

Visco-elastic properties of OMMT filled fractioned bleached crepe rubber

H.G.I.M. Wijesinghe, A.G.A.W. Alakolanga, N.S. Withanage
Faculty of Animal Science and Export Agriculture, Uva Wellassa University of Sri Lanka

and

U.N. Ratnayake
Rubber Research Institute, Thelawala Road, Ratmalane, Sri Lanka

Introduction

Natural Rubber (NR) latex tapped from *Hevea brasiliensis* converts into an important engineering material for different applications. NR latex pale crepe, the purest form of NR produced by Sri Lanka, is mainly used in pharmaceutical and surgical applications, infant toys, food contact rubber articles and adhesives, (Senevirthne and Kumara, 2003). Natural Rubber has a higher greenstrength as but it is soft and has lower dimension stability (Cohan and Spielman, 1948) which is one of the major draw backs in NR for engineering application.

Recently, Nanoclays such as montmorillonite clay are attracted as an alternative filler to achieve the reinforcement of rubber compounds by replacing conventional fillers (Ratnayake and Peiris, 2010). Study the effect of Organo-montmorillonite (OMMT) on the visco elastic properties of fractioned bleached crepe rubber will helpful for the advancement of the raw rubber industry as value addition. In this study, OMMT dispersion in the rubber matrix has studied not only by Mooney viscosity and stress relaxation properties but also by the physical properties of vulcanizates. Therefore this study may help to have an advantage for the development of crepe rubber industry and product manufacturing industry in Sri Lanka.

Material and Methods

NR field latex was obtained from NR processing factory at Rubber Research Institute, Dartonfield, Agalawaththe. Montmorillonite clay modified with quaternary alkyl ammonium salt (OMMT) was used as the nanofiller. Other general chemicals and laboratory equipment were obtained from Rubber Research Institute, Rathmalana.

Initially, 5%(w/w) aqueous dispersion of OMMT was prepared using a surface active agent as a dispersing agent. Latex mixing/intercalation method (Gatos and Kocsis, 2010) was carried out to prepare OMMT filled fractioned bleached crepe rubber (OFBCR). Dry rubber content (DRC) of fractionated bleached latex was diluted up to 10% and subsequently OMMT dispersion was incorporated to latex samples at OMMT loading from 0 to 8 phr with an interval of 2 phr, with simultaneous stirring. Standard latex crepe manufacturing procedure was adopted to prepare OFBCR (Senevirthne and Kumara, 2003). Laces were dried in the drying tower at 34°C for three days. Complete randomized design was applied to assign treatments, T₀(0 phr), T₂ (2 phr), T₄ (4 phr), T₆ (6 phr) and T₈ (8 phr).

The NR was characterized based on DRC and the OMMT was characterized by the ash content. Mooney viscosity and stress relaxation of OFBCRs were measured according to the [ISO/R 289-1963] by the Ektron Mooney viscometer. Then the OFBCR samples were compounded according to the pre-determined formulation. Curing characteristics of the OFBCR samples were measured by using MDR 2000 (moving die rheometer, M/S Alpha Technologies, USA) at

150°C according to the ISO 3417:2008 procedure. OFBCR samples were moulded by hydraulic hot press at 150°C temperature and 20MPa pressure for optimum cure time derived from the cure characteristics data. The tensile properties of OFBCR samples were determined by “Instron 3300 Series” material testing machine at a crosshead speed of 500 mm/min as per ISO 37:2011.

The hardness of the samples were determined using Elastocon bares digi hardness tester according to the ISO 48:2010. Compression set at constant strain was measured according to ISO 815-1:2008 test method and tear strength of OFBCR samples were determined by “Instron 3300 Series” material testing machine at a crosshead speed of 500 mm/min according to ISO 34-1:2011. All tests were carried out at 27±2°C and each test was replicated at least 3 times. Data were analyzed by using the Minitab 16 statistical software with the use of General Liner Model (GLM) with Tukey’s all pair wise comparison tests at 95% confidence interval.

Results and Discussion

Field latex used for the preparation of nano crepe rubber showed the dry rubber content of 30%. OMMT clay has modified with quaternary alkyl ammonium salts. The ignition weight loss of OMMT is 43%–48%. Ash content of clay is 52%–58%. This ash content represents the amount of silicates and other inorganic metal amount in the clay. Ignition weight loss is correlated to the amount of quaternary ammonium alkyl modifier and adsorbed moisture amount in the clay.

Mooney viscometer is an instrument to measure the 'stiffness' of uncured compounds, the result of that viscosity is called as Mooney viscosity at ML 1+4 (100°C). Mooney stress relaxation coefficient is the slope of the power law model when it is in logarithmic scale ($\log M = a(\log t) + \log k$) where M- torque units from the Mooney stress relaxation test, k- a constant equal to torque 1 s after the rotor has stopped, 'a'- an exponent that measures the rate of stress relaxation and t- testing time. Also elasticity of rubber material is inversely proportionate to the 'a' and lower elasticity improves the mixing of rubber and processing, especially extrusion and calendaring. Malac J., (2009).

Clay loading level (phr) has significantly affected to the Mooney viscosity expressed as ML (1+4) 100°C of OFBCR samples (p-0.000). Only T₆ and T₈ has not indicated a significant difference (p-0.0569) between them with respect the Mooney viscosity but all other treatment levels are significantly different among (p-0.000). Mooney viscosities for T₀, T₂, T₄, T₆ and T₈ are presented in Figure 1. The reason for the reduction of Mooney viscosity is, when increasing the OMMT loading, the plasticization of rubber material by OMMT and may possibly be the chain slippage over the clay platelets (Kader *et al.*, 2010).

As reported in Figure 2, the stress relaxation coefficient has increased up to 4 phr and there after it reduces. The maximum stress relaxation coefficient has indicated at the 4 phr clay loading level, therefore, it can be concluded that OFBCR with 4 phr OMMT clay loading has a better processability than other samples. Long relaxation times and high amplitudes of stress relaxation suggest the mechanism of structural relaxation involving large-scale displacements of isolated clusters of nanoparticles within the rubber matrix and vice versa (Dick, 2010).

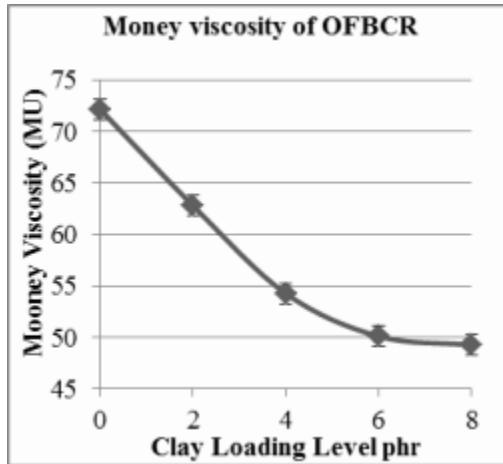


Figure 1. Mooney viscosity T_0 , T_2 , T_4 , T_6 and T_8

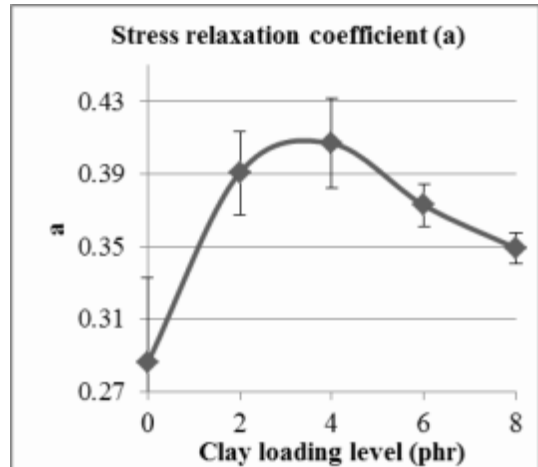


Figure 2. Stress relaxation coefficient for T_0 , T_2 , T_4 , T_6 and T_8

Curing characteristics of OFBCR samples have indicated the increasing cure rate index (CRI), maximum torques (MH) and reducing scorch time (t_{s2}) (Figure 3). Reason for the increasing CRI may be the acceleration of curing reaction by organic modifier; simultaneously it can reduce the t_{s2} .

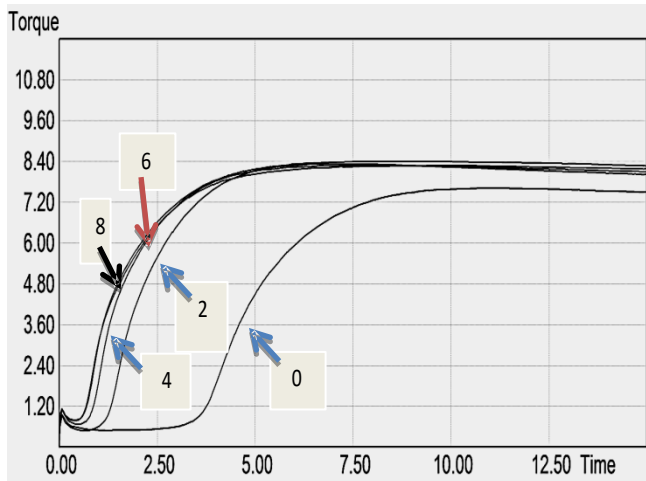


Figure 3. Cure curves for T₀, T₂, T₄, T₆ and T₈

Clay loading level has not significantly affected to the tensile strength of OFBCR materials (0.181). The reason for this may be the uneven distribution of organoclay in the rubber matrix. But 26.56 % increase has indicated at T₆ clay loading level compared to T₀. Also clay loading level has significantly affected to the modulus at 300 % (0.009). Modulus at 300% has indicated an increasing trend up to T₆ and there after it reduces. The modulus has increased by 37.22% at T₆ compared to T₀. When

consider the modulus at 300% at the T₆, the reason for this increase may be the optimum dispersion of organoclay in the rubber matrix. Therefore, it can be concluded that the elastic modulus has improved by OMMT at T₆. Also the elongation at break has not affected significantly by the clay loading level (0.135).

Compression set percentage has significantly affected by the clay loading level (0.000). Maximum compression set has indicated at T₆, but it does not significantly different to T₄ (0.090). Compression set indicates the elastic properties of vulcanizates. Compression set has increased up to T₆ and then it reduces. Therefore, it can be concluded that the elasticity has reduced when the filler loading is increased up to T₆. The reason for increase the compression set may be the better dispersion of the organoclay in the rubber matrix. Hardness of the OFBCR vulcanizate has increased with respond to the clay loading level and has indicated 22% increase at T₆ compared to T₀. The hardness has increased rapidly up to T₄ and thereafter it has indicated more or less same values for T₄, T₆ and T₈ indicating that optimum dispersion of OMMT clay was achieved with 4 phr. clay loading (0.000). Entanglement of rubber molecule with OMMT may be the reason for the improvement of hardness.

Table 1. Physical properties of OFBCR

Property	Clay loading phr				
	T ₀	T ₂	T ₄	T ₆	T ₈
Tensile strength (MPa)	23.72	24.88	23.53	24.35	25.08
Mod @ 300 % (MPa)	4.54	5.10	5.45	6.23	5.72
Elongation @ break	448.5	433	448.84	434.3	452.3
Compression set %	4.06	7.49	12.55	15.28	9.5
Hardness (IRHD)	37.21	42.02	44.16	45.39	45.8
Tear strength (N/mm)	31.65	32.01	35.61	34.98	33.98

Maximum tear strength has indicated at T₄. Even dispersion of OMMT could be improved the tear strength. When the filler loading is increased over the 4 phr, the re-aggregation of wide stacks of clay platelets could be taken place. Therefore the crack initiation and propagation can

be accelerated by reducing the tortuous path length. Shortening the stack-stack distance can lead to a greater resistance to crack propagation (Gatos and Kocsis, 2010). Due to the high aspect ratio of the clays their optimum dispersion is reached at a smaller amount (Gatos and Kocsis, 2010).

Conclusions

According to the Mooney stress relaxation information, clay loading levels at 4 phr (T₄) have indicated better processability as filled raw rubber material called OFBCR. Also physical properties have shown that T₄ and T₆ treatments have given optimum dispersion of OMMT in rubber matrices.

Acknowledgments

Authors would like to acknowledge the technical support and the materials given by the Rubber Research Institute, Ratmalana and University of Uva Wellassa, Sri Lanka.

References

- Cohan, L.H. and. Spielman, R. (1948). *Indu. Eng. Chem* 40: 2204.
- Gatos, K.G. and Kocsis, J.K. (2010). *Rubber/Clay Nanocomposites: Preparation, Properties and Applications*. In: Sabu Thomas, Ranimol Stephen *Rubber Nanocomposites*. Singapore: John Wiley & Sons (Asia) Pte Ltd. 169 - 175.
- Malac, J. (2009). *Viscosity, Relaxation and Stability of Natural Rubber*. *The Open Macromolecules Journal*, 3, 41-44. Retrieved August 22, 2014, from the World Wide Web: <http://www.benthamopen.com/tomacroj/articles/V003/41TOMACROJ.pdf>
- Ratnayake U.N. and Peiris, C. (2010). *Natural Rubber/Layered Silicate Nanocomposite for Building Applications*. *International Conference on Sustainable Built Environment*, 69-76. Retrieved May 27, 2014, from the World Wide Web: http://www.civil.mrt.ac.lk/conference/ICSBE_2010/vol_03/11.pdf
- Senevirthne W.M.G. and Kumara P.H.S. (2003) *Handbook of Rubber-Processing Technology: Pale crepe and Sole crepe*. (2), 34-57. United Printers, Moratuwa.