

Morphological, Dynamic Mechanical, and Mechanical Properties of Natural Rubber and Poly (Vinyl Alcohol) Blends

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Abstract. Biopolymer blends of natural rubber (NR) latex and poly (vinyl alcohol) (PVA) were prepared using the latex blending method. The influence of solid content of NR latex on morphological, dynamic mechanical, mechanical and thermal properties of NR/PVA films was investigated. The results showed that the solid content of NR latex was consistent with morphology, dynamic mechanical and mechanical properties of the NR/PVA films. Reduction of NR particle size in NR/PVA blend, increasing trend of tensile strength and elongation at break and changing of glass transition temperature (T_g) of PVA phase in the NR/PVA blend were observed with increasing solid content of NR latex.

1. Introduction

Nowadays, the increasing demand of polymer products increases garbage from their wastes, which is a widely recognized source of pollution. Since most of thermoplastic and elastic materials do not decompose easily, elimination of their wastes is a serious environmental concern. To minimize this problem, many researchers have been developed a new material by blending of conventional polymer with biodegradable polymer [1, 2]. There are variety of biodegradable polymers obtained from natural product such as starch, cellulose, chitin and chitosan, from microbial fermentation, such as polyhydroxybutyrate or obtained by chemical synthesis such as polylactic acid, polycaprolactone, poly (vinyl alcohol), poly (vinyl chloride) and polysaccharides [3-6]. Among these, poly (vinyl alcohol) (PVA) is one of the most frequently chosen polymers for biodegradable polymer blend researches [5, 6]. PVA is a non-toxic water-soluble polymer extensively used in paper coating, textile sizing, flexible water-soluble packaging films and also in food chemistry, pharmaceuticals and biomedical applications. PVA could be considered as a good host material in polymer blend due to good thermo-stability, chemical resistance and film forming ability [7].

Natural rubber (NR) is one of important renewable resource elastomers used in many manufactures, i.e. rubber tires, gloves, condoms and foam products, due to its good elastic properties, good resilience and damping behavior. Many researchers have been reported blending of natural rubber with various types of thermoplastic in molten state to improve mechanical properties of natural rubber including polystyrene, poly(vinyl chloride) and poly(vinyl alcohol) [8-10].

Recently, interpenetrating polymer network (IPN) of NR/PVA in latex stage with different types of crosslinking agents has been studied at various blend compositions for dielectric materials, bioadhesive and antimicrobial films [11-15]. Improvement of mechanical properties of natural rubber by increasing PVA content has been reported. However, the study of variation of water concentrations in the blends has never been reported. In this study, latex stage blending of NR and PVA at a blend composition of 50/50 w/w was prepared without using of crosslinking agent. The influence of solid content of NR latex on phase morphology and physical properties of NR/PVA blends was investigated by complimentary characterization techniques.

2. Experimental

2.1. Materials

Poly (vinyl alcohol) (PVA) (Sigma- Aldrich Inc., Saint Louis, USA) with average molecular weight of 85,000-124,000 and degree of hydrolysis varying from 87-89% was used for the experiment without future purification. Centrifuged natural rubber (NR) latex with 60% of dry rubber content was supplied by Qianjin State Rubber Farm (Zhanjiang, China).

2.2. Preparation of 50/50 NR/PVA blends

The NR latexes at concentrations of 10, 20, 30, 40, 50 and 60 wt% (according to solid content) were prepared by dilution of centrifuged NRL with de-ionized water. The certain amount of PVA (5 wt%) was dissolved in de-ionized water and stirred at 65°C for 2 h. The PVA solution was kept at room temperature for 24 h before use. The 50/50 w/w of NR/PVA blends were prepared by adding NR latex into the PVA solution and mixed by using magnetic stirrer at room temperature for 30 min. The NR/PVA latex was cast in glass mold and dried at room temperature for 48 h. After that, the sample was dried in hot air oven at 50°C for another 48 h.

2.3. Characterization

The viscosity of NR latex was measured by a LVT E3209 Brookfield viscometer (Brook-field Viscometers Ltd., Harlow, UK) at 25°C.

The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques were used to visualize the morphology of 50/50 NR/PVA film. For TEM measurement, the NR/PVA latex samples were diluted and dropped onto carbon coated copper grids to obtain approximately 60-80 nm thickness film. The micrographs were then recorded using a JEM-1400 TEM (JEOL, Tokyo, Japan) at an accelerated voltage of 80 kV. For SEM measurement, the film samples were cryogenic fractured in liquid nitrogen and coated the surface by Cu/Pd before characterized using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) (Hitachi, Tokyo, Japan) with an accelerating voltage of 1.0 kV.

Mechanical properties of dried film were analysed by a Hounsfield H10KS universal testing machine (Hounsfield Test Equipment, Redhill, UK) at room temperature and a crosshead speed of 500 mm/min. The samples were prepared following ASTM D412. The average of five tests was reported here.

Dynamic mechanical properties of PVA, NR and their blends were determined using a DMTA 8000 (Perkin Elmer Inc., MA, USA). The dual cantilever mode of deformation was used under the test temperature range from -100 to 100°C with a heating rate of 3°C/min at a frequency of 1 Hz under liquid nitrogen flow.

3. Results and discussion

3.1. Viscosity of NR latex

Figure 1 shows the viscosities of NR latexes at various solid contents measured at different rotational speeds. All samples show shear thinning non-Newtonian rheological behavior. The viscosity of NR latex increased with increasing solid content, especially at 60 wt%. This is attributed to the increasing of particles in the system. The viscosity of colloidal solution is a linear function of the volume fraction of dispersed particles according to Einstein equation [16]:

$$\eta_r = 1 + 2.5 \phi \phi_0 \quad (1)$$

where η_r is the viscosity of the dispersion relative to the viscosity of the solvent and ϕ is the volume fraction of spherical particles in suspension.

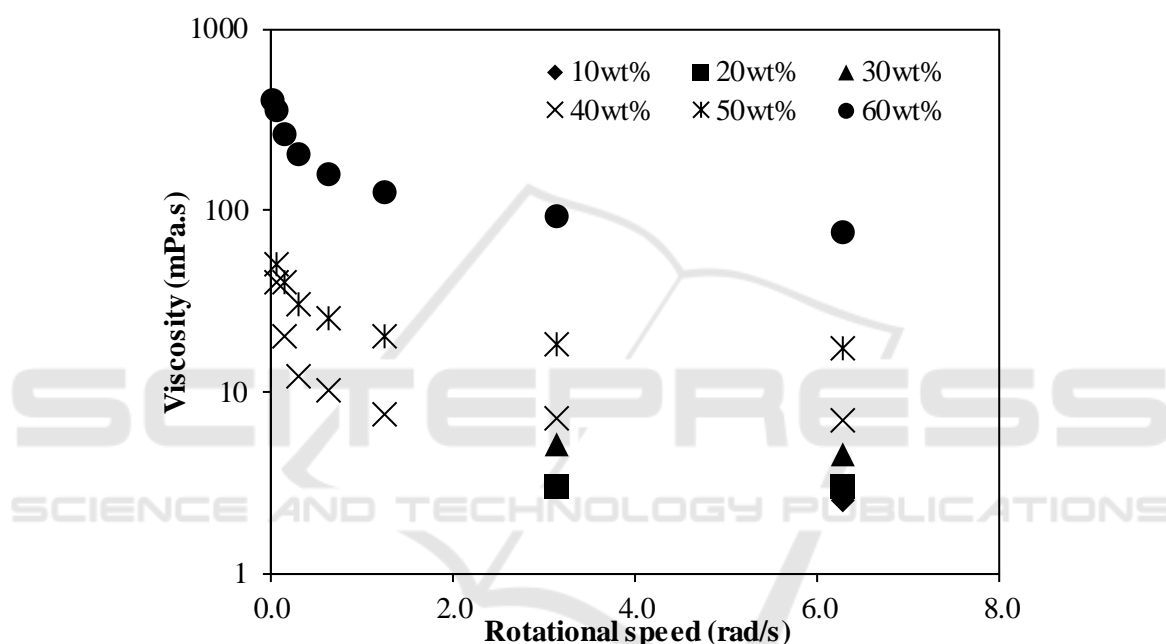


Figure 1. Viscosity of different NR latexes at various rotational speeds.

3.2. Morphology of NR/PVA blends

In order to evidence phase morphology and size of NR particles in 50/50 w/w NR/PVA blends, all samples were examined using TEM and SEM. Figure 2 shows the TEM images of pure 5 wt% PVA solution and 60 wt% NR latex. It is seen that there was no particle observed in PVA film, while various sizes of the NR particles were visible as spherical dark spots in the micrograph of NR film.

The TEM micrographs of NR/PVA blends at various solid contents of NR latex are given in Figure 3. All samples showed the dispersion of dark spots on white background. As compared with the TEM result of pure polymers in Figure 2., it is indicated that NR particles dispersed in PVA matrix. The SEM result of fractured surface of NR/PVA blend as shown in Figure 4 also implied the immiscible between NR and PVA. Particle size of NR in NR/PVA varied from 0.5-2.0 μm . Smaller size of NR particles was observed for the blend obtained from higher solid content of NR latex.

Generally, the stability of colloidal particles is controlled by the balance between repulsive and attractive forces involved in the system. If the attractive forces, which are assumed to be of London van der Waals type, are larger than the repulsive forces (i.e., electrostatic, steric, solvation and

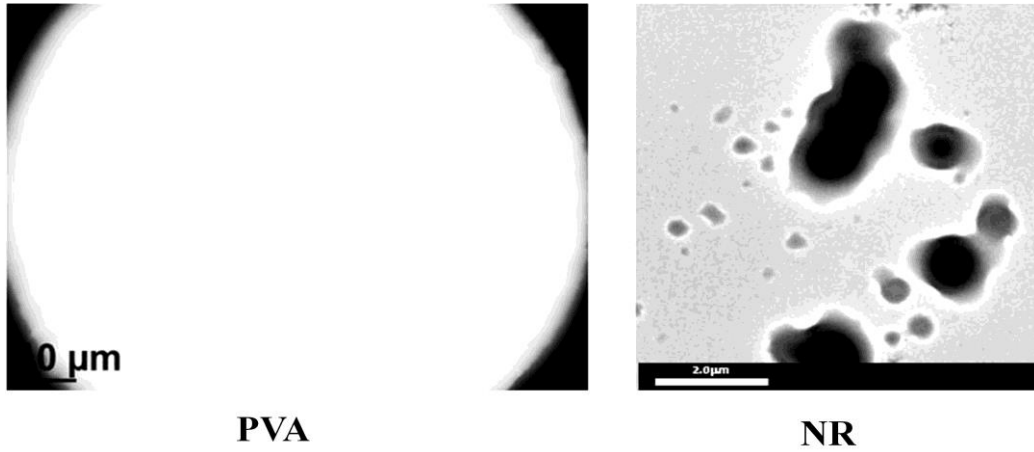


Figure 2. TEM micrographs of pure PVA and NR.

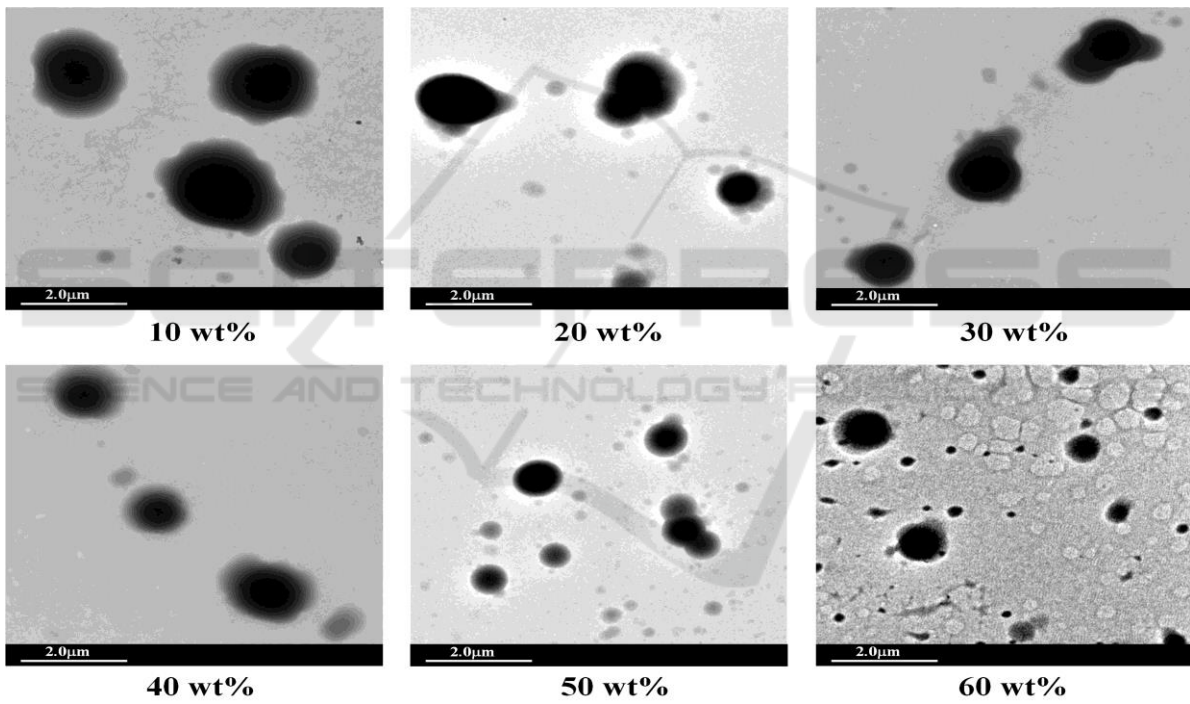


Figure 3. TEM micrographs of 50/50 w/w NR/PVA blends at various solid contents of NR latex.

depletion stabilizations), interaction between two or more particles may first cohere to give a loose aggregate and then subsequently to give a little larger particle [17].

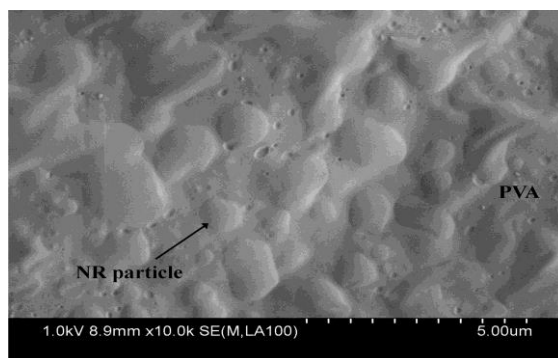


Figure 4. SEM micrograph of fractured surface of 50/50 w/w NR/PVA.

In NR/PVA latex system, the PVA can dissolve well in water medium and act as stabilizer for NR particles, which hinders the aggregation of NR particles during mixing and film formation. At higher solid content of NR, the system has higher viscosity and shorter distance between NR particles and PVA molecules. Therefore, it is possible that the PVA molecules can be adsorbed on NR particles easier than the NR/PVA system with lower solid content. This caused the increment of repulsive force between NR particles leading to stabilization of NR particles. In contrast, the dilution of NR latex by de-ionized water (low solid content of NR) might cause the elimination of repulsive force between NR particles, which induces to form aggregates of NR particles. This led to the presence of large NR particles at lower solid content of NR. The proposed aggregation and stabilization of NR particles by adsorbed PVA molecules during mixing and film formation are depicted in Figure 5.

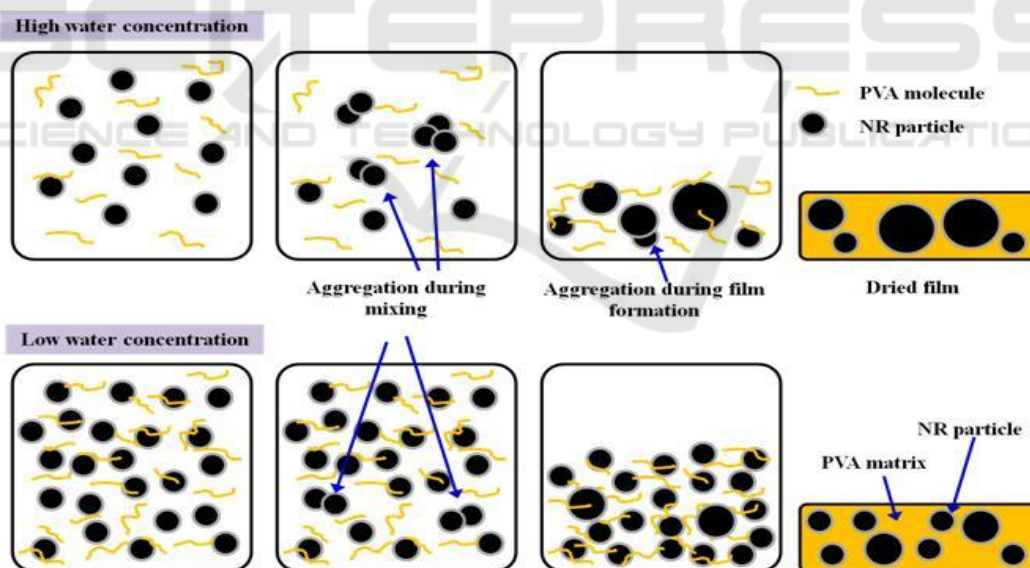


Figure 5. Schematic diagram of proposed aggregation and stabilization of NR particles during mixing and film formation.

3.3. Mechanical properties

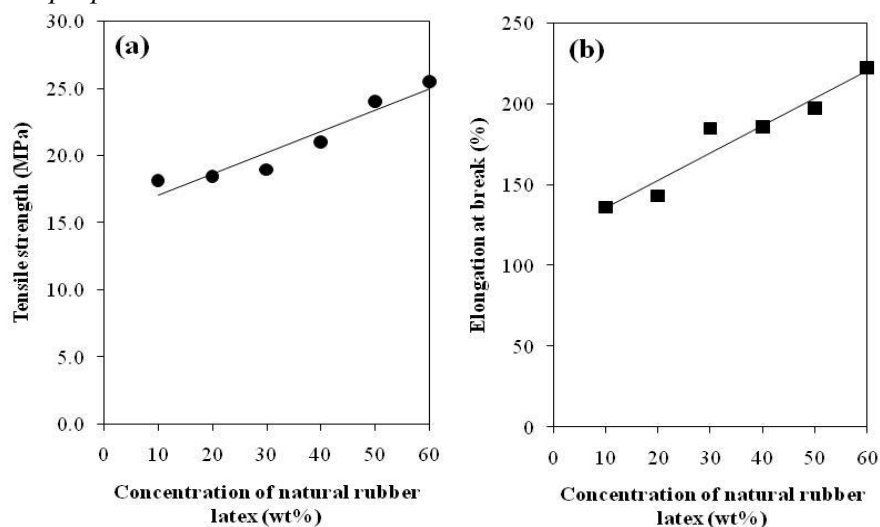


Figure 6. Mechanical properties of 50/50 w/w NR/PVA at various solid contents of NR latex: (a) tensile strength and (b) elongation at break.

In Figures 6a and 6b, it was found that both tensile strength and elongation at break of NR/PVA blends showed an increase trend with increasing solid content of NR latex. It can be explained by the reduction of rubber particle size in the NR/PVA blends, as shown in Figure 3. Decreasing content of rubber particles in the blend increased interfacial area between dispersed NR and PVA matrix, which enhanced force transfer between two phases and then provided improvement of mechanical properties.

3.4. Dynamic mechanical properties

Figure 7 represents the variation of storage modulus (E') and loss modulus (E'') as a function of temperature in the range of -100°C to 100°C . In Figure 7a, it is seen that the E' values of PVA were maximum, while NR showed minimum values. The E' values of the blends were found to be intermediate between those of pure components. The NR/PVA blends prepared by using 60 wt% solid content of NR latex showed higher values of E' compared with those of 30 wt% solid content indicating higher stiffness of NR/PVA blends.

The influence of temperature on the loss modulus of the samples is shown in Figure 7b. The T_g was selected as the peak position of E'' . The E'' curves of NR/PVA blends clearly appeared two distinct and separate peaks corresponding to the T_g 's of NR and PVA. This indicates immiscible properties between NR and PVA in the NR/PVA blends. However, it is noted that the T_g 's of NR and PVA in NR/PVA blends were shifted toward each other implying partially compatible between two phases [18, 19]. In addition, T_g of PVA phase in NR/PVA blends shifted toward lower temperature as the solid content of NR latex increased from 30 wt% to 60 wt%. It might be due to higher surface area of NR particles at higher solid content of NR latex, which restricted mobility of PVA molecules and induced greater energy dissipation. This result is in agreement with morphological and mechanical properties as discussed above.

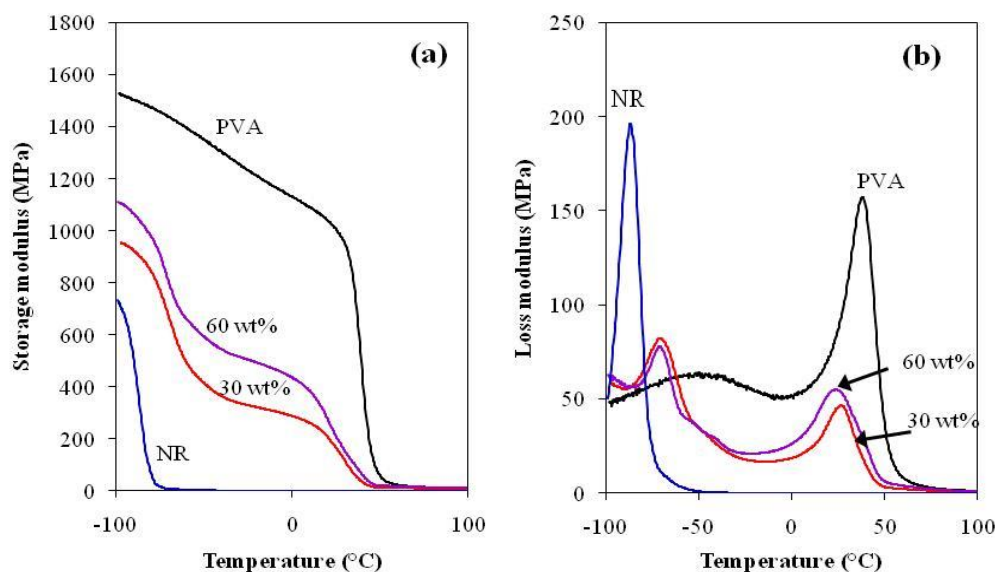


Figure 7. Temperature dependence of (a) storage and (b) loss moduli of PVA, NR and 50/50 w/w NR/PVA blends.

4. Conclusions

From these results, it can be concluded that the solid content of NR latex showed significant effect on morphology, mechanical and dynamic mechanical properties of the 50/50 NR/PVA blends. Increasing solid content of NR latex exhibited reduction of NR particle size in the blends leading to increase in tensile strength and elongation at break of the blends. Moreover, increasing solid content of NR latex from 30 wt% to 60 wt% caused increasing of elastic modulus and shifting of T_g of PVA phase toward lower temperature indicating the enhanced compatibility between NR and PVA phases.

Acknowledgments

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