Foamability of Natural rubber (NR)/Poly(butylene adipate-co-terephthalate) (PBAT) Thermoplastic Vulcanizate with OBSH as a blowing agent

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Abstract. Natural rubber, NR, is bio-based material that is generally used for foam preparation as it results in good softness and high resilience. Among many applications, NR foam/sponge is often used for shoe sole either insole or outsole. Likewise, rubber sponge is very important for healing Plantar Fasciitis as rubber sponge is soft, elastic and capable in impact absorption. NR is in fact non-biodegradable resulting in increasing of waste which is a hot issue at present. Huge interest has paid attention in using biodegradable polymer in various products and applications. Polybutylene adipate-co-terephthalate, PBAT, is one of many bioplastics that possesses biodegradability characteristic. It also shows excellent flexibility similar to elastomer. Many attempts have been focus on blending this polymer to improve toughness in brittle plastic. Our research is aimed to incorporate PBAT into NR and producing thermoplastic vulcanizate. NR/PBAT TPV foam is then produced using 4,4’-Oxybisbenzenesulfonyl hydrazide (OBSH) as a blowing agent. The ratios of NR/PBAT are varied as follow: 70/30 65/35 60/40 55/45 50/50 45/55. The polymer blends were mixed on a two-roll mill with the formulation of ZnO 3 phr, luperox 101 1 phr and OBSH 10 phr. Compression molding was used in order to prepare rubber sponge at 160 °C, 1500 psi. Cell size, cell size distribution, density and compression set of NR/PBAT foam were investigated.

1. Introduction

Rubber foams, or sponge, have been known for their excellent absorption properties, light weight soft, low density and well supports weight. They often used for products such as pillows, mattresses, seat cushions, insoles, packaging, agriculture, construction, transportation, thermal and acoustic insulation and other fields. Nowadays, plastic foam such as PS foam, PU foam is popular nonetheless they cause huge wastes and pollution. Polybutylene adipate-co-terephthalate, PBAT is semi-crystalline biodegradable polyester but its crystallinity is quite low due to the structural crystallization obstruction. The elastomeric like characteristic of PBAT is interesting that it is able to apply for thermoplastic elastomer. Thongpin and Buaksuntear prepared thermoplastic elastomers from natural rubber and Poly(butylene adipate-co-terephthalate), NR/PBAT blends [1]. They found an excellent elastomeric behavior and they continue their study in preparation of NR/PBAT thermoplastic vulcanizate [2]. It showed also good tension set of the prepared TPV. Previous studies have brought us...
to this that aims to apply NR/PBAT TPV for foam formation using 4,4'-Oxybis-benzenesulfonylhydrazide, OBSH, as a blowing agent. In recent study, the effect of PBAT phase on foaming ability on foam properties will be reported.

2. Experimental

2.1. Materials
Natural rubber (STR5L) was obtained from CHAREON TUT Co. Ltd. Thailand. Polybutylene Adipate-co-Terephthalate (PBAT), Ecoflex F blend with the grade of C1200 was obtained from POLYMAT Co. Ltd. Thailand. 4,4'-Oxybis-benzenesulfonylhydrazides, OBSH, used as a blowing agent and ZnO were kindly supplied by Chemical Innovation group, Thailand. 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane) has code name of Luperox 101 was obtained from SIGMA-ALDRICH Co. Ltd. Thailand.

2.2. Preparation of PBAT modified
PBAT and NR were dried in an oven at 80 °C for 6 h before blending to minimize the effect of moisture. PBAT and luperox 101 1 phr were fed into an internal mixer (Brabender Mixer Docking Station W50EH series) at 160°C for 10 min with a rotor speed of 100 rpm. Confirming the crosslinking reaction between PBAT and luperox 101 by examining its gel content.

2.3. Gel fraction measurement
The gel fraction of PBAT and PBAT modified was determined by equation (1) using dichloromethane as solvent. Reacted PBAT was soaked and kept in a vial. Subsequently PBAT gel was dried in a hot air oven at 80 °C for 6 hrs.

\[
\text{Gel fraction} = \frac{W_g}{W_0} \times 100\% \quad \text{eq. 1}
\]

Where \(W_0\) is original weight of sample, \(W_g\) is dried insoluble gel.

2.4. Preparation rubber compound and rubber foam
NR was masticated on a two-roll mill (Labtech Co. Ltd. Thailand) for 30 min at 50 °C then PBAT was fed into the masticated on the roll at 130 °C. The ratios of NR/PBAT are as follows: 70/30, 65/35, 60/40, 55/45, 50/50, 45/55. 3 phr of ZnO was then added. After decreasing of roll temperature, 1 phr of Luperox 101 and 10 phr of OBSH were filled and mixed thoroughly. Other compounds were mixed in the same manner except for PBAT in which reacted PBAT was used instead of PBAT pellet. After obtaining NR/PBAT compounds, they were tested using MDR, Gotech2000, Taiwan, at 160 °C to evaluate characteristic parameters. Then foaming process was carried out using compression molding (CHAREON TUT Co. Ltd. series PR1D-W300L350 Thailand) at 160 °C under pressure of 1,500 psi.

2.5. Characterization

2.5.1. Tensile properties
Tensile properties of NR/PBAT foams were conducted according to ASTM D 412-06a using universal testing machine (Instron Crop, model 5969) with a load cell of 5 kN and crosshead speed of 500 mm/min. Modulus of elasticity, ultimate tensile strength and percentage elongation at break were obtained.

2.5.2. Foam density
The density of NR/PBAT foams was measured using Mettler Toledo JE 703 C Carat Scale with Internal Calibration, density kits and accessories were used for determined density in water.

2.5.3. Compression set
Foams were cut into the 2.0 cm × 2.0 cm × 1.0 cm. The compression set was conducted according to ASTM D3574. The specimens were compressed to 50% compressive strain specimens were kept between the plates and put in a hot air oven at 70°C for 22 hrs. After that the samples were taken out
from the oven and released from the plates. The specimens were allowed to recover for 30 min at ambient temperature. The compression set value \( C_t \) was then calculated by using equation (2)

\[
C_t = \frac{(H_0 - H_f)}{(H_0 - H_w)} \times 100\%
\]

eq. 2

Where \( H_0 \) is original height of sample, \( H_f \) is final height of sample, \( H_w \) is height of compressed specimen.

2.5.4. Morphology Investigation

Gold sputtered Scalpel cut foams were examined for their morphology in cross-section area using Hitachi TM3030 scanning electron microscopy under an accelerating voltage of 15 kV. The cell size of foam was measured from SEM micrographs using Image J program to determine cell size of foam. The measurement was carried out from the cell foam at least 100-150 cells.

3. Results and discussion

3.1 Morphology of NR/PBAT TPV foam

The cell morphology of NR/PBAT TPV foam and NR/modified PBAT TPV foam are displayed in Figure 1 and 2. Generally foamability of crosslinked polymer is dependent upon gas produced from blowing agent, distribution of blowing agent in polymer and viscosity of crosslinked polymer [3]. Elasticity of polymer also affect foam characteristic [4]. It is noticeable from Figure 2 (a) – (c) that cell size of NR/PBAT foam is increased with NR content. This could be due to the solubility of blowing agent in NR is better than in PBAT [5, 6]. Moreover, under processing in compression mold PBAT was in melted state whereas viscosity of NR was increased while crosslinking reaction was increased. Thus, NR phase could hold gas produced from decomposition of blowing agent better than PBAT. As shown, high PBAT content, foam cell skin is thicker than high NR content [7].

![Figure 1. Morphology of NR/modified PBAT TPV foam with various ratio at (a) 70/30, (b) 65/35, (c) 60/40, (d) 55/45, (e) 50/50, (f) 45/55](image)

In the case of foam prepared from NR/modified PBAT, cell size distribution seems to show binodal distribution. Structure of foam cell was found to be changed from the previous TPV system. Luperox101 modified PBAT melted mixed with NR compound resulted in the elongated cell foam structure rather than spherical cell foam. In fact, the presence of peroxide in PBAT not only lead to crosslinking of PBAT but also degradation of PBAT [8]. The evidence confirmed by onset temperature under TGA experiment from Table 1. The degraded PBAT could act a either plasticization or lubrication during foaming of NR/modified PBAT hence the viscosity of polymers
during foaming was lower than NR/PBAT. The pressure gas produced could expand foam skin. Nonetheless foam skin could not expanded in the direction perpendicular to mold surface whereas it could in the transverse direction to the mold. The foam structure obtained could be schematically drawn and depicted in Figure 4.

![Figure 2. Cell morphology of NR/PBAT TPV foam, NR/PBAT TPV ratio follow by (a)70/30, (b)65/35, (c)60/40, (d)55/45, (e)50/50, (f)45/55](image)

**Figure 2.** Cell morphology of NR/PBAT TPV foam, NR/PBAT TPV ratio follow by (a)70/30, (b)65/35, (c)60/40, (d)55/45, (e)50/50, (f)45/55

![Figure 3. TGA thermograms of modified PBAT TPV and PBAT TPV](image)

**Figure 3.** TGA thermograms of modified PBAT TPV and PBAT TPV

| Formular      | T_{onset} (°C) | T_{d} (°C) | T_{endset} (°C) |
|---------------|---------------|------------|-----------------|
| modified PBAT TPV | 360.18       | 404.56     | 427.26          |
| PBAT TPV      | 374.17        | 405.85     | 430.96          |

**Table 1.** TGA data of modified PBAT TPV and PBAT TPV

In addition, phase morphology of foam cell skin showed phase separation between NR and modified PBAT. This could be due to the crosslinked PBAT possessed high viscosity intensify incompatibility between NR and PBAT phases.
3.2 Density of NR/PBAT TPV foam
Density of NR/PBAT TPV foam compared with NR/modified PBAT TPV foam are presented in Figure 5. It should be reminded that cell structure of NR/modified PBAT and its morphology should be elongate and phase separated respectively. These should affect its lowered in bulk density of the foam.

![Figure 5. Cell density and bulk density of NR/PBAT TPV foam compared with NR/modified PBAT TPV foam.](image)

3.3 Tensile properties of NR/PBAT foam
Tensile properties, i.e. Young’s modulus, tensile strength and elongation at break, of NR/PBAT TPV foam compared with NR/modified PBAT TPV foam are present in Figure 6 (a)-(c). Considering Young’s modulus of the foams showed in Figure 6 (a), they tend to be increased with PBAT contents due to PBAT having higher modulus than NR [9]. NR/PBAT TPV foams show higher Young’s modulus in all NR/PBAT contents that the foam with modified PBAT. As mentioned earlier that PBAT could also be degraded by the addition of peroxide and disadvantaged on both Young’s modulus and tensile strength of the foam containing modified PBAT. In term of Elongation at break of the foam, although skin of cell foam thickness was increased with PBAT content, elongation at break was still decreased. This was caused by the phase separation between these two polymers. In the foam system containing modified PBAT, phase separation between crosslinked PBAT and NR are intensified, as seen from SEM micrographs. This consequently resulted in lowering in elongation at break of NR/PBAT TPV foam than NR/modified PBAT TPV foam.
Figure 6. The tensile properties of NR/PBAT TPV foam compared with NR/modified PBAT TPV foam (a) tensile modulus, (b) tensile strength and (c) elongation at break.

3.4 Compression set of NR/PBAT foam

It is generally known that factors that affected compression are Low compression set values that indicate excellent elasticity and durability for long-term supporting material [10]. The results from Figure 7 shows that the higher the NR content the lower compression set. This indicates that NR has excellent elasticity and resilience. After compressive load releasing, foam can be recovered to nearly original dimension. Generally, good TPV should possess compression set less than 50% [11]. In addition, NR/modified PBAT TPV foam seems to showed even low compression set. This could be due to thicker skin of cell foam in NR/PBAT TPV foam than the other foam system. In which, they can support long term compression loading [12].

Figure 7. Compression set of NR/PBAT TPV foam compared with NR/modified PBAT TPV foam.

4. Conclusion

The NR/PBAT TPV and NR/modified PBAT TPV foams were successfully prepared using OSH as a blowing agent. The foamability of both foams systems was compared. SEM micrographs show foams morphology and cell size of the foams. The results also show that cell morphology and cell size distribution are dependent both on NR/PBAT contents and modification of PBAT. Luperox101 treated PBAT resulted in crosslinking as well as degradation of PBAT and this affected the viscosity of blown polymer during foaming in the mould. The crosslink PBAT domains caused phase separation between NR and PBAT and hence cell foam structure. The cell foam skin thickness also changed from spherical like cell structure to elongated cell foam structure. These also resulted in the lowered density for NR/modified PBAT TPV foam. In term of tensile properties, Young’s modulus of NR/PBAT TPV foam is higher than that NR/modified PBAT TPV foam. Due to the elongation at break of both foam systems are decreased thus tensile strength of the foam are also decreased due to stress-induced crystallization of cell foam skin was obstructed by the present of PBAT. Compression set of NR/modified PBAT TPV foam were improved compared to NR/PBAT TPV foam due to the thick foam cell skin. From this primarily study shows that NR/PBAT TPV foam could be able to foam with carefully control condition and our further study will be reported.
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