

Improvement of toughness and water resistance of bioplastic based on wheat gluten using epoxidized natural rubber

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Abstract. Novel blends based on wheat gluten (WG) and epoxidized natural rubber (ENR) were fabricated with different ENR contents of 10, 20 and 30 wt% in an internal mixer. Sulfur vulcanization was used to crosslink the ENR phase in the blends. Comparatively, blends of WG and natural rubber (WG/NR) were prepared in the same condition as the WG/ENR blends. Tensile mechanical properties and impact strength of the WG/ENR blends were investigated and compared with the WG/NR blends as well as pure WG. Moreover, water absorption of pure WG and the WG/ENR blends was also tested. As investigated by scanning electron microscopy (SEM), the results revealed more compatibility between WG and ENR compared with NR. The elongation at break, impact strength and water resistance of the WG/ENR blends were found to remarkably increase with respect to the pure WG. Thus, incorporation of ENR into WG could improve toughness and water resistance of WG. Furthermore, the effect of adding glycerol acting as a plasticizer on the mechanical properties and impact strength of the WG/ENR blends was also studied. The blends with glycerol-plasticized WG (WG-Gly/ENR) showed more homogeneous morphologies and superior results in the mechanical properties and impact strength compared with the WG/ENR blends.

1. Introduction

During the past years, bio-based polymers from renewable natural resources have attracted much attention for academia and industry because of increasing environmental problems. Plant protein-based biopolymers can serve as an alternative to conventional petroleum-based plastics because of their low cost, large-scale availability, nontoxic, and environmentally friendly properties. Compared with other plant proteins, the wheat gluten (WG) has a relative cheap cost, good stability to heat, strong tensile strength and excellent barrier properties [1-3]. However, major drawbacks of WG-based plastics to prevent them from a wide range of applications are their inherent brittleness and high water absorption after being processed. This is due to high degree of the three-dimensional protein network formed by heat-induced covalent crosslinking through disulfide bonds (S-S) of thiol groups (-SH) of cysteine residues in WG peptides and due to hydrophilic nature (polar amino acids) of the protein [4]. To improve the mechanical properties and water resistance of WG plastics, there are various approaches to expand its usefulness in an even wider variety of applications. Plasticizers are widely

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used to add into WG for improving flexibility of the WG plastics. Such plasticizers include glycerol, sorbitol, sucrose, diethanolamine and triethanolamine, and saturated fatty acid [5-8]. However, these plasticizers do not improve the water resistance of the WG, except the later plasticizer. Blending WG with other polymers is one practical way to achieve new polymeric materials with tailor-made properties. Many polymers have been reported to blend with WG in order improve mechanical properties of the protein, for instance, aliphatic polyester [9], poly (hydroxyl ester ether) [10], polycaprolactone [11] and maleic anhydride-modified polycaprolactone [12], poly (vinyl alcohol) [2, 13] and thiolated (vinyl alcohol) [14] and cassava starch [15].

Epoxidized natural rubber (ENR) is a commercial modified natural rubber which is prepared by reacting natural rubber (NR) latex with peroxy acid. ENR possesses excellent elastic properties and toughness, high strength, oil resistance and adhesive properties, and a high degree of damping [16]. Epoxy groups in ENR would improve the polarity of rubber, thereby promoting compatibility with polar polymers in polymer blends. ENR is a promising material acting as toughening agent for many polymers. Some studies on blending of ENR to improve flexibility and impact strength have been reported with polystyrene (PS) [17], poly (vinyl chloride) (PVC) [18], nylon 6 [19], poly (ethylene-co-acrylic acid) [20] and poly (lactic acid) (PLA) [21].

As noted above, many studies have reported blending WG with various thermoplastic polymers. However, based on our knowledge, there have been no reports on blending ENR elastomer into WG. Thus, the objective of this research is to fabricate a new WG/ENR blend which is expected to exhibit good flexibility, impact strength and water resistance with respect to pure WG plastic. In this work, mechanical properties, including tensile mechanical properties and impact strength, as well as water absorption of the blends were investigated. Comparison between WG/NR and WG/ENR blends was also described in terms of mechanical properties and morphology. Moreover, the effect of plasticization of WG by using glycerol as a plasticizer on mechanical properties, morphology and water resistance in the WG/ENR polymer blends is discussed in detail.

2. Experimental

2.1. Materials

Wheat gluten (WG) was supplied by Zhangjiagang HengFeng Starch Products Co. Ltd., China. Natural rubber (NR) of STR 5L grade (Standard Thai Rubber 5 L) was purchased from PI Industry Co. Ltd., Thailand. Epoxidized natural rubber containing 50 mol% of epoxidation (ENR50) was produced by Muang Mai Guthrie Public Co. Ltd., Thailand. Glycerol (Gly) used as a plasticizer, was obtained from Fisher Scientific. In this work, conventional vulcanization (CV) was used to vulcanize ENR phase to enhance tensile strength properties of polymer blends. All chemicals for the conventional vulcanization in ENR including zinc oxide (ZnO), stearic acid (SA), tetramethylthiuram disulfide (TMTD), *N*-tert-butyl-2-benzothiazolesulfenamide (TBBS) and sulfur were used as received. Zinc oxide and stearic acid were used as activators, TMTD and TBBS were added as accelerators, and sulfur was used as a curing agent to vulcanize the rubber phase.

2.2. Preparation of WG/ENR blends

WG was dried in an oven at 80 °C for 24 hr to remove moisture before use. ENR was masticated in an internal mixer (Brabender W50EHT, Germany) at 70°C for 15 min with a rotating speed of 70 rpm. WG and the masticated ENR with various ratios of 100/0, 90/10, 80/20 and 70/30 by weight were mixed together in the internal mixer at 70°C with a rotating speed of 70 rpm for 10 min to prepare premixed blends. To prepare pre-vulcanized WG/ENR blends, all chemicals for curing ENR including zinc oxide (5 phr), stearic acid (1.5 phr), TMTD (0.4 phr), TBBS (0.6 phr) and sulfur (2.5 phr) were added sequentially into the premixed WG/ENR blends for 5 min for each chemical. Moreover, to compare with the WG/ENR blends, the WG/NR blends were prepared at the same condition as described above. In order to study effect of a plasticizer on mechanical properties of the WG/ENR blends, a 20% of glycerol by weight based on WG was homogeneously mixed with WG for 5 min in

Philips Blender HR2115 to obtain glycerol-plasticized WG (WG-Gly) first. The WG-Gly was mixed with the masticated ENR to prepare the premixed WG-Gly/ENR blends and then followed by adding the curative agents into the WG-Gly/ENR blends at the same condition as described above. All blends were compression- molded at 150°C for 5 min at pressure of 1,500 psi by using LabTech compression molding machine to prepare sample specimens for mechanical property and water absorption testing.

2.3. Mechanical property testing

2.3.1. Tensile testing. A universal testing machine (Instron 5969) was used to investigate tensile properties according to ASTM D638-10 type IV. The tensile tests were conducted under ambient condition with a 5 kN load cell and the crosshead speed of 50 mm/min. At least ten specimens were performed for each blend.

2.3.2. Izod impact testing. Izod impact testing, according to ASTM D256-10, was performed on notched impact specimens by using a pendulum impact tester (Zwick model B5102.202 Izod Pendulum 4 J). For each blend, fifteen specimens were tested and the average value of impact energy in kJ/m² was recorded.

2.4. Morphology

Morphology studies of WG and the WG/ENR blends with different ratios were carried out using a scanning electron microscope (SEM; Hitachi Model S3400N instrument). Cryogenic fractured surface of the polymer blends were used to study the morphology of the blends coated with platinum.

2.5. Water absorption testing

All samples of WG and WG/ENR as well as WG-Gly/ENR blends with dimensions of 64.0 x 12.60 x 2.00 mm were dried in an oven at 80°C for 24 hr to remove moisture in the specimens and the original weight of the samples was recorded. Then, the specimens were horizontally submerged in deionized water at a room temperature. At certain times of 5, 15, 25, 35, 50, 60, 120, 180, 240, 720, 1440 and 2880 min, the specimens were taken out from water. The excess surface water was removed with a tissue and weight of the specimen was immediately measured as a function of time. Three replicates were measured for each material at each time point. The percentage of water absorption (%WA) was calculated as shown in equation (1).

$$\% \text{ WA} = [(W_s - W_0)/W_0] \times 100 \quad (1)$$

where W_s and W_0 are weight of a specimen after submersion and before submersion, respectively.

3. Results and discussion

Generally, NR and ENR must be vulcanized to provide the better physical and mechanical properties for engineering application. From this reason, in this work, vulcanized NR and ENR by sulfur was used to improve tensile properties. Typically, rubbers can be vulcanized by two systems: sulfur-cured and peroxide-cured systems. The sulfur vulcanization provides high chain flexibility of the polymer network in the rubber phase due to formation of the mono, di and polysulphidic linkages (C-S-C, C-S-S-C and C-S_x-C, respectively), which more stable than rigid C-C linkages in the peroxide vulcanization [18]. Moreover, in this work, the temperature used for mixing all vulcanizing chemicals and the premixed WG/ENR or WG/NR blends to prepare the pre-vulcanized blends in the internal mixer was 70°C. At this temperature, which is lower than a range of use temperature of sulfur to vulcanize the rubber (120-150°C), possible crosslinking accidents of ENR or NR phase in the blends is avoided during the mixing step.

3.1. Comparison of WG/NR and WG/ENR blends

3.1.1. Morphology of the WG/NR and WG/ENR blends. Scanning electron micrographs of cryogenic fractured surfaces of the WG/NR and WG/ENR blends with ratios of 90/10 and 70/30 are given in figure 1. Regardless of the rubber types, obvious agglomeration of WG on the fractured surfaces and a continuous structure of rubber phase were observed in all blends (figures 1a-1d). Typically, in polymer blends containing rubber, the rubber phase is in form dispersed particles in a matrix after vulcanization. However, the rubber component in our blends was a continuous phase. This observation is similar to PLA/NR blends reported by Yuan et al [22]. This might be because, in fact, the WG mixed into the rubber phase was in powder form. The WG could not melt during the mixing step in the internal mixer, thus it formed agglomeration dispersed in the blends. Compared to the WG/ENR blends (figure 1b), the WG/NR blend with 10 wt% content of NR (figure 1a) showed clearly an appearance of a large number of cracks as well as holes between WG aggregates and NR phase. When NR content in the blends increased (30 wt% content of NR) as shown in figure 1c, some cracks and cavities between WG agglomerations and NR domain were observed. Comparatively, in the 70/30 WG/ENR blend (figure 1d) the size of WG aggregates became smaller than that of the 70/30 WG/NR blend as presented in figure 1c. Moreover, in the 70/30 WG/ENR blend, the ENR domain appeared smooth, while the rough NR domain on the fracture surface was observed in the corresponding WG/NR blend. These results indicated a better compatible morphology as well as a better interfacial adhesion in the WG/ENR blends relative to the WG/NR blends. This might be because the ENR is polar rubber due to a presence of epoxy groups in its structure, while the NR is non-polarity. Hence, blending polar wheat protein and non-polar NR led to incompatible blend due to a great difference in polarity of such polymers. In contrast, in the case of the WG/ENR blend, there is similarity in polarity between WG and ENR and there might be molecular interaction between epoxy groups of ENR and polar amino acids in WG, resulting in an enhancement in compatibility between WG and ENR.

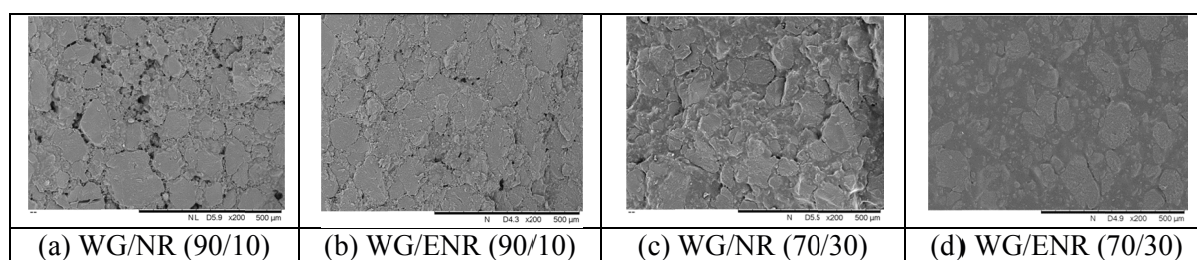


Figure 1. SEM images of cryogenic fractured surfaces: (a) WG/NR (90/10), (b) WG/ENR (90/10), (c) WG/NR (70/30) and (d) WG/ENR (70/30) (x200 magnification).

3.1.2. Mechanical Properties of the WG/NR and WG/ENR blends. Tensile mechanical properties and impact strength of the WG/NR and WG/ENR blends prepared under the same condition are summarized in table 1. Obviously, the addition of either NR or ENR into WG decreased modulus and maximum tensile strength of WG due to a result of the low modulus of the rubbers. In contrast, elongation at break and impact strength of both blends were higher than those of pure WG. Considering the effect of weight percent of the rubbers on the mechanical properties of the blends, it can be seen that modulus and tensile strength continuously decreased but elongation and impact strength values significantly increased as the rubber content increased. However, the WG/ENR blends provided superior results for all tensile mechanical properties and impact strength compared to the WG/NR blends. This is attributed to more compatibility of WG and ENR as illustrated in the previous SEM images in figure 1.

As shown in table 1, incorporating the ENR component into the brittle WG dramatically enhanced elongation at break and also impact strength of the wheat protein. For instance, the WG/ENR blend at ratio of 80/20 provided remarkable improvement of elongation at break from 1.76 to 20.30% (around 12 times) and impact strength from 0.47 to 5.15 kJ/m² (around 11 times) with respect to pure WG.

Table 1. Tensile properties and impact strength of WG/NR and WG/ENR blends.

Polymer blends	Ratio (wt/wt)	Modulus (MPa)	Maximum Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)
WG/NR	100/0	1668.20 ± 142.15	37.70 ± 3.54	1.76 ± 0.20	0.47 ± 0.13
	90/10	415.32 ± 76.10	3.48 ± 0.65	1.08 ± 0.26	1.07 ± 0.29
	80/20	114.31 ± 2.29	2.63 ± 0.41	4.98 ± 0.57	2.95 ± 0.88
	70/30	24.87 ± 2.76	1.92 ± 0.34	18.38 ± 3.68	5.04 ± 0.54
WG/ENR	100/0	1668.20 ± 142.15	37.70 ± 3.54	1.76 ± 0.20	0.47 ± 0.13
	90/10	792.16 ± 42.29	8.83 ± 0.97	1.90 ± 0.19	1.88 ± 0.34
	80/20	286.40 ± 37.95	6.71 ± 0.55	20.30 ± 2.31	5.15 ± 0.21
	70/30	49.17 ± 8.74	4.56 ± 0.63	41.10 ± 3.97	8.34 ± 0.65

3.2. Comparison of WG/ENR and WG-Gly/ENR blends

3.2.1. Morphology of the WG/ENR and WG-Gly/ENR blends. Figure 2 illustrates the SEM images of scanning electron micrographs of cryogenic fractured surfaces of the WG/ENR and WG-Gly/ENR blends with ratios of 90/10, 80/20 and 70/30.

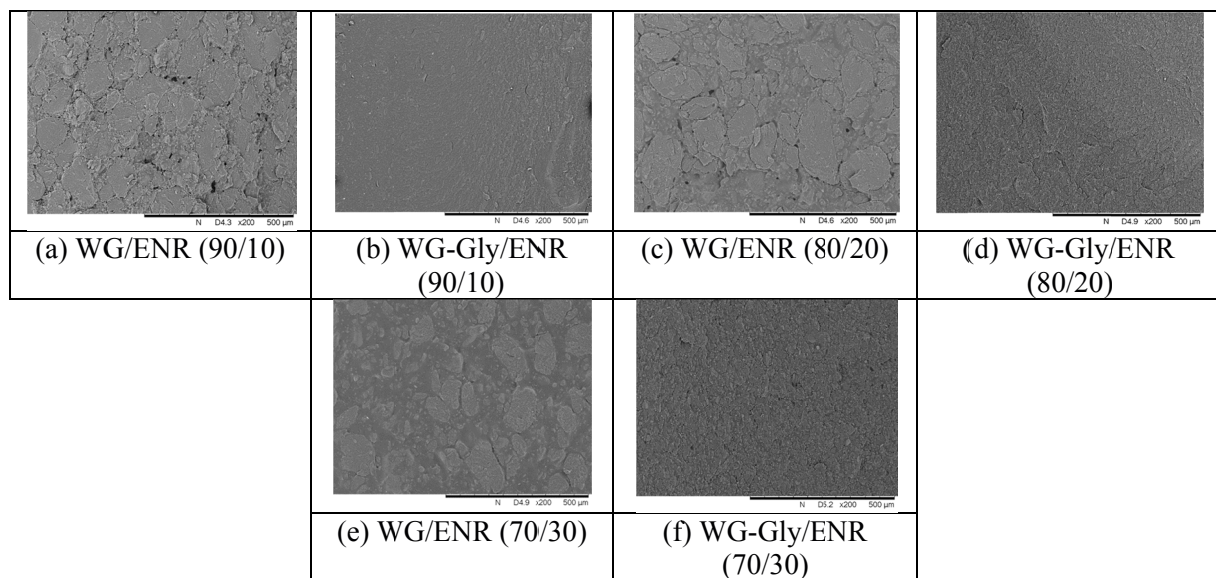


Figure 2. SEM images of cryogenic fractured surfaces: (a) WG/ENR (90/10), (b) WG-Gly/ENR (90/10), (c) WG/ENR (80/20), (d) WG-Gly/ENR (80/20), (e) WG/ENR (70/30) and (f) WG-Gly/ENR (70/30) (x2 00magnification).

Interestingly, it can see clearly that in the blends prepared from plasticized WG as shown in figures 2b, 2d and 2f, there is no appearance of large WG agglomeration compared to the blends prepared from WG without plasticization. The WG-Gly/ENR blend with ratio of 90/10 showed smooth surface whereas rough surfaces were observed in the blends with ratios of 80/20 and 70/30. No appearance of

the large WG aggregates in the WG-Gly/ENR blends is because incorporation of glycerol acting as a plasticizer into WG led to not only a decrease in intermolecular forces, especially hydrogen bonding and electrostatic interactions, between protein chains but also an increase in polymer mobility in WG [23, 24], and thereby providing the better dispersion of WG in the ENR phase during the blending preparation. Therefore, plasticization of WG with glycerol is necessary in order to reduce size of WG aggregates in the blends, resulting in providing more homogeneous blends with respect to WG/ENR blends without plasticization.

3.2.2. Mechanical Properties of the WG/ENR and WG-Gly/ENR blends. The tensile modulus, maximum tensile strength, elongation at break and notch Izod impact strength of pure WG, plasticized WG (WG-Gly) and all blends including the WG/ENR and WG-Gly/ENR blends with various ratios is shown in table 2. As expected, in the WG-Gly, the modulus and maximum tensile strength reduced while the elongation at break and impact strength increased with respect to pure WG. The reduction of the modulus and tensile strength in WG-Gly can be attributed to the fact is that glycerol acting as a plasticizer decreases the glass transition temperature (T_g) of WG, resulting in higher chain mobility of WG. Comparatively, it was found that the all tensile mechanical properties and impact strength of the WG-Gly/ENR blends were higher than of the WG/ENR blends. For instance, the tensile strength, elongation and impact strength of the WG-Gly/ENR blends at low ENR content of 10 wt% increased around 2, 4 and 2.5 times, respectively with respect to the WG/ENR blends at the same rubber content. This result indicated that the plasticization of WG by glycerol significantly enhanced the mechanical and impact properties of the WG-Gly/ENR blends compared to the blends without plasticization. It was well known the mechanical properties of polymer blends depend largely on the resulting the phase structure and morphologies of such blends. Hence, the improvement of the mechanical and impact properties of the WG-Gly/ENR blends resulting from size reduction of WG aggregates in the blends due to the plasticization effect of glycerol in WG as shown in the aforementioned SEM micrographs in figure 2.

Table 2. Tensile properties and impact strength of WG/ENR and WG-Gly/ENR blends.

Polymer blends	Ratio (wt/wt)	Modulus (MPa)	Maximum Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)
WG/ENR	100/0	1668.20 ± 142.15	37.70 ± 3.54	1.76 ± 0.20	0.47 ± 0.13
	90/10	792.16 ± 42.29	8.83 ± 0.97	1.90 ± 0.19	1.88 ± 0.34
	80/20	286.40 ± 37.95	6.71 ± 0.55	20.30 ± 2.31	5.15 ± 0.21
	70/30	49.17 ± 8.74	4.56 ± 0.63	41.10 ± 3.97	8.34 ± 0.65
WG-Gly/ENR	100/0	601.20 ± 48.34	20.92 ± 4.46	3.68 ± 0.34	1.54 ± 0.69
	90/10	508.82 ± 12.31	18.10 ± 1.24	7.91 ± 1.30	4.68 ± 0.23
	80/20	428.40 ± 29.20	14.61 ± 0.87	13.9 ± 1.52	10.53 ± 0.87
	70/30	96.25 ± 15.48	9.54 ± 0.99	29.6 ± 3.04	15.04 ± 0.59

Figure 3 shows typical stress-strain curves of pure WG, glycerol-plasticized WG (WG-Gly) and the WG-Gly/ENR blends with different ENR contents. Obviously, compared to the WG-Gly/ENR blends, the WG-Gly showed more brittle fracture with high modulus and tensile strength but low elongation. In contrast, when the ENR was added into the plasticized WG, more ductility was observed. Considering areas under the stress-strain curves of all samples, it was found that the area under the

curve, correlated to toughness of the sample increased as the concentration of ENR in the blends, indicating that incorporation of elastomeric ENR into WG remarkably enhanced toughness in the polymer blends.

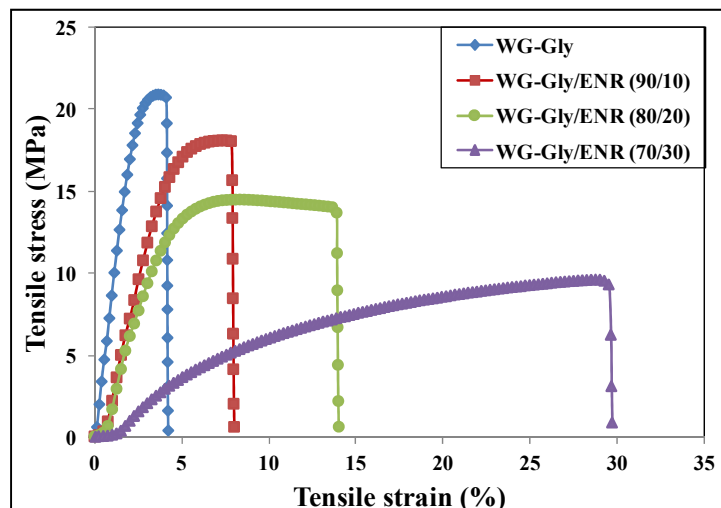


Figure 3. Typical stress-strain curves of WG-Gly and the WG-Gly/ENR blends with different ENR contents.

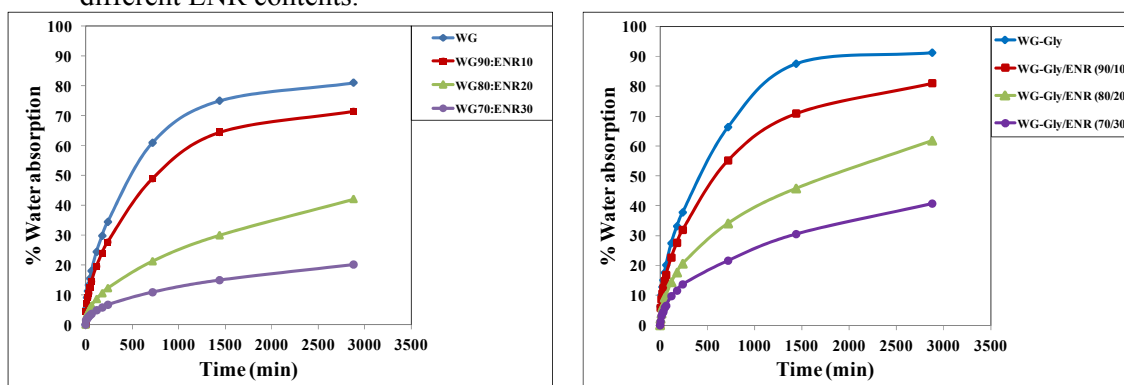


Figure 4. %Water absorption of a) WG/ENR blends and b) glycerol-plasticized WG/ENR blends.

3.3. Water absorption property

Water absorption of polymer blends is one of important properties for evaluating their stability on water affecting their long-term performance. The result of the percent water absorption (%WA) data of pure WG and the WG/ENR blends is illustrated in figure 4a, while %WA data of glycerol-plasticized WG (WG-Gly) and glycerol-plasticized blends (WG-Gly/ENR) is presented in figure 4b. From figure 4a, it can be clearly seen that pure WG absorbed much more water than did the WG/ENR blends. During 2 days of the testing, WG absorbed 80% of its original weight in water, indicating very poor water resistance of the WG plastic whereas %WAs of the blends were lower than 70%. Thus, incorporation of ENR rubber into WG significantly improved the water resistance of the blends compared with that of the pure WG because ENR is the hydrophobic natural rubber, while WG has hydrophilic nature due to polar amino acids in WG structure, resulting in a high degree of water absorption. Considering the WG/ENR blends, %WAs of the blends with ratios of 90/10, 80/20 and 70/30 were around 70, 40 and 20%, respectively. Thus, the water resistance of the blends increased with an increase of rubber content in the blends due to a presence of higher non-polar rubber content in the blends, thereby reducing water diffusion in the blends. In the case of the WG-Gly/ENR blends (figure 4b), a decrease in the water absorption as the rubber content was observed, similar to the result

of the WG/ENR blends. For comparison of %WA of the WG/ENR and the WG-Gly/ENR blends, the WG-Gly/ENR blends provided higher water absorption with respect to the WG/ENR blend without the plasticizer. This might be because hydrophilic hydroxyl groups in glycerol molecules can absorb water, resulting in a high degree of water absorption in the plasticized WG-Gly/ENR blends.

4. Conclusions

The WG/ENR and WG/NR blends with various weight ratios of 90/10, 80/20 and 70/30 were fabricated in this work. The ENR provided more compatibility with WG than did NR as shown in the SEM results. More compatibility of the WG/ENR blends led to higher mechanical properties and impact strength of with respect to the WG/NR blends. Moreover, the influence of addition of ENR on mechanical and impact properties, morphologies and water absorption of the blends were studied compared with the pure WG. Incorporation of ENR tremendously enhanced the elongation at break, impact strength and water resistance of the blends compared with the pure WG. On the other hand, modulus and maximum tensile strength decreased as an increase in ENR content. Hence, addition of ENR into WG led to an enhancement of the flexibility and water resistance in the blends with respect to pure WG. The effect of adding glycerol plasticizer to WG on the tensile mechanical properties, toughness and water absorption were also investigated with respect to the blends without plasticization. From the SEM micrographs, compared to the WG/ENR blends, it was found that the aggregate size of WG in the blends dramatically decreased and more homogeneous morphologies was observed in the WG-Gly/ENR blends. This is due to a plasticization effect, which reduced intermolecular forces, such as hydrogen bonding and electrostatic interactions between the protein chains. From this result, the mechanical properties and toughness of the WG-Gly/ENR blends were higher than those of the WG/ENR blends. However, the WG-Gly/ENR blends showed lower the water resistance than the blends without glycerol plasticization due to a presence of hydrophilic glycerol in the blends.

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