Thermoplastic natural rubber based on linear-low-density polyethylene

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Abstract. Thermoplastic natural rubber (TPNR) is one of the alternative natural rubber (NR) products obtained by blending NR with any compatible thermoplastics, e.g., high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear-low-density polyethylene (LLDPE), polystyrene (PS), polylactic acid (PLA) at the temperature above the melting point of plastics, which is always above the softening point of NR. Unlike vulcanized NR, TPNR is recyclable and convertible to the final articles using the existing plastic technologies, including extrusion and injection molding. TPNR materials based on NR/LLDPE blends filled with two types of inorganic fillers, i.e., titanium dioxide and silica, were prepared and their properties were discussed in the current work. Silica provided a better reinforcing effect to the NR/LLDPE blends, whereas the blends filled with titanium dioxide exhibited excellent UVA and weather resistance. The resulting NR/LLDPE blends filled with inorganic fillers can be injection molded to form the products with desired shapes.

1. Introduction

Natural rubber (NR) is a biobased polymeric material from the Para rubber tree (Hevea brasiliensis). NR has high molecular weight and exhibits excellent water resistance, but low grease resistance. Furthermore, NR is sensitive to oxidation because of unsaturated double bonds; metal, light, and heat can accelerate the oxidation of NR as well. Consequently, NR properties may be changed over time during outdoor uses.

Thermoplastic natural rubber (TPNR) is a kind of thermoplastic elastomer, which is one of the alternative NR products obtained by blending NR with any compatible thermoplastics, e.g., high-density polyethylene (HDPE) [1], low-density polyethylene (LDPE) [2], linear-low-density polyethylene (LLDPE) [3], polystyrene (PS) [4], polylactic acid (PLA) [5] at the temperature above the melting point of plastics, which is always above the softening point of NR. Unlike vulcanized NR, TPNR is recyclable and convertible to the final articles using the existing plastic technologies, including extrusion and injection molding.

Herein, TPNR materials based on NR/LLDPE blends filled with two types of inorganic fillers, i.e., titanium dioxide and silica were prepared and their properties, including mechanical, morphological, and QUV and weather-resistant ones were discussed.

2. Experimental

2.1. Preparation of NR/LLDPE blends filled with TiO₂ and/or SiO₂

Natural rubber (NR, STR 5CV60, Natural Art and Technology Co., Ltd., Thailand) was first masticated in an internal mixer (KD-3-20, Kneader Machinery, Japan) at 70°C for 2 min. Antioxidant and
antiozonant (1 phr each, Behn Meyer Chemicals (Thailand) Co., Ltd., Thailand) were added into the masticated NR and their mixing was performed at 70°C for 2 min. The mixture was then cut into small pieces using a plastic crusher to obtain NRC (NR without the addition of inorganic fillers). On the other hand, NR, antioxidant (1 phr), and antiozonant (1 phr) were compounded with inorganic fillers (20 wt%), i.e., TiO$_2$ (TIOXIDE® TR92, Venator Materials Corporation Huntsman, Malaysia), SiO$_2$ (TOKUSIL® 255, OSC Siam Silica Co., Ltd, Thailand), or TiO$_2$/SiO$_2$ (1:1 w/w) in an internal mixer at 70°C for 5 min. These compounds were prepared into small pieces using the same processes as those for NRC to obtain NRT (NR containing TiO$_2$), NRS (NR containing SiO$_2$), and NRTS (NR containing equal amount of TiO$_2$ and SiO$_2$), respectively.

The as-prepared NRT, NRS, or NRTS flakes were subsequently blended with NRC flakes and linear-low-density polyethylene (LLDPE, InnoPlus LL8420A, PTT Global Chemical Public Company Limited, Thailand) in an internal mixer at 110–140°C for 5 min to obtain NR/LLDPE/TiO$_2$, NR/LLDPE/SiO$_2$, and NR/LLDPE/TiO$_2$/SiO$_2$, respectively. A series of NR/LLDPE/TiO$_2$, NR/LLDPE/SiO$_2$, and NR/LLDPE/TiO$_2$/SiO$_2$ was prepared by varying weight fractions of the above three components. The final samples possessed a constant NR/LLDPE weight fraction of 60/40 and different concentrations of TiO$_2$; SiO$_2$, or TiO$_2$/SiO$_2$ (1/1 w/w) of 2.5, 5, and 10 wt.%. Each sample was then compressed at 100°C by a compression molding machine (CC-HIM-2060, Chaicharoen, Thailand) and then die cut into test specimens.

2.2. Characterization and property testing of NR/LLDPE blends filled with TiO$_2$ and/or SiO$_2$

The tensile property was tested according to ISO37:2011 using an Instron universal testing machine (Instron, USA) with a test speed of 500 mm/min and a gauge length of 30 mm. Tensile strength, Young’s modulus, and elongation at break of each sample were reported as averages from the measurement of three specimens. Shore A hardness of the sample was tested according to the ASTM D2240-05 using a G8-719N Durometer (Teclock, Japan).

Morphological characteristics at tensile fractured surfaces of the samples were examined using a JSM-6610 series scanning electron microscope (SEM, JEOL, USA) at an acceleration voltage of 10 kV. The SEM micrographs were taken at a magnification of 500. The sample surfaces were coated with a thin layer of gold to prevent charging before observation.

Ozone resistance test was performed according to ISO1431-1:2004. Samples were stretched to 120% of their original length and then exposed to the ozone with a concentration of 50 ppdm at 40°C for 7 h. The crack of the samples was then observed.

QUV and weathering resistance determination was carried out according to ASTM G154-16. The sample specimens were exposed to UVA at 60°C for 8 h and punctuated with 50°C of water vapor for 4 h for the overall test period of 168 h using an Accelerated Weathering Tester (QUV/spray, Q-LAB, USA). The color of each specimen was then examined using a spectrophotometer (Miniscan EZ, HunterLab, USA) and the change in color as compared with the unexposed specimen was observed.

The results were statistically analyzed using IBM SPSS Statistics Version 20 (Statsoft, Oklahoma), with analysis of variance (ANOVA) and Duncan’s test at significant differences at 5% level.

3. Results and discussion

The tensile properties and hardness of all samples were shown in Figure 1. Although tensile properties and hardness of NR/LLDPE blend and NR/LLDPE/inorganic filler composites were insignificantly different, tensile strength, Young’s modulus, and hardness of the composites tended to increase with increasing inorganic filler concentration. It should be pointed that elongation at break of the composites was lower than that of the blend and hardly changed as a function of inorganic fillers concentrations. The results implied that the composites became more rigid due to the reinforcing effect.

SEM images at tensile fracture surfaces also supported the above mechanical property results as demonstrated in Figure 2. NR/LLDPE blend shows rough tensile fractured surface, reflecting extensible
material. However, the roughness of tensile fractured surfaces slightly decreased when inorganic fillers were added, corresponding to stiffer material. The reduction of surface roughness was more outstanding in the composite filled with SiO$_2$, particularly with increasing SiO$_2$ concentration.

**Figure 1.** (A) Tensile strength, (B) Young’s modulus, (C) elongation at break, and (D) hardness of (I) NR/LLDPE, (II) NR/LLDPE/TiO$_2$, (III) NR/LLDPE/SiO$_2$, and (IV) NR/LLDPE/TiO$_2$/SiO$_2$.

**Figure 2.** SEM images ($\times$500) at tensile fractured surfaces of (I) NR/LLDPE, (II) NR/LLDPE/TiO$_2$, (III) NR/LLDPE/SiO$_2$, and (IV) NR/LLDPE/TiO$_2$/SiO$_2$. 
QUV and weathering resistance properties of the blend and composites were evaluated by the difference in CIELAB color space value before and after exposure to the UVA, water vapor, and heat. The smaller difference indicates the better resistances. Figure 3A-C shows that the difference in CIELAB color space (L’, a’, and b’) values of the composites filled with TiO₂ was lower than those of the blend and the composites filled with SiO₂, suggesting that TiO₂ provided the best resistance against UVA and weather to the NR/LLDPE blend. The result in Figure 3D was also in good agreement with the CIELAB color space as the composites filled with TiO₂ possessed a higher Grey Scale value than others, reflecting less change in color after UVA and water vapor exposure.

**Figure 3.** (A) L’, (B) a’, and (C) b’ values before (left bar) and after (right bar) exposing to UVA at 60°C for 8 h alternating with water vapor at 50°C for 4 h, total exposure time of 168 h, and (D) Grey Scale of (I) NR/LLDPE, (II) NR/LLDPE/TiO₂, (III) NR/LLDPE/SiO₂, and (IV) NR/LLDPE/TiO₂/SiO₂.

### 4. Conclusions

TPNR materials based on LLDPE were successfully prepared. Two types of inorganic fillers, i.e., TiO₂ and SiO₂, were incorporated. The obtained NR/LLDPE composites filled with inorganic additives showed slightly increased tensile strength, Young’s modulus, and hardness, which were in good agreement with the morphology observed by SEM. SiO₂ provided the composites with better mechanical properties, whereas TiO₂ improved their QUV and weather resistance.

### Acknowledgment

This work was financially supported by the Thailand Research Fund, Thailand, and the Graduate Program Scholarship from The Graduate School, Kasetsart University, Thailand.

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