Bio-based thermoplastic vulcanizates from natural rubber (bioplastic/NR)

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Abstract. Thermoplastic vulcanizates (TPV) is a class of thermoplastic elastomer of which generally consists of polyolefin phase, mainly PP or PE, with dynamically cured elastomer phase such as EPDM. The elastomer should be well dispersed in the polyolefin matrix which facilitates thermoplastic like processing of elastomer. The properties of TPV are mainly governed by properties of thermoplastic matrix and vulcanized rubber phases including curing system used for dynamic vulcanization. As environmental problem has been an important issue, application of bioplastic in thermoplastic elastomer is an interesting issue. The blending of NR with various bioplastics has been studied in our work and the system should classify as bioplastics/NR. Dynamic vulcanization of NR during melt blending of NR with various bioplastics was also studied. In this report, the melt blending system of PBAT/NR; PCL/NR and PBS/NR were carried out. The batch melt blending in an internal mixer were performed with various NR and bioplastics compositions. Dynamic vulcanization of NR phase, using Luperox® 101 as curing agent, was also occurred in the mixer during melt blending. Except for PBS/NR TPV system where dicumyl peroxide was used as curing agent. This will advantage for foam preparation in further foaming step. The results showed that PBAT/NR TPV with NR content as high as 70% possessed tension set less than 20% and elongation at break under tension was higher than 600%. For PCL/NR system at the same composition, the tension set was also found at 20%, elongation at break under tension was as high as 1000%. The TPV system of PBAT/NR and PCL/NR were also extrudable. Tension set for NR/PBS TPV system was found at about 30% and the elongation at break under tension was about 600%. From the mentioned basic properties of biobased TPV in our researches, it presents that they could propose the promising qualified TPV, in term of reprocess ability and advantage for the sake of biodegradability.

Note: PBAT, PCL and PBS stand for poly(butylene adipate-co-terephthalate, polycaprolactone, and poly(butylene succinate) respectively.

1. Introduction
Elastomer is a class of polymeric materials that can be deformed at room temperature and can be reverted quickly to nearly original size and form after unloading. In fact, elastic recovery under
compression and tension is its predominant properties. Generally, elastomer can be stretched as twice as its original length. Resilient property is also an important property of elastomer. Elastomer could be thermoplastic and thermoset polymers. Thermoplastic elastomers can be processed using conventional processing techniques for thermoplastics such as extrusion and injection molding. The scrap from the processes can be recycled. There are various classes of thermoplastic elastomers which are styrene block copolymers (TPS), thermoplastic polyolefin elastomers (TPO), thermoplastic polyurethanes (TPU), thermoplastic copolyester (TPC), thermoplastic polyamides (TPA) and thermoplastic vulcanizates (TPV). As it is generally known that rubber, both synthetic and natural rubber, show viscoelastic properties which can be applied for specific applications especially for vibration and shock isolation. Coran and Patel [1] reported that blending EPDM with thermoplastic polyolefin with fully cured EPDM referred as thermoplastic vulcanizate having superior strength, high temperature mechanical properties and good compression set. There has been number of researches studied on TPV prepared from thermoplastic and natural rubber (NR) including polyolefin/NR and polyester/NR [2, 3]. Even though NR is not 100% biodegraded (only protein attached to polymer chain could be biodegraded) TPV prepared from bioplastic/NR blend with bio-based NR should be able to encourage circular economy in Thailand.

2. Experimental

2.1. Materials

Natural rubber (NR) STR5L used in this research is high in its specification with low contamination and color and was purchased from Chareon Tut Co., Ltd., Thailand. It was purchased from PJ Rubber Co., Ltd (Thailand). Poly (butylene adipate-co-terephthalate), (PBAT) or Ecoflex® F Muleh C1201 with MFR 2.7-4.9 g/10 min (at 190°C; 2.16 kg), density 1.25-1.27 g/cm³, melting point 110-120°C was purchased from POLYMATS Co., Ltd. (Thailand). Granule form of PCL (CAPA 6800) was purchased from Perstorp, UK. PCL has a molecular weight and melt flow index (MFI) is 80,000 g/mol and 3 g/10 min at 160˚C/2.16 kg, respectively. The PBS (BioPBS™ FZ71PM) was purchased from PTT MCC Biochem Company by Thailand of which the melting point is 115°C, density is 1.26 g/cm³. Its melt flow index (MFI) is 22 g/10 min.

2.2. Preparation of TPV

Bioplastic which are PBAT, PCL and PBS were dried at 50°C under vacuum for 6 h before use. NR was masticated on a two-roll mill for 30 min before mixing with PBAT. PBAT/NR and PCL/NR were melted mixing in an internal mixer (PLASTI-CORDER, Brabender, Germany) at 140°C with the various rotor speeds. The mixing was performed at 140°C until plasticisation of thermoplastic had occurred for 2 min and then 1, Germany) with the blend ratios of PBAT/NR as follows 60/40, 55/45, 50/50, 45/55, 40/60, 35/65 and 30/70% by weight. The blends were melted at and Luperox® 101 (Lup) as a curing agent was added. The rotor speed of mixing was also varied. PBAT/NR vulcanizates were then being compressed to sheets by compression molding in a hot-plate hydraulic press (Scientific, Labtech Engineering, Thailand) at 140°C. After hot pressing, the sheet was allowed to cool to room temperature under pressure of 1,000 psi.

NR/PCL: Dried NR and dried PCL were also melted blended in at 140°C with the rotor speed of 80 rpm using also Luperox101 as curing agent. The mixing time was carried on for 15 min. The compositions of NR/PCL were as follow: 70/30, 65/35, 60/40, 55/45, 50/50, 45/55, 40/60, 35/65 and 30/70% by weight. The obtained NR/PCL vulcanizates was then being compressed in a compression-molded with the temperature of 140°C and the pressure of 1,000 psi.

NR/PBS: In this system, NR was masticated and being compounded with 1.5 phr. of dicumyl peroxide (DCP) before melted blending with PBS in an internal mixer at 140°C for 15 min. before dispatching the TPV from the internal mixer chamber. The ratios of NR/PBS are as follows: 50/50, 50/40, 70/30 and 80/20% by weight. The obtained TPV were then compress in a compression molding at 150°C under the pressure of 1,000 psi.
2.3. Characterization

The tensile properties, i.e. initial modulus, tensile strength and elongation at break of the TPV were performed under universal testing machine (UTM; Instron 5969, USA). Dumbbell specimens were tested at room temperature according to ASTM D638. Furthermore, tension set were also determined according to ASTM D412 and performed on dumbbell specimen. The dumbbell specimens were tensioned to 200% and kept under tension for 10 min. The length of the specimen was measured and compared between before and after elongation. The tension was then calculated followed equation (1):

\[ \% \text{Tension set} = \frac{l_2 - l_0}{l_1 - l_0} \times 100 \]  

3. Results and discussion

Mechanical properties of TPV are generally governed by many factors such as types of thermoplastic, vulcanizing system in rubber phase and importantly the phase morphology of thermoplastic and vulcanized rubber in TPV [4]. The morphology of the TPV was not only governed by the melt viscosity of thermoplastic but also the speed of rotor in mixing chamber. PBAT/NR TPV system was selected to report the effect of rotor speed of mixing as shown in Figure 1 which presents tensile strength, Figure 1 (a) and tension set, Figure 1 (b), of TPV obtained from tensile testing of TPV containing various ratios of PBAT and NR. The results show that mixing with low rotor speed of 60 and 80 rpm, PBAT/NR vulcanizates could not be elongated due to the large particle size of crosslinked NR particles. In fact, stress-strain curves of PBAT/NR TPV mixing with rotor speed of 100 rpm showed strain hardening behaviour under tensioning. The tensile strength behaviour of PBAT/NR also implied that at low rotor speed of mixing, i.e. 60 and 80 rpm, poor dispersion of NR phase was obtained and resulted in the low tensile properties [5]. Mixing PBAT and NR at high rotor speed, i.e. 100 rpm, the size of NR phase was reduced and completely dispersed led to the improvement in the tensile properties. It should be point out here that, at high rotor speed of mixing, shear heating and heat produced during dynamic vulcanization were also affected properties of TPV [5]. It was noticeable (the results could not be shown) that at 100 rpm, crosslinking (torque increment) occurred earlier than that at 60 and 80 rpm. In term of elastomeric property, tension set of the TPV should be lower than 50% meaning that the produced materials should not show permanent deformation higher than 50 % [6]. It was found that PBAT/NR with higher NR contents shows lower tension set. Also, the higher rotor speed resulted in lower tension set. This advantaged for elastomer applications.

![Figure 1](image_url)

**Figure 1.** Tensile strength and tension set of PBAT/NR TPV dynamic vulcanized in internal mixer with Luperox101® 1 phr, various PBAT/NR ratio and various rotor speed.
The degree of crosslinking in rubber phase is also important for TPV properties [7]. We investigated the effect peroxide content on tensile properties and tension set of TPV prepared from dynamic vulcanization of PCL/NR. As melting temperature of PCL is as low as 61 °C [8], we investigate the effect of peroxide content from 1, 1.5 to 2 phr by melt mixing NR and PCL at 140 °C with rotor speed of 80 rpm for 10 minutes in an internal mixer. At this condition PCL was not yet crosslinked by peroxide. The tensile properties and tension set are presented in Figure 2. In order to avoid the effect of stress induced crystallization and yielding of PCL phase, tensile stress at 800 % strain are reported. Tensile strength of PCL/NR TPV was decreased with NR content this is due to the high crystallinity of PCL (50% crystallinity) [8]. The increased in Luperox101 led to the increased in crosslink density and hence stress hardening of crosslink NR phase. Therefore, tensile strength of NR/PCL TPV was increased with the content of Luperox101. It must be noted that the properties of NR/PCL would be different if the temperature and time of mixing were increased due to the crosslinking of PCL phase. In term of tension set, crosslink density affected the properties of elastomer, i.e. elasticity of rubber phase as shown by the decreased of tension set. In this particular TPV system, PCL present as continuous phase in all composition ratios.

![Figure 2](image-url)

Figure 2. Tensile strength at 800% strain (a), tension set (b) of NR/PCL TPV dynamically vulcanized with various Luperox101 contents.

NR/PBS dynamically vulcanized using DCP as a curing agent was also investigated. This system was carried out in order to prepare TPV for NR/PBS foam sponge. Tensile strength of NR/PBS was increased with PBS content due to its high crystallinity (more than 60%) [9]. It was found that high rotor speed of mixing, high tensile strength NR/PBS TPV was obtained. It was noticed from the torque-time mixing curve that at higher rotor speed curing has occurred earlier than lower rotor speed. This was due to the shear heating during shearing in an internal mixer and leading to high crosslinking and hence high elasticity. This is responsible for the low tension of this system.

4. Conclusion
Thermoplastic vulcanizates derived from various Bioplastic/NR were successfully prepared and investigated for their tensile properties and tension set. It was clear that phase morphology between bioplastic and NR are very important for their properties especially elastic recovery reported by their tension set. Rotor speed of 100 rpm was found to be suitable for mixing bioplastic/NR during which dynamic vulcanization had occurred. Although higher rotor speed of mixing may be performed but shear heating occurred during mixing had to be attentive by the excess crosslinking and degradation of bioplastic. Indeed, degree of crosslink in NR phase can be increased by the peroxide content.
nonetheless shear heating occurred during melt mixing could also accelerate crosslinking reaction during mixing.

Figure 3. Tensile strength and tension set of PBS/NR TPV dynamic vulcanized in internal mixer with DCP 1.5 phr, various PBS/NR ration and various rotor speed.

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Acknowledgement
The authors would like to thank department of materials science and engineering for the supports throughout the works. The authors are also in debt to PETROMAT for the financial support.