro, and J. Noordermeer, "Effect of different types of peroxides on rheological, mechanical, and morphological properties of thermoplastic vulcanizates based on natural rubber/polypropylene blends," *Polymer Testing*, Vol. 26, No. 4, pp. 537-546, 2007.

[10] H. Ismail, D. Galpaya, and Z. Ahmad, "The compatibilizing effect of epoxy resin (EP) on polypropylene(PP)/recycled acrylonitrile butadiene rubber (NBRr) blends," *Polymer Testing*, Vol. 28, No. 4, pp. 363-370, 2009.

[11] C.L.Zhang, L.F. Feng, X.P. Gu, S. Hoppe, and G.H. Hu, "Blend composition dependence of the compatibilizing efficiency of graft copolymers for immiscible polymer blends," *Polymer Engineering and Science,* Vol. 50, No. 11, pp. 2243-2251, 2010.

[12] N. Papke, and J. Karger-Kocsis, "Thermoplastic elastomers based on compatibilized poly(ethylene terephthalate) blends: Effect of rubber type and dynamic curing," *Polymer*, Vol. 42, No. 3, pp. 1109-1120, 2001.

[13] R.G. Larson, *The Structure and Rheology of Complex Fluids,* Oxford University Press Inc., New York, United States, 1999.

[14] B. Adhikari, D. De, and S. Maiti, "Reclamation and recycling of waste rubber," *Progress in Polymer Science,* Vol. 25, No. 7, pp. 909-948, 2000.

[15] V.V. Rajan, W.K. Dierkes, R. Joseph, and J.W.M. Noordermeer, "Science and technology of rubber reclamation with special attention to NR-based waste latex products," *Progress in Polymer Science*, Vol. 31, No. 9, pp. 811-834, 2006.

[16] S.H. El-Sabbagh, "Compatibility study of natural rubber and ethylene–propylene diene rubber blends," *Polymer Testing*, Vol. 22, No. 1, pp. 93-100, 2003.

[17] T. Caykara, S. Demirci, and O. Kantoglu, "Thermal, spectroscopic, and mechanical properties of blend films of poly(N-Vinyl-2-Pyrrolidone) and sodium alginate," *Polymer-Plastics Technology and Engineering*, Vol. 46, No. 7, pp. 737-741, 2007.

[18] A.A. Yehia, A.A. Mansour, and B. Stoll, "Detection of compatibility of some rubber blends by DSC," *Journal of Thermal Analysis*, Vol. 48, No. 6, pp. 1299-1310, 1997.

[19] P.A. Nelson, and S.K.N. Kutty, "Cure characteristics and mechanical properties of maleic anhydride grafted reclaimed rubber/styrene butadiene rubber blends," *Polymer- Plastics Technology and Engineering*, Vol. 43, No. 1, pp. 245-260, 2004.