Enhancing Properties of Cured NR/PVA Blends Using Glutaraldehyde as a Crosslinking Agent: Effect of Nano-Clay Loading

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Abstract. A novel and inexpensive method to vulcanize natural rubber (NR) was successfully developed and reported in our previous work. NR can be easily vulcanized using glutaraldehyde (GA) at low temperature without adding any specific activators. However, there is some limitation (i.e., poor film formation and properties) to apply as many product items. Therefore, the main objective of this work is to improve the properties and film formation of this cured system. The effect of loading levels of nano-clay on the properties of GA cured NR/PVA blends has been investigated. Mechanical, thermal and morphological properties were characterized. From the overall characterization, cured NR/PVA blends with 1 phr of nano-clay exhibited the highest tensile strength, elongation at break and hardness of 8.02 MPa, 690% and 62.4 shore A, respectively. Enhancing in thermal stability of the sample was confirmation by shifting of degradation temperature based TGA technique. The experimental results reveal that the properties and film formation of this system can be developed with the proper additives in the preparation. From obtained knowledge, it is interesting due to it can be applied for various industrial applications with eases of producing at low temperature and cost.

Keywords: Natural rubber, Nano-clay, Glutaraldehyde, Cured NR/PVA blends, Vulcanization.

1. Introduction

Natural rubber (NR) is a natural material which is derived from typical plants. NR is normally known as cis-1,4-poly (isoprene) [1]. It is an unsaturated elastomer with many superior properties such as high strength, outstanding resilience, and high elongation at break [2]. In addition, these properties can be improved by different methods such as grafting, blending, addition of fillers etc. Blending is a mechanical mixture of more than two polymers and it is a convenient route for the modification of properties to meet
specific need and reasonable demands of the polymers [3]. The common way is blending with other latex or water soluble polymer to obtain better performance or fabrications. Polyvinyl alcohol has good water solubility, film-forming property, adhesive force and emulsification [4]. However, the natural rubber is a non-polar polymer, whereas the PVA is a polar polymer. Therefore, NR/PVA blend could be partial compatibility, leading to low physical properties. Nowadays there is great interest in the development of rubber composites using nano-clay as reinforcing material [5]. The functional properties such as mechanical properties, barrier resistance and flame retardancy can be enhanced considerably at lower loading level of nano clay due to their high aspect ratio [6]. The reinforced rubber depends on several factors: filler particle size, concentration, aspect ratio, dispersion and morphology. All these factors lead to the concept of filler network formation and enhancing the mechanical properties of rubber matrix. It makes the final products less expensive [7]. However, the vulcanization process is very important for rubber applications. Mechanical properties of NR increase during the vulcanization process due to the cross-linking of NR chains [1]. In general, there are many potential vulcanization techniques including sulfur, peroxide, and phenolic resin curing [8]. These curing systems need high temperature together with various chemicals, i.e., activators and accelerators. Natural rubber can be easily vulcanized using glutaraldehyde (GA) at low temperature without adding any specific activators, which is highly favorable to the environment [9]. According to this study, glutaraldehyde initially reacts with ammonia present in the natural rubber latex and generates pentane-1,5-diylidenediamine. It has been shown that, this curing system provides better thermal stability than that of the sulfur cured system with greater ease of processing. However, the GA-cured system exhibits low mechanical properties [10]. The aim of this study is to reinforce nano-clay into NR/PVA blends to improve the properties and stability of the blends using glutaraldehyde as a crosslinking agent.

2. Experimental method

2.1 Materials
Commercial high ammonia latex (HA Latex) with 60% dry rubber content (DRC) was purchased from Chalong Latex Industry, Thailand. Glutaraldehyde (GA) and Polyvinyl alcohol (PVA) were purchased from Boss Official Limited Partnership, Songkhla, Thailand.

2.2 Preparation of nano-clay dispersion
The nano-clay (Cloisite 30B) used in this study was collected from Rockwood Clay Additives, GmbH, Germany. The aqueous dispersion of 30 wt% nano-clay was prepared by conventional ball milling technique for 72 h.

2.3 Preparation of Cured NR with various nano-clay contents using Glutaraldehyde
12.5% Glutaraldehyde (GA) solution was prepared by diluting in distilled water. The ammonia content present in natural rubber was estimated according ASTM D-1076-02 into the mixture of NR/PVA blends with 90/10 weight ratios. Nano-clay was added into the mixture of NR/PVA blends with various loading levels under continuously stirring at room temperature. Glutaraldehyde solution was slowly added into the reinforced latex using continuously stirring at a mole ratio 1:1 between ammonia and glutaraldehyde. The mixture was cast on a glass plate and dried in hot air oven at 50 °C for 24 hours [8]. The samples were introduced for testing and characterization.

2.4 Characterization
The overall chemical composition of the filler was determined by an EDX spectrometer attached to scanning electron microscope (SEM). The specimens were mounted on aluminum stubs using carbon tape and then coated with a thin layer of gold to prevent charging before the observation. Swelling measurement was
carried out in engine oil as a test liquid at room temperature for 24 h. The degree of swelling was calculated
by using Equation (1).

\[
\text{Change in weight (\%) = } \frac{W_s - W_o}{W_o} \times 100
\]  

(1)

where \( W_o \) and \( W_s \) are the weight of the specimen before and after immersion in the test liquid, respectively.

The tensile strength was performed according to the ASTM D 412 method using dumbbell-shaped test
specimens at a crosshead speed of 500 mm/min using a universal testing machine. Indentation hardness was
tested using a Shore A durometer according to ASTM D2240. The thermal properties were characterized
using thermogravimetric analysis (TGA). A small amount (1–10 mg) of sample was taken in a crucible and
placed inside the machine from 40°C to 800°C at a rate of 10°C/min in oxygen atmosphere.

3. Results and discussion

3.1 Scanning Electron Microscopy

The overall chemical composition of the cured NR/PVA blends with various nano-clay contents is identified
and qualified by EDX spectrometry and SEM. The SEM image of the cured NR (Figure 1a) reveals a very
smooth surface. Figure 1b shows that the nano-clay is dispersed uniformly in the NR matrix. Figure 1c
shows the nano-clay particles are poorly dispersed and agglomerated due to the higher content of nano-clay.
The presence of overall chemical composition of nano-clay in the NR/PVA blends matrix has been
confirmed by EDX analysis (Table 1). EDX profile concludes that skeleton of nano-clay is composed of
elements: mainly silicon, second most oxygen, third most aluminum and finally carbon. The amount of these
elements is increased with increase in nano-clay content. Especially, the percentage of silicon and aluminum
atom increases with increasing the amount of nano-clay into NR/PVA blends (Figure 2). In addition, the
distribution of silicon and aluminum atoms further support the observation of aggregates of nano-clay in the
matrix. Better dispersion can be seen in the cured NR with 1 phr nano-clay compared to the composite with
2.5 phr nano-clay. However, the analysis shows an increase in the percentage of carbon atom for all samples.
This may be due to the presence of long chains molecules of natural rubber (polyisoprene) in the sample.

![Figure 1. SEM images of cured NR/PVA blends with various nano-clay contents: (a) 0 phr (b) 1 phr and (c) 2.5 phr.](image-url)
Figure 2. Mapping of the elements found on the image of cured NR/PVA blends with various nano-clay content using GA as crosslinking agent; Si: silicon and Al: aluminum: (a) 1 phr and (b) 2.5 phr.

Table 1. Overall chemical composition obtained by EDX spectrometry.

| Elements     | 0 phr (%) | 1 phr (%) | 2.5 phr (%) |
|--------------|-----------|-----------|-------------|
| Carbon (C)   | 94.0      | 95.4      | 94.3        |
| Oxygen (O)   | 6.0       | 4.4       | 5.4         |
| Silicon (Si) | 0         | 0.1       | 0.3         |
| Aluminum (Al)| 0         | 0.1       | 0.1         |

3.2 Swelling Behaviors

Figure 3 shows the degree of swelling of the cured NR/PVA blends with nano-clay for 0, 1 and 2.5 phr in engine oil. It is seen that the degree of swelling of cured NR with 1 phr nano-clay are found to be much less when compared to the NR with 0 phr and 2.5 phr. This can be explained in terms of the composite materials containing layered silicate with a high aspect ratio, it strongly limits the deformation of macromolecules due to a highly efficient stress transfer [11]. In addition, the reduction of swelling upon the addition of layered silicates is due to the enhanced rubber/filler interaction. The reduction in solvent transport can be explained in terms of tortuosity of the path and decreased transport area in the membrane. However, the degree of swelling for cured NR with 2.5 phr nano-clay shows higher values because of the weak interface and poor clay dispersion. As a result, the available free voids within the matrix increase. Therefore, diffusion of solvent molecules through rubbery polymers is easy. This result confirms the fine dispersion of nano-clay in the NR matrix. However, crosslinking reduces the rubber chain mobility and thus reduces the transport of solvent through the rubber. In our previously published article [9], it was reported that the cured NR prepared using glutaraldehyde exhibited better oil resistance properties than of the pure NR. It is seen that glutaraldehyde vulcanizes rubber phase and does not allow the chains to rearrange easily under solvent stress.
3.3 Mechanical properties

Mechanical properties of the cured rubber with nano-clay varying from 0 to 2.5 phr are listed in Table 2. Improvement in the properties of NR/PVA blends can be seen by adding nano-clay. The highest tensile strength and elongation at break are observed at clay loading of 1 phr (Figure 4). This is directly related to the dispersion and distribution of nano-clay as shown in previous part. For higher loading level (2.5 phr), the failure of sample may be due to the agglomerations and the formation of filler–filler networks in NR/PVA blends matrix. The proposed model of interaction between matrix and nano fillers are shown in Figure 7. Incorporation of filler into the NR/PVA blends matrix reduces the elasticity of rubber chains and the resulting composite becomes more rigid [12]. Rigidity of the material leads to increase in modulus and hardness with increasing the percentage of nano-clay (Figure 5). In addition, it might be attributed by the effect of PVA which consists of coarse crystalline phase. Formation of cross-links in PVA and NR phases when it is crosslinked with glutaraldehyde enhances the stability. Crosslinking of natural rubber is occured by the reaction between rubber and pentane 1,5-diylidenediamine as shown in Figure 7. It leads to the formation of three-dimensional network and restricts the movement of rubber chains. From the overall results, it is found that the sample with 1 phr nano-clay loading level exhibited higher mechanical properties. It is clearly confirmed from the fine and uniform dispersion of nano-clay in the rubber matrix by SEM image (Figure 1b and Figure 7).
Table 2. Mechanical properties of cured NR with different nano-clay content.

| Amount of nano-clay (phr) | 100% modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Hardness (Shore A) |
|---------------------------|--------------------|------------------------|-------------------------|-------------------|
| 0                         | 2.37               | 4.46                   | 438                     | 61.20             |
| 1.0                       | 2.51               | 8.02                   | 690                     | 62.40             |
| 2.5                       | 2.64               | 5.61                   | 503                     | 68.40             |

Figure 4. Tensile strength and elongation at break of cured NR/PVA blends using GA as crosslinking agent with different nano-clay content.

Figure 5. 100% modulus and hardness of cured NR/PVA blends using GA as crosslinking agent with different nano-clay content.

3.4 Thermal properties

Results of TGA for the composites with various percentages of nano-clay are shown in Figure 6. The onset degradation temperature of cured NR/PVA blends with 2.5 phr nano-clay contents is higher (245 °C) when compared to composites with 0 and 1 phr (230 and 233 °C). The results show that the thermal stability increases with the addition of nano-clay. Due to the barrier effect from nano-clay may hinder diffusion of small molecules generated during thermal decomposition. Lengthened paths of diffused low molecular gases in the polymeric matrix from the uniform distribution of the layered silicates delay the degradation of the cured NR/PVA blends [13]. In addition to this, vulcanization of rubber phase with glutaraldehyde in the presence of ammonia increases the thermal stability. Newly generated three-dimensional networks between rubber molecules is also a reason for the enhancement in the thermal stability of rubber. Reaction between rubber and pentane 1,5-diylidenediamine molecules crosslinks natural rubber (Figure 7).
Figure 6. TGA curves for cured NR/PVA blends using GA as crosslinking agent with various amounts of nano-clay.

Figure 7. Proposed mechanism of cured NR with various nano-clay content using GA as crosslinking agent (a) 0 phr, (b) 1 phr and (c) 2.5 phr.
4. Conclusion
Cured NR/PVA blends with various nano-clay contents using glutaraldehyde as curing agent was successfully prepared at low temperature. Dispersion of nano-clay was studied using SEM and EDX. Addition of nano-clay into cured NR samples provided better swelling, mechanical and thermal properties. However, loading of 1 phr nano-clay into cured NR/PVA blends exhibited the best properties due to the fine and uniform distribution of filler particles. These NR based composites can be applied for various industrial applications.

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References
[1] O. Sivaraman, N. Ghosh, S. Gayathri, P. Sudhakara, S. K. Misra, and J. Jayaramudu, “Natural Rubber Nanoblends: Preparation, Characterization and Applications,” Polymer and Composite Materials, 2017. DOI 10.1007/978-3-319-48720-5_2
[2] T. A. Dung et al., “Modification of Vietnam natural rubber via graft copolymerization with styrene,” J. Braz. Chem. Soc., vol. 28, no. 4, pp. 669–675, 2017. DOI:10.21577/0103-5053.20160217
[3] M. A. Haque, M. U. Ahmad, F. Akhtar, N. C. Dafader, and M. E. Haque, “Improvement of physicochemical properties of natural rubber and polyvinyl alcohol blends by radiation vulcanization,” Polym. - Plast. Technol. Eng., vol. 46, no. 10, pp. 927–931, 2007. DOI: 10.1080/03602550701280323
[4] K. Chen and R. Wang, “The Mechanical and Aging Properties of the Natural Rubber/Polyvinyl Alcohol (NR/PVA) Blends,” Adv. Mater. Res., vol. 1073–1076, pp. 12–15, 2014. DOI:10.4028/www.scientific.net/AMR.1073-1076.12
[5] S. Mathew and S. Varghese, “Natural Rubber Latex-based Nanocomposites with Layered Silicates,” J. Rubb. Res., vol. 8, no. 1, pp. 1–15, 2016. DOI: 10.13140/RG.2.1.2189.2726
[6] A. Amarasiri, U. N. Ratnayake, U. K. De Silva, S. Walpalage, and S. Siriwardene, “Natural rubber latex-clay nanocomposite: Use of montmorillonite clay as an alternative for conventional CaCO₃,” J. Natl. Sci. Found. Sri Lanka, vol. 41, no. 4, pp. 293–302, 2013. DOI: http://dx.doi.org/10.4038/jnsfsr.v41i4.6258
[7] T. Pojanavaraphan and R. Magaraphan, “Prevulcanized natural rubber latex/clay aerogel nanocomposites,” Eur. Polym. J., vol. 44, no. 7, pp. 1968–1977, 2008. DOI:10.1016/j.eurpolymj.2008.04.039
[8] E. Kalkornsuran, W. Yung-Aoon, B. Thongnuanchan, A. Thitithammawong, C. Nakason, and J. Johns, “Influence of grafting content on the properties of cured natural rubber grafted with PMMAs using glutaraldehyde as a cross-linking agent,” Adv. Polym. Technol., 2017. DOI 10.1002/adp.21806
[9] A. Johns, M. P. S. Aan, J. Johns, M. S. Bhayashkar, C. Nakason, and E. Kalkornsuranpranee, “Optimization study of ammonia and glutaraldehyde contents on vulcanization of natural rubber latex,” Iran. Polym. J. English Ed., vol. 24, no. 11, pp. 901–909, 2015. DOI 10.1007/s13726-015-0382-8
[10] E. Kalkornsuranpranee, W. Yung-Aoon, L. Songtipya, and J. Johns, “Effect of processing parameters on the vulcanisation of natural rubber using glutaraldehyde,” Plast. Rubber Compos., vol. 46, no. 6, pp. 258–265, 2017. DOI: 10.1080/14658011.2017.1323610
[11] Kong, Lingxue, Chen, Ying, Peng, Zhen and Li, Puwang, “Latex-based nanocomposites,” Progress in Polymer Nanocomposite Research., Hauppauge, N.Y., pp.83-104, 2008. ISBN: 978-1-60456-484-6

[12] C. M. Ewulonu, C. M. Obele, I. O. Arukalam, and S. R. Odera, “Effects of local clay incorporation technique on the mechanical properties of natural rubber vulcanizates,” vol. 4, no. 3, pp. 307–320, 2015. DOI: 10.6088.ijaser.04031

[13] C. Zhang and J. Wang, “Natural rubber/dendrimer modified montmorillonite nanocomposites: Mechanical and flame-retardant properties,” Materials (Basel),, vol. 11, no. 1, 2017. DOI: 10.3390/ma11010041