Effect of Glycerol on Gluten filled in Natural Rubber/WG Blend

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Abstract. In recently, a large number of utilization of NR has been found in several applications such as foam, insole but they do not provide good properties. In order to improve mechanical properties, in this work, wheat gluten (WG) which is a complex protein derived from wheat was used as a reinforcement. Furthermore, NR with WG (plasticized WG) can reduce costs of materials and easily degrade. NR-WG blend was prepared by mixed NR and WG, plasticized by glycerol, then mixed each other by using two rolls mill and compressed to get specimens. SEM, MDR, tensile testing and tear testing were used to characterize compounds. The effect of glycerol contents added and acting as plasticizer were also studied. The results show that the presence of glycerol also affected vulcanization behavior of rubber matrix. The increasing of glycerol content can also improve dispersion of WG in rubber matrix and indeed improve mechanical properties of NR.

1. Introduction

Natural rubber (NR) is widely used in several because its available is chosen for its resilience, resistance to fatigue, low heat built up, to be able to apply over a wide range of operating temperatures. Nevertheless, its vulcanizate is not good enough properties any applications [1-2]. WG is low cost, has good film forming ability and oxygen barrier properties, and has been explored as a biodegradable packaging material. WG can be compressed in a compression mold, which encourages hydrophobic interactions and can induce aggregation and crosslinking, thereby increasing tensile strength while lowering elongation to break [3]. Commercial applications require the stability and reliability for their raw materials sources. Wheat is desirable feedstock for commercial applications because its supply is stable. Wheat gluten is among the largest and most complex protein networks in nature with molecular weight of more than 10 million and is consisted of spherical gluten particles. Wheat gluten is also a low cost raw material and is rarely studied as reinforcements in rubbers. Dry wheat gluten is rigid with a storage modulus of 1 GPa and therefore should provide reinforcement for soft polymers such as rubbers. Reinforcement fillers from natural sources are sustainable, light weight, carbon neutral, biodegradable, and renewable [4-5]. Wheat gluten containing plasticizer is able to form network upon thermosetting. Glycerol is usually used as a plasticizer to reduce intermolecular forces and the glass transition so as to increase chain mobility of proteins [6].

As noted above, some studies have reported about blending WG with various thermoplastic polymers. However, based on our knowledge, there have been no reports on blending WG into NR. Thus, the objective of this research is to fabricate a new NR/WG blend which is expected to present good mechanical properties with respect to NR pure. In this work, mechanical properties, including
2. Experimental

2.1 Materials

Wheat gluten (WG) was supplied by Chemipan Co. Ltd., Thailand. Natural rubber was produced by Muang Mai Guthrie Public Co. Ltd., Thailand. In this work, to improve mechanical properties of blends, conventional vulcanization (CV) was used to cure NR phases in blends. All chemicals for vulcanization in the rubber phase were used as received including activators, Zinc oxide (ZnO) and stearic acid, accelerators, tetramethyl thiuram disulfide (TMTD) and 2-Mercaptobenzothiazole (MBT) and sulfur as a vulcanizing agent.

2.2 Preparations

Firstly, wheat gluten (WG) was mixed with glycerol with the content of glycerol of 25, 30, 35, 40, 45 and 50 phr. with respect to WG. WG and glycerol were hand-mixed in a bowl to form glycerol plasticized WG. The samples were rested overnight at room temperature before mixing with NR. The 30 percent by weight of WG (after plasticization) was mixed with NR and masticated on a two roll mill (Lab Tech, Thailand) at 60 °C for 40 min. After that the temperature of rolls was set to 40 °C before the incorporation of the following vulcanizing agents which are ZnO (3 phr.), stearic acid (2 phr.), MBT (1.5 phr.), TMTD (0.2 phr.) and sulfur (2 phr.) were added consecutively into the masticated NR/WG blends. The vulcanization behavior of all blends were investigated using MDR (Moving Die Rheometer, Go Tech M2000), at 150 °C, to estimate scorch time (t_s2) and cure time (t_c90) which the latter characteristic time will be used as vulcanization time in compression molding machine. All NR/WG with various glycerol contents were compressed at 150 °C under 1500 psi using compression molding machine (Lab Tech. Thailand). The vulcanized NR/WG slabs were obtained and used to prepare test specimens for tensile testing, tear testing.

2.3 Characterization

2.3.1 Tensile testing

Vulcanized NR/WG was shaped into dog bone specimens (follow ASTM D412) using pneumatic cutting machine (Chareon Tut, Thailand). Tensile test was conducted according to ASTM D-412 using a universal machine (Instron Crop, model 5969) at room temperature with a 5 kN load cell and test speed of 500 mm/min.

2.3.2 Tear testing

Tear specimens were also obtained by cutting vulcanized NR/WG blends using pneumatic cutting machine. Tear test was conducted according to ASTM D-624 using a universal machine at room temperature with a 5 kN load cell and test speed of 500 mm/min.

2.3.3 Morphological testing

A scanning electron microscope (SEM, Hitachi TM3030) was used to investigate the surface morphology of cryogenic fractured vulcanized NR/WG blends. The fractured surfaces of all specimens were gold sputtered in order to induce surface conductivity before investigation under SEM.

3. Results and discussion

3.1. Cure Characteristic parameters of NR/WG blends

In term of rubber goods, rubber compounds are needed to be examined for their vulcanization characteristic such as, scorch time (t_s2), cure time (t_c90). These parameters are related to reaction induction time and curing time used for vulcanization of rubber compounds. Moreover rheological properties of rubber compounds such as minimum torques, ML, and maximum torque, MH, of rubber compound and vulcanized rubber under disc rotating are also investigated. NR/WG blend with various glycerol examined under MDR obtain t_s2, t_c90, ML, MH and cure rate index, CRI. The results are showed Figure 1 and Figure 2. The difference between MH and ML denoted as different torque, DT, which is related to modulus of vulcanized rubber, is also obtained ad showed in Figure 2.
It could be seen from the results in Figure 1 (a) that the presence of WG results in slightly decreased of scorch time. Kongkaew and coworkers [7] has reported that the presence of protein in rubber could shorten in scorch time due to maillard effect of protein in which protein could undergo crosslinking. While the glycerol content is increased, the decreased in scorch time was resulted. This could be due to the plasticization of WG and could be able to be sheared during mixing to small particles. The small particles led to being increased surface area of WG particles. This results in the increase in the interaction between WG and curing agents. In the case of NR/glycerol 30 phr., scorch time appeared to be very short. It is important to note that glycerol could also plasticize NR matrix and facilitate the dispersion of curing additive to localize in rubber matrix. Hence the vulcanization induction time is shortened. It was not the case for cure time, Figure 1 (b) where additives undergo chemical reaction with rubber molecules. Glycerol could interact with fatty acid as well as with accelerator thus vulcanization reaction was retarded led to prolong of t₉₀.

**Figure 1** Cure characteristics of NR/WG compound with various glycerol contents in WG (a) Scorch time, tₛ₂ (a) and (b) cure time for 90% vulcanization, t₉₀.

In term of rheological parameter, as shown in Figure 2 (a), i.e. minimum torques, ML, which indicated the viscosity of rubber compound including filler distribution during disk oscillation in MDR. NR compound shows ML around 0.125 N-m whereas the presence of WG leads to increasing of ML. This is due to the obstruction of large WG particle, as can be seen from SEM micrograph in the next section, and hence results in slightly increased ML. The well distribution of WG would also results in difficulty of rubber flow during oscillating shear and results in increased ML. The more dispersion the more rubber flow obstruction occurred. Hence high glycerol content lead to better dispersion and distribution of WG occurred and consequently increased ML. However, ML of NR/WG with glycerol contents seem to show relatively unchanged at glycerol content from 30 phr. In the case of NR/Glycerol, ML is very low compared to other NR/WG compounds. This should be due to the plasticization effect of glycerol on NR. In term of maximum torque, MH, it is important to note that maximum torque is related to stiffness of vulcanized rubber. The addition of reinforcement into vulcanized rubber should result in high MH. In addition, degree of crosslink should also lead to high MH. As shown in Figure 2 (b), addition of WG leads to increased in MH. This is owing to the high strength of WG. The improved dispersion and distribution of glycerol plasticized WG in NR result in better adhesion and hence promoted reinforcing effect of WG in NR. The increased of maximum torques, MH then obtained. Generally gluten could be crosslinked during kneading [8] that also result in increasing of MH. In fact delta torque, DL, relates to crosslink density of the vulcanized rubber. Thus it should show the same trend as MH. Excess glycerol could also act as plasticizer for NR [9] and this could result in slightly decreased in MH for NR containing WG plasticized with glycerol 50 phr.
In the case of cure rate index which obtain from the following equation; \( \frac{100}{(t_{90}-t_{2})} \), relate to curing reaction rate of rubber compound. The result is presented in Figure 2 (d) and indicated that vulcanization reaction might be retarded by glycerol localized in WG phase.

Figure 2 (a) Minimum torque (ML), (b) maximum torque, (c) delta torque (DT) and (c) Cure rate index (CRI) of NR, NR/30Glycerol, NR/WG with various glycerol contents.

3.2. Morphology of NR-WG

SEM images of cryogenic fractured surface of NR/WG with various contents of glycerol are shown in Figure 3. The results show that NR and WG are immiscible blend due to the high polarity of WG therefore they are not compatible. Glycerol has been one of many plasticizer used for WG. The addition of glycerol into WG, it could be soften and consequently broken to smaller particles and enhance distribution of WG in NR as could be elucidated from Figure 3 (a)-(f). The particles size of WG was decreased with the contents of glycerol. As could be seen from WG particle presents in Figure 3 (a) that it was reduced from 60 \( \mu \)m to about 3 \( \mu \)m in Figure 1 (e). With high plasticizer content, such as at 50 phr., WG started to swell and could be sheared into smaller particles as seen in Figure 3 (f) where the particle size are less than 3 \( \mu \)m. In addition, at high glycerol content could lead to elongated WG particles, as seen from the Figure. Excess of glycerol could also plasticizes NR matrix as shown by the tensile properties, especially elongation at break, see section 3.3.
3.3. Tensile Properties

The results from tensile stress and tensile strain curves of NR/WG blends with various contents of glycerol depicted in Figure 4 (a). The results show that the increased in glycerol content self reinforcement of vulcanized NR/WG increased. This could be due to the plasticization effect of WG by the addition of glycerol. As shown in SEM that the higher the glycerol added the WG particles will be sheared to small particles and well distributed in NR matrix. This results in increasing reinforcing effect of WG on NR matrix, as shown in the increasing of secant modulus at 100% tensile strain. Furthermore, increased contents of glycerol enhance tensile stress due to the stress induced crystallization of NR matrix which was promoted also by the well distribution of WG. The ability to elongate, inducing rubber chain to be aligned parallel with stress direction, should be facilitated by the plasticization effect of glycerol. The plasticization effect including well distribution and dispersion of WG particles results in increased elongation at break of NR/WG blend. However, at 50 phr. of added glycerol, with respect to WG, gave rise to largest elongation at break due to excess plasticization effect of glycerol on NR matrix, i.e. facilitating rubber molecules to be slippage under tension. At this glycerol content may slightly affect secant modulus of the vulcanized rubber. This is general for polymer that the addition of plasticizer could result in low modulus [10-11]. For stress induced crystallization of vulcanized rubber, it is not the same case as ductile plastic, as vulcanized rubber is an elastomer which it could be stretched to more than 1000 % elongation. This is because the polymer chains, i.e. rubber chains, are in rubbery state. Hence the crosslinked chains could be conformed in to a large number of conformations and the stretched specimen size is reduced during being stretched. Crosslink points in the specimen act as linkage to resist stretching of the chain. This is the reason why rubber chains that being stretched to the higher strain will exhibit high resistance to elongate. Schematic picture explains how crosslink in vulcanized rubber affect the high stress at break, tensile strength, is showed in Figure 5. After understanding in stress (or strain) induced crystallization of vulcanized rubber under tension (stretching), one should consider effect of plasticizer that it facilitates the mobility of chain segments [12]. Hence polymer molecules should be able to be stretched to higher strain and consequently enhanced stress induced crystallization. It should also comprehend that stress (or strain) induced crystallization could also know as stress (or strain hardening).
Figure 4 (a) Stress-strain curves, (b) secant modulus, (c) tensile strength and (d) elongation at break of NR/WG with glycerol content at 25-50 phr. with respect to WG.

Figure 5 Relatively short chains are drawn as thick lines. Filled circles represent crosslinks. (a) Before deformation (b) after deformation just before the onset stress induced crystallization and (c) the fully stretched chains have acted as chains alignment (shaded parts). [12]

3.4. Tear Testing
Tear resistance, presented by tear strength, of NR/WG with various plasticization of WG by adding various content of glycerol is depicted in Figure 6. It can be seen that tear strength was increased with the increased contents of glycerol added into WG. This could be due to two reasons. Firstly, as glycerol content was increased WG would be well distributed and dispersed in NR matrix resulting in the promoted adhesion between WG and NR. Also the mallard reaction in WG could lead to the increased in tear resistance of NR/WG blend.
4. Conclusions

It should be bear in mind that this part of the work, we studied effect of glycerol contents on NR/WG blend vulcanizate where WG content is fixed at 30 % by weight. The fabrication of NR/WG blends with various contents glycerol in WG was varied as 25, 30, 35, 40, 45 and 50 phr. with respect to WG were carried out. The higher contents glycerol added to WG lead to more plasticization of WG and softening of WG. This gives rise to well dispersion and distribution of WG in NR as evidence by SEM micrographs. The distribution and dispersion of WG in NR will result in adhesion and compatibility between WG and NR results. The adhesion between NR and WG led to enhancement in tensile properties and tear properties.

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