

Effect Of Epoxidized Natural Rubber (Enr) on Film and Adhesive Properties of Polyvinyl Alcohol (Pva)



Engineering

KEYWORDS : Polyvinyl alcohol (PVA); epoxidized natural rubber (ENR); blend; adhesive and mechanical properties

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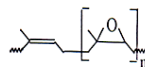
ABSTRACT

Effect of epoxidized natural rubber (ENR) (ENR-12, ENR-27 and ENR-42) incorporated in polyvinyl alcohol (PVA) at various ratios (PVA/ENR = 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100) on adhesive and film properties of different PVA (BF-17, BP-17 and BF-26) was investigated. Incorporation of ENR at 10-30% could improve the film mechanical properties (i.e., increased tensile strength and elongation at break) and adhesion properties (i.e., increased adhesive shear strength and elongation) of the PVA. In particular, PVA/ENR blend prepared from PVA-BF26 and ENR-12 at PVA/ENR ratio of 80/20 exhibited the best adhesive properties. This blend also showed the greatest improvement of mechanical properties of the resulting film, compared to the PVA without ENR incorporation.

1. INTRODUCTION

Poly (vinyl alcohol) (PVA) (Figure 1A) is a biodegradable synthetic polymer which is dissolvable in water and resistant to organic solvents due to its hydrophilicity (Ai et al, 2008). PVA can be used to produce a film for food packaging and widely used to make glue or water-based adhesive applied for papers and woods (DeMerlis and Schoneker, 2003). The properties of PVA vary depending on the molecular weight and degree of hydrolysis, which determine their applications (Skeist, 1990). PVA film is generally tough, clear and resistant to gas and aroma permeation. PVA adhesive possesses high adhesive strength when applied on hydrophilic substrates. In dried state PVA can undergo crystallization and has high interaction between the molecules. Therefore, this sometime makes adhesive from PVA too stiff and rigid. Moreover, PVA is sensitive to water due to its hydrophilicity. As a result, implementation of PVA in the form of film or adhesive at high humidity conditions may encounter a problem due to its swelling and peeling off. Therefore, incorporation of other polymers that are flexible and less sensitive to water into PVA may be the simple mean to improve the properties.

Natural rubber (NR) is a polymer that is soft, flexible and had lower water permeability, which can be incorporated in PVA. However, PVA is a molecule with high polarity or hydrophilicity while the natural rubber molecules are non-polar. Blend of PVA and NR is thus incompatible. Therefore, it requires a chemical structure modification of NR prior to use. Epoxidized natural rubber (ENR) (Figure 1B) is a modified natural rubber in which the epoxy group is incorporated in the structure of NR, which makes it polar. The polarity of the ENR depends on the amount of epoxy content within the molecule and results in different properties (Burfield et al., 1984). Therefore, incorporation of ENR into PVA might improve film and adhesive properties especially the flexibility of PVA. The objective of this study was to investigate the effect of blend composition and different ENR containing various epoxy contents on film and adhesive properties of PVA of different types.



ENR-25 (n = 0.5)

ENR-50 (n = 1.0)

(B)

Figure 1 Molecular structures of PVA (A) and ENR (B) molecules.

2. MATERIALS AND METHOD

2.1 Chemical

Different types of PVA were purchased from Chang Chun Plastic Company (Taipei, Taiwan). The latexes of ENR containing different epoxy contents were prepared according to the standard method reported by Nuntawong (2007). Characteristics and properties of PVA and ENR used in this study are presented in Table 1.

2.2 Preparation of PVA/ENR blends

2.2.1 Preparation of PVA solution

PVA (BF-17, BP-17 or BF-26) was mixed with distilled water at the concentration of 10% (w/v). The mixture was heated at 85 °C with agitation until totally dissolved. The PVA solution was then cooled down to room temperature.

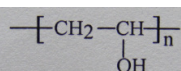
2.2.2 Blending of PVA and ENR

The PVA/ENR blends were prepared in the latex state. Different ENR latexes (ENR-12, ENR-27 and ENR-42) containing 10% dry rubber content were added to the PVA solutions to obtain the final PVA/ENR ratios of 100:0, 90: 10, 80: 20, 70: 30, 60: 40, 50: 50 and 0: 100 by dry weight. The concentration of the blend mixtures was kept constant at 10% (w/v). The mixture was then mixed at 60 °C for 30 min. The blend mixtures were subjected to analysis for adhesive properties. Film samples of 0.100±0.050 mm thickness were prepared from the blend mixtures by casting onto a glass plate (15x15 cm²) at ambient condition (28±3 °C and 72±5% relative humidity (RH)) for 5 days. The dried films were then subjected to mechanical property testing.

2.3 Analysis of the properties of PVA/ENR blends

Properties of PVA/ENR blends were determined in comparison with the control PVA and ENR as following.

2.3.1 Adhesive properties (adhesive test)



(n = 98.5-99.2 %mol)

(A)

Adhesive properties of the blends were determined on plywood substrate. The blend mixture of 2 ml was applied and spread evenly on surface of plywood (2 mm thick). The area of adhesion was 1 x 0.5 inch² (Fig. 2). Then, it was pressed with weight of 5 kg and allowed to adhere and dry for 24 h before testing. Prior to adhesive testing, the obtained samples were conditioned at 25 °C and 50±5% (RH) for 48 h. The adhesive shear strength test was performed on the samples by using Lap shear test according to the ASTM-D1002 method by using a Universal Testing Machine (Lloyd Instruments, Hampshire, UK). The adhesive shear strength (AST) was calculated by the following equation:

$$AST = \frac{F_{\max}}{A}$$

Where, F_{\max} is maximum force and A is lap adhesion area. The elongation at adhesive failure (EAF) was also recorded.

2.3.2 Mechanical properties of the film

Tensile properties of the films were determined according to the standard ASTM-D638 method using a Universal Testing Machine. Prior to testing, the films were conditioned at 25 °C and 50±5% RH for 48 h. The film sample with the gage length of 50 mm was clamped to the load cell of 500 N and subjected to tensile deformation at the cross-head speed of 5 mm/min until the sample was broken. The maximum load and the final extension at break were used for calculation of tensile strength (TS) and elongation at break (EAB), respectively.

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Table 1 Properties of PVA and ENR used in this study.

Properties/characteristics	PVA			ENR		
	PVA-BF17	PVA-BF26	PVA-BP17	ENR-12	ENR-27	ENR-42
Types of PVA	Fully hydrolyzed	Fully hydrolyzed	Partially hydrolyzed	-	-	-
Degree of hydrolysis (%mol)	98.5-99.2%	98.5-99.2%	86-89%	-	-	-
Degree of polymerization	~ 1700	~ 2600	~ 1700	-	-	-
Molecular weight	75,000-80,000	112,000-120,000	84,000-89,000	-	-	-
Epoxy content (%mol)	-	-	-	12±3	27±5	42±5

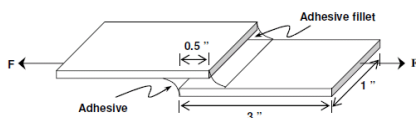


Figure 2 Test specimen used for adhesive shear strength measurement according to the ASTM-D1002.

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sample was broken. The maximum load and the final extension at break were used for calculation of tensile strength (TS) and elongation at break (EAB), respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of types and levels of ENR on properties of PVA with different degrees of hydrolysis (DH)

3.1.1 Adhesive property

Adhesive properties (adhesive shear strength: AST, and elongation at adhesive failure: EAF) of medium-molecular-weight PVA with different DH (fully-hydrolyzed PVA (PVA-BF17) and partially-hydrolyzed PVA (PVA-BP17)) incorporated without and with different types of ENR at various PVA/ENR ratios are depicted in Fig. 3. Regardless of epoxy contents of ENR used, the adhesive shear strength (AST) of both PVA continuously increased when the level of incorporated ENR increased from 0 to 30% (i.e. PVA/ENR = 100/0 to 70/30). For the same PVA type and PVA/ENR ratio, addition of ENR-42 yielded the PVA/ENR blend with higher AST as compared to those incorporated with ENR-12 and ENR-27, respectively. For the same type of ENR incorporated, the PVA/ENR blend using PVA-BF17 (fully hydrolyzed PVA) exhibited higher AST than the blend using PVA-BP17 (partially hydrolyzed PVA). For elongation before adhesive failure (EAF) (Fig. 3B), incorporation of ENR resulted in increased EAF of PVA/ENR blend with increasing ENR levels, compared to that of the control PVA without ENR, irrespective of PVA types. However, when ENR-42 was used, the EAF of PVA/ENR-42 blend decreased as PVA/ENR-42 ratio increased to 60/40 and 50/50. In addition, with the same ENR used, the blend prepared from fully hydrolyzed PVA (PVA-BF17) had higher EAF than did the blend from partially hydrolyzed PVA (PVA-BP17). This result was due to the fact that PVA-BF17 has higher hydroxyl group than did PVA-BP17. This was more likely resulted in higher interaction with epoxy group of ENR (Nakason et al., 2001) and also stronger interaction with cellulose molecules in the plywood, attributed to better adhesive properties.

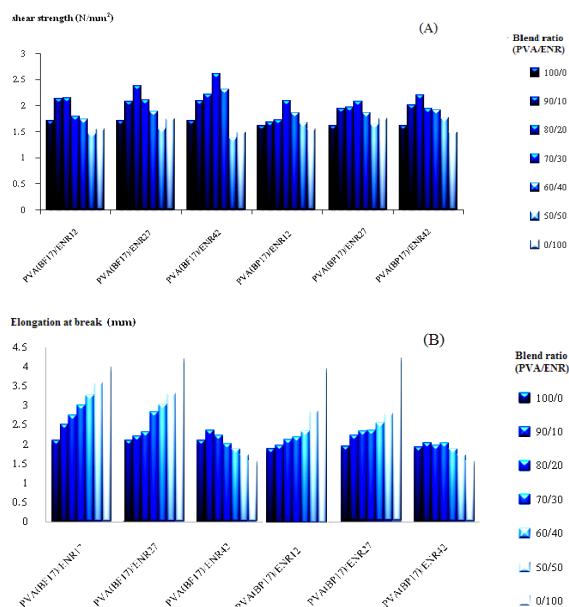


Figure 3 Adhesive shear strength (A) and elongation at adhesive failure (B) of adhesion on plywood of PVA-BF17 and PVA-BP17 incorporated without and with different ENR at various PVA/ENR ratios.

3.1.2 Mechanical properties of the film

Tensile strength (TS) and elongation at break (EAB) of films prepared from medium-molecular-weight PVA of different DH (PVA-BF17 and PVA-BP17) incorporated without and with different types of ENR at various PVA/ENR ratios are shown in Fig. 4. TS of the PVA/ENR blend films increased when the level of incorporated ENR increased up to 30% and then decreased when ENR at higher level was added, regardless of ENR and PVA

types. When compared the properties of PVA/ENR blend films prepared from the same PVA type and PVA/ENR ratio, slight differences in TS were observed in PVA/ENR blend films containing different ENR types. However, for the same ENR used but different PVA, the blend films prepared from PVA-BF17 had higher TS than did those prepared from PVA-BP17.

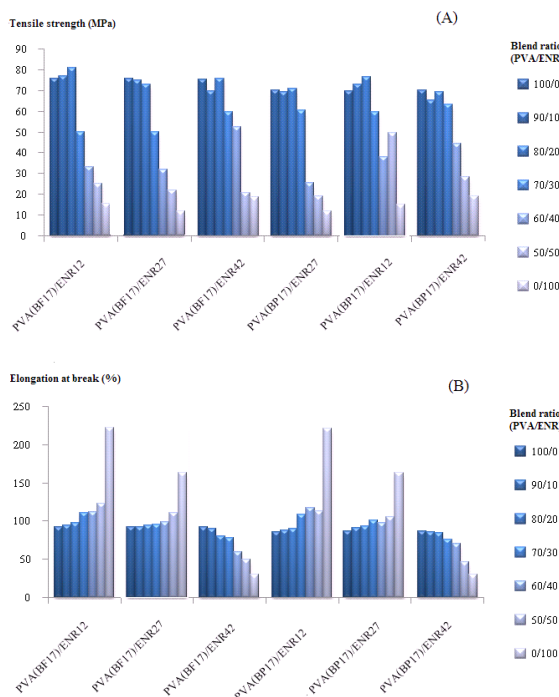


Figure 4 Tensile strength (A) and elongation at break (B) of films from PVA-BF17 and PVA-BP17 incorporated without and with different ENR at various PVA/ENR ratios.

For EAB of the films (Fig. 4B), the blend films prepared from both PVA incorporated with ENR-12 and ENR-27 exhibited increased EAB with continuous increasing level of those ENR used. However, EAB of blend films containing ENR-42 trended to decrease when the level of ENR-42 incorporated increased, especially at the PVA/ENR-42 ratios of 60/40 and 50/50. This was more likely resulted from the larger domain of phase separation. ENR-42 molecules which possess high numbers of epoxy group might prone to interact with themselves and thus forming a large ENR domain. For the same type and level of ENR used but different PVA types, the PVA film and PVA/ENR blend films prepared from PVA-BF17 had higher EBA than did those from PVA-BP17. This was possibly caused by higher amount of OH groups in fully hydrolyzed PVA, which could undergo more interaction with epoxy groups of ENR (Nakason et al., 2001). As a result, the PVA-BF/ENR blend films were generally stronger and tougher than the PVA-BP/ENR counter parts.

3.2 Effect of types and levels of ENR on properties of PVA of different molecular weights

3.2.1 Adhesive property

Figure 5A and 5B show adhesive shear strength (AST) and elongation at adhesive failure (EAF), respectively, of the blends prepared from fully hydrolyzed PVA (PVA-BF) of different molecular weights (PVA-BF17 and PVA-BF26) incorporated without and with different types of ENR at various PVA/ENR ratios. It was found that addition of different ENR types in both PVA resulted in increased AST when the ENR level increased from 10% to 30%. However, the AST of the PVA/ENR blends was decreased when ENR was incorporated at higher levels, most likely due to the larger agglomeration of ENR. For the same type of PVA and PVA/ENR ratio, the blend added with ENR-12 exhibited higher AST than the blends using ENR-27 and ENR-42. The PVA/ENR blends prepared from high-molecular-weight PVA (i.e., PVA-BF26) had higher AST than did the blends obtained from

low-molecular-weight PVA (i.e., PVA-BF17). For the EAF value of adhesion (Fig. 5B), the PVA/ENR blends containing ENR-12 and ENR-27 showed increased EAF with an increase in level of ENR used, irrespective of molecular weights of PVA tested. However, use of ENR-42 at PVA/ENR ratios of 60/40 and 50/50 attributed to decreased EAF of the resulting blends. For the same type of ENR added, the EAF of blends prepared from PVA-BF26 was higher than that of blends from PVA-BF17. This indicated the better adhesive properties toward plywood of higher molecular weight PVA compared to lower molecular weight PVA. Higher amount of OH groups was presumably found in larger size PVA molecules, resulting in greater interaction with the epoxy groups of ENR as well as interaction with hydroxyl and carbonyl moieties of cellulose in plywood at the interface (Nakason et al., 2001). This resulted in better adhesive properties of high-molecular-weight PVA and its blend as compared to low-molecular-weight PVA.

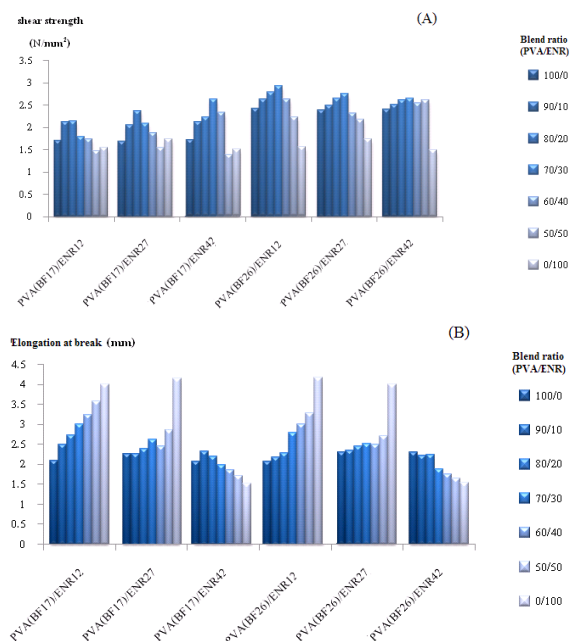


Figure 5 Adhesive shear strength (A) and elongation at adhesive failure (B) of adhesion on plywood of PVA-BF17 and PVA-BF26 incorporated without and with different ENR at various PVA/ENR ratios.

3.2.2 Mechanical properties of the film

Tensile properties of PVA/ENR blends prepared from fully hydrolyzed PVA (PVA-BF) of different molecular weights (PVA-BF17 and PVA-BF26) incorporated without and with different types of ENR at various PVA/ENR ratios were shown in Fig. 6. PVA/ENR blend films showed increased TS with increase in PVA/ENR ratios in the range 90/10 to 70/30, irrespective of ENR and PVA types (Fig. 6A). For the same PVA and PVA/ENR ratio, different types of ENR used showed slight effect on TS of the resulting blend films. However, TS of bend films was dependent on molecular weight of the PVA used. For the same type of ENR and PVA/ENR ratio, the blend films obtained from high-molecular-weight PVA (PVA-BF26) had higher TS than did those from low-molecular-weight PVA (PVA-BF17). When the EAB of films was observed, incorporation of ENR-12 and ENR-27 in both PVA types caused an increased in EAB of resulting PVA/ENR blend films with increasing the ENR levels (Fig. 6B). In contrast, the blend films added with ENR-42 at PVA/ENR-42 ratios of 60/40 and 50/50 showed the decrease in EAB. For the blend films incorporated with the same ENR type and level, those with PVA-BF26 (high molecular weight) had higher EAB as compared to those with PVA-BF17 (low molecular weight). Therefore, tensile performance of the PVA/ENR blend films depended on molecular weight of PVA as well as epoxy content and level of ENR incorporated.

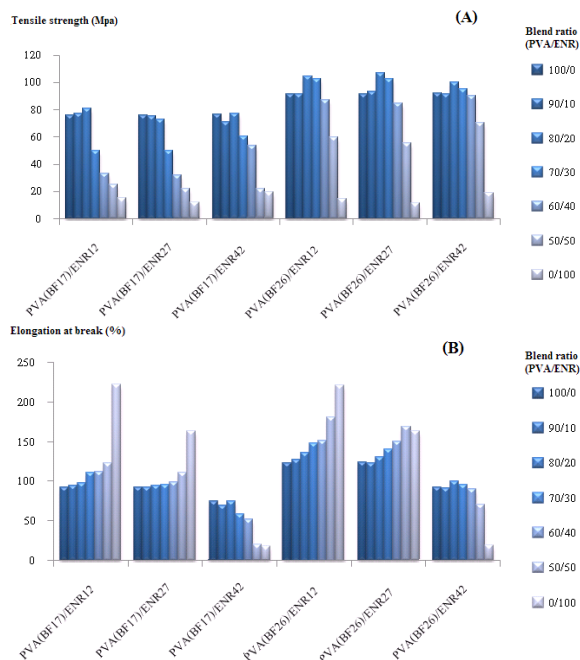


Figure 6 Tensile strength (A) and elongation at break (B) of films from of PVA-BF17 and PVA-BF26 incorporated with-out and with different ENR at various PVA/ENR ratios.

4. CONCLUSIONS

Incorporation of appropriate type of ENR at optimal level could improve the adhesive and mechanical properties of PVA. The properties of resulting PVA/ENR blends were depending on PVA type and molecular weight as well as ENR type (epoxy content) and blend composition. The PVA/ENR blend at 80/20 (w/w) prepared from high molecular weight PVA (i.e., PVA-BF26) and ENR-12 with low epoxy content but more elasticity exhibited the greatest property improvement of PVA in terms of film mechanical properties and adhesive properties. These improved properties were ascribed to the greater interaction between hydroxyl group in PVA and epoxy group in ENR.

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