

Mechanical, Thermal and Fire Retardant Characteristics of NR/PP/ATH Thermoplastic Vulcanizates

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Abstract

Blends of natural rubber (NR) and polypropylene (PP) were melt-mixed with phenolic resin crosslinking agent to obtain thermoplastic vulcanizates (TPVs). The blend composition of NR and PP was at 60/40 %wt. Alumina trihydrate (ATH) was incorporated into the blends to improve the flame retardancy, and the effect of ATH incorporation at different levels (20 - 120 PHP, part per hundred polymers) on blend morphology, ATH dispersion, mechanical properties, thermal resistance and flame retardancy was investigated. Analyses by transmission electron microscopy (TEM) and energy dispersive X-ray-scanning electron microscopy (EDX-SEM) revealed the dispersed phase-like morphology of 60/40 NR/PP TPVs. The presence of ATH in the TPVs did not have much influence on morphology of 60/40 NR/PP blends. Increasing ATH content decreased the dispersion level of ATH, which caused a decrease of tensile strength and elongation at break. Furthermore, an addition of ATH into the NR/PP blends resulted in lower elastic recovery, but slight increase of hardness. It was also found that the ATH suppressed the intensity of mass loss rate of NR and PP, resulting slower thermo-oxidative decomposition process of the blend materials. Limiting oxygen index (LOI) and UL94-V rate were enhanced with more incorporated ATH content. According to the results present in this study, the addition level of ATH for development of flame retardant NR/PP blend-based TPVs with acceptable elastomeric properties was recommended at 100 PHP.

Keywords: Natural rubber, polypropylene, thermoplastic vulcanizates, flame retardancy, morphology

Introduction

Thermoplastic vulcanizates (TPVs) are one of special class of rubber materials that have attracted the attention of many researchers and industrialists due to a combination of rubbery character along with their thermoplastic properties. TPVs have been prepared from various rubber/plastic blends by undergoing a special chemical process called dynamic vulcanization to introduce the chemical bonds between the rubber molecules [1,2]. The dynamic vulcanization during melt mixing of rubber and plastics induces a stable structure of crosslinked rubber particles within a continuous plastics [3]. At present, commercialized dynamic vulcanizates are mostly produced from blends of various synthetic rubbers and polypropylene (PP), and mainly used to make automotive parts, medical products, electronic appliances etc.

In addition to synthetic rubber, natural rubber (NR) has become a potential candidate to be used as blend component in the TPVs, not because of the renewable resource but also its excellent elasticity and dynamic performance. The functional properties of unfilled NR/PP TPVs were reported by the authors [4-

6]. Their properties were drastically changed if the NR concentration, crosslinking level of NR phase and phase structure of NR/PP blend were modified. The addition of filler could also adjust the properties of NR/PP blends [7-9]. Lopattananon *et al.* [8] showed that the tensile strength, thermal stability and oil resistance of dynamic crosslinked 60/40 NR/PP blends were enhanced through incorporation of nanoclay at concentration ranging from 2 - 10 phr. This was due to an improvement in blend morphology, i.e., smaller crosslinked NR phase when that of the corresponding neat blend was compared with. A highest improvement in tensile strength was attained when the addition level of nanoclay concentration was 5 phr. Recently, Masa *et al.* [9] also showed that the tensile strength, elongation at break and oil resistance of 80/20 NR/PP blend were significantly improved over the neat counterpart due to finer blend morphology accelerated by clay addition at concentration of 5 phr. However, the NR/PP TPVs use components that are highly combustible, and emit smoke under burning process causing increase of fire hazard [10]. Therefore, the flammable property restricts their further application in final products such as automotive components and electrical insulation.

ATH (alumina trihydrate, $\text{Al}(\text{OH})_3$), a hydrated mineral filler, has currently been widely used in producing fire-safe polymers because of effective fire protection performance, low cost and low toxicity [11,12]. ATH also has additional benefit of suppressing smoke during polymer combustion [12,13]. The most important contribution of hydrated filler is the endothermic release of water, which removes heat from the system [14,15]. For polymer with processing temperature below dehydration temperature of ATH (200 °C), ATH provides adequate processing coupled with enhanced flame retardancy. Flame retardancy effect of ATH incorporation in different rubbers/thermoplastics has been studied [12,16-23]. Owing to these studies, it was found that the final properties such as strength, flexibility, density and flammability of these materials largely depend on the additive level of ATH and its size. Moreover, in the flame retardant polymers, the additive level could be different due to the variation in their decomposition mechanism [13]. Canaud *et al.* [16] used ATH to exert the fire-retardant effect of carbon black filled ethylene-propylene-diene monomer rubber (EDPM). They suggested that the EDPM compounds with 160/15 and 170/7 phr/phr ATH/carbon black were the most suitable to be used in wire and cable under low and medium voltage. Zhang *et al.* [17] showed that the increasing addition of ATH (20 - 60 wt%) in ethylene-vinyl acetate (EVA) decreased the modulus, tensile strength and elongation at break, but significantly increased the thermal and flame-resistant properties. A study by Farzad *et al.* [19] showed that the flammability of EDPM/PP blends greatly decreased with increasing addition of ATH up to 75 phr, but further increasing ATH content had less effect on the flammability of EDPM/PP blends. Sabet *et al.* [12] reported the results in case of ATH filled linear low-density polyethylene (LDPE) with different contents (50 - 340 part per hundred polymers, PHP) and particle sizes (2, 10, 20 and 55 μm), which showed that the flame resistant properties and smoke density improved with increasing amount of ATH and decreasing size of ATH particles. Sonneir *et al.* [20] modified the fire performance of EVA by incorporating ATH (20, 40 and 60 wt%) into EVA. They found that increasing ATH content could increase time-to-ignition and decrease combustion heat due to the release of water, which diluted the fuel during combustion of EVA. Lopattananon and co-workers [22] attempted to fabricate fire retardant 60/40 NR/PP TPV by association of 60 PHP ATH and maleic anhydride grafted polypropylene (MAH-g-PP) at different concentrations to improve mechanical properties and flame retardant. However, the flame retardancy of 60 PHP ATH filled NR/PP TPVs was not efficient for fire retardant materials.

Therefore, to control over fire resistance and useful properties of the NR/PP TPV, the effect of ATH addition on the properties are important points to study. In this study, the TPVs were prepared from NR and PP blends. The ATH of various amounts was added into the TPV compounds. The blend structure, dispersion of ATH filler, mechanical properties, thermal properties and flame retardancy of TPVs filled with ATH were examined.

Materials and methods

Materials and chemicals

Natural rubber (NR, Ribbed smoked sheet, RSS#3) with Mooney viscosity (ML 1+4 (100°C)) of 80, was purchased from Rubber Farmer Organization of Khokpho-Maelarn (Pattani, Thailand). Polypropylene (PP 1102H for compression molding grade) with melt flow index of 2 g/10 min (230°C/2.16 kg) was supplied by IRPC Public Co., Ltd. (Thailand). Dimethylol phenolic resin (HRJ-10518) was manufactured by Schenectady International (NY, USA) and used as a curing agent. The melting point and density of the HRJ-10518 was 140 °C and 1.05 g/cm³, respectively. Stannous chloride (SnCl₂·2H₂O) with melting temperature of 37 °C and density of 2.71 g/cm³ was manufactured by QREC Chemical (New Zealand). It was used as a catalyst for phenolic curing system. 2, 2, 2-Trimethyl-1, 2-dihydroquinoline (TMQ) was supplied by Flexys (US) and used as anti-oxidant for NR. Ultra-blend™6000 (Performance Additives Sdn Bhd, Malaysia) was used as blend homogenizer. It is the mixture of light coloured, aliphatic hydrocarbon resins. Paraffinic oil (White oil grade A no. 15, China Petrochemical International Co., Ltd, China) was used as processing aid. Compatibilizer used for promoting interfacial interaction between NR and PP in the blend was phenolic grafted PP (Ph-g-PP). It was prepared by melt compounding ingredients in the following order: PP, SnCl₂·2H₂O and HRJ-10518. The mixing was carried out in the internal mixer with temperature of 180 °C, rotor speed of 60 rpm and mixing time of 6 mins according to a method described in publication [24]. Aluminium trihydrate (ATH) with density of 2.42 g/cm³ and pH of 10.4 was supplied by Zibo Co., Ltd. (China). It has irregular particle-shaped structure with diameter of 1-2 µm.

Preparation of ATH filled NR/PP TPVs

The ATH filled NR/PP TPVs were prepared by melt mixing in Brabender plastograph model 815653 (Brabender GmbH&Co. Ko, Germany) at 180°C with rotor speed of 60 rpm. The NR/PP composition was selected at 60/40 %wt due to balance of elastomeric and processing properties [4-6]. The ingredients for fabrication of the filled NR/PP TPV are given in **Table 1**. The filled TPVs were prepared by mixing step represented in **Figure 1**. The dynamically crosslinked NR/PP blends were compression molded to obtain sheets under pressure of 120 bar at 180 °C for 22 min. The unfilled TPVs were also prepared as reference for comparison purpose by using the same formulation and mixing step as given in **Table 1** and **Figure 1**, respectively. The total mixing time of TPV compounding was kept constant for 20 min.

Table 1 Formulation of ATH filled 60/40 NR/PP TPV.

Ingredients	Quantities (parts per hundred parts of polymer, PHP)
NR/PP	100.00
Ph-g-PP	2.00
TMQ	0.60
Ultra-blend™6000	4.00
ATH filler	20,40, 60, 80, 100 and 120
Paraffinic oil	20.00
SnCl ₂ ·2H ₂ O	0.36
HRJ-10518	5.40

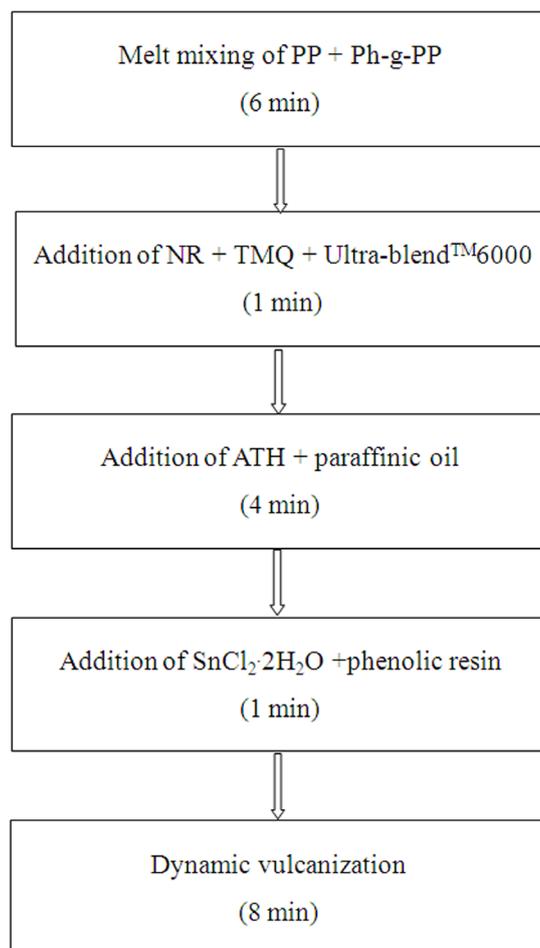


Figure 1 Schematic diagram illustrating fabrication of ATH filled 60/40 NR/PP TPV.

Characterizations

Mechanical property measurement

The tensile test was conducted on Hounsfield Tensometer model H10KS (*Hounsfield Test Equipment Co., Ltd, UK*) at room temperature (25 ± 2 °C) with extension rate of 500 ± 50 mm/min in accordance with ASTM D412. Dumb-bell shaped specimens were cut from TPV sheets. Reported results were an average of at least 5 tests. Tension set at 100 % elongation as an index of elastomeric property was determined at room temperature according to ASTM D412. For the measurement, the samples were stretched to 100 % of their original length for 10 min, and they were relaxed after being exposed to specific deformation for 10 min. Afterward, the changes in the sample dimensions were determined. Hardness (Shore A) was measured using a hardness tester (TOYOSEIKI, Japan) in accordance with ASTM D2240.

Electron microscopy analysis

The blend morphology of NR/PP blends were examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For the TEM analyses, the unfilled and filled samples were cut to thin section (75 nm) at temperature of -120 °C by an ultramicrotome model RMC MT-XL

(RMC Products Group, Ventana Medical System, Inc., US), followed by staining with OsO₄. The ultrathin sections were examined by a JOEL model JEM-2010 (JOEL Co., Ltd, Japan) operating at an accelerating voltage of 160 kV. The ATH dispersion in the NR/PP TPVs was also examined by X-ray mapping of aluminium in the TPV composites. The analyses were performed by using Oxford Energy Dispersive X-ray Spectroscopy (EDS) system attached to the SEM microscope (JOEL model JSM-5800 LV, JOEL Co., Ltd, Japan).

Thermogravimetric analysis (TGA)

Thermal stability was carried out by Thermogravimetric Analyzer (TGA 7, Perkin Elmer, USA). The TGA studies were operated in oxygen current at flow rate of 20 ml/min. The samples (about 20 mg) were heated from 50 - 800 °C at the rate of 10 °C/min.

Flammability tests

The resistance to fire of the samples was carried out by 2 technical methods, Limiting Oxygen Index (LOI) measurement and UL94 vertical (UL94-V) test. The LOI test was conducted in accordance with ASTM D2863. The samples with dimensions of 10×150×3 mm³ were placed vertically in a glass column. A mixture of nitrogen and oxygen were supplied into the glass column, and the samples were ignited. The oxygen concentration was regulated so that the minimum oxygen concentration in nitrogen was obtained to support the combustion of the samples. The UL94 vertical (UL94-V) test was carried out using a sample with a dimension of 13×125×3 mm³ according to ASTM D3801. The test flame was applied under the lower end of the vertical samples for 10 s, and then removed. After removal of test flame, the burning time was recorded, and the burning particle fall from the samples was noted if any. Five specimens were tested. The test results were classified by burning ratings: V-0, V-1 or V-2. V-0 rating represents the best flame retardancy of the materials, while V-1 and V-2 ratings indicate the intermediate and poor flame retardancy of the materials, respectively.

Results and discussion

Phase morphology of NR/PP TPVs and ATH filler dispersion

It has been shown by a number of studies that the functional properties of both filled and unfilled TPVs were well correlated to their blend morphological characteristics, i.e., phase structure, size of rubber particle, particle size distribution and filler dispersion [8,25,26]. To check the effect of ATH addition on the blend morphology of the 60/40 NR/PP TPV compounds, different microscopic techniques were performed.

Figure 2 shows TEM images of the neat TPV and the TPVs filled with ATH contents of 20 and 60 PHP. The TEM images of the TPVs containing ATH contents greater than 60 PHP were not observed in this study due to difficulties in sample preparation for TEM examination. In these TEM images, the dark regions represented the crosslinked NR phase and the light regions are the PP phase. Apparently, for both filled and unfilled samples, the blend of NR and PP showed a structure typical to a dispersed phase-like morphology, in which the NR domains were distributed across the continuous PP phase. For the ATH filled blends, the ATH was dispersed mainly in the NR phases. In this study, the domain size of NR in **Figure 2** was also measured by using image J software, and it was found that the average sizes of the crosslinked NR domains for each TPV were not significantly different, and the size distribution was comparable among various kinds of TPVs. For example, the unfilled TPV, 20 PHP and 60 PHP ATH filled TPVs had an average size of NR phase of 2.01, 2.05 and 2.06 μm as well as their NR particle size distribution laid in the range of 0.59 - 4.19 μm, 0.75 - 3.90 μm and 0.74 - 4.49 μm, respectively. Therefore, the morphology and the NR particle size were apparently unchanged with addition of different ATH content. These results indicated that the ATH incorporation had no influence on the mixing process of NR and PP and the dynamic crosslinking of the NR phase. However, at higher ATH content, the particle size of ATH tended to increase due to filler-filler interaction among ATH, resulting in filler agglomeration as shown in **Figures 2(B) - (C)**. To confirm the filler-filler interaction in the ATH filled 60/40 NR/PP TPVs, the X-ray mapping of the aluminium (Al) element in the neat and filled TPVs was

performed to study the effect of ATH content on dispersion state in the larger area than TEM analysis. The results are shown in **Figure 3**.

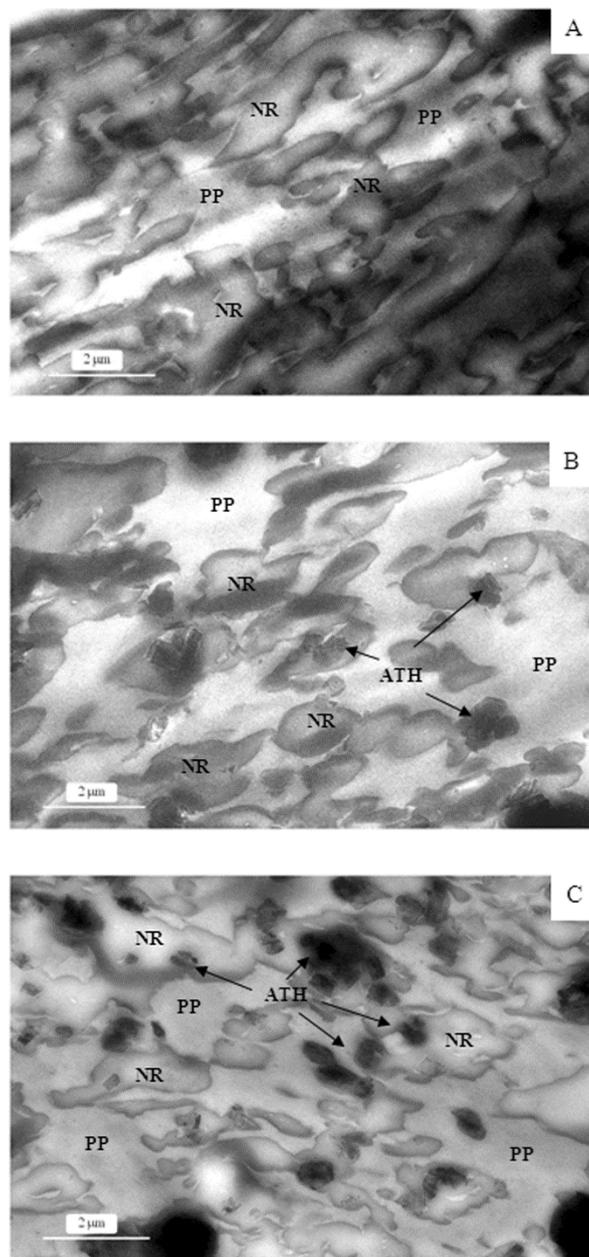


Figure 2 TEM photomicrographs of (A) neat 60/40 NR/PP TPV, (B) 20 PHP ATH filled 60/40 NR/PP TPV and (C) 60 PHP ATH filled 60/40 NR/PP TPV at magnification 5000X.

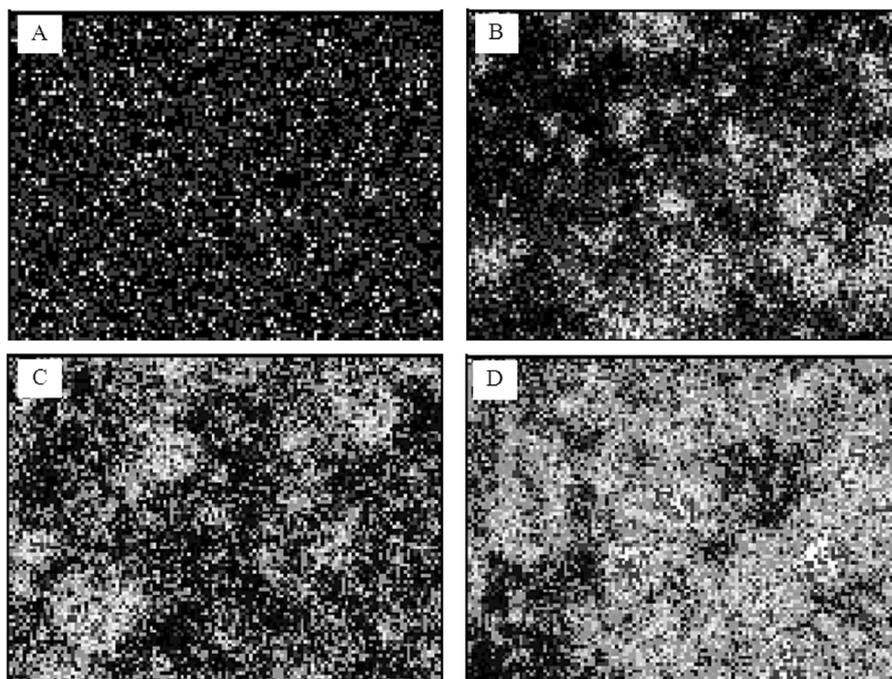


Figure 3 X-ray aluminium mapping images of (A) neat 60/40 NR/PP blend, (B) 20 PHP ATH filled 60/40 TPV, (C) 60 PHP ATH filled 60/40 NR/PP TPV and (D) 100 PHP ATH filled NR/PP TPV.

From **Figure 3**, the bright-contrast area over a dark background represents the group of the aluminium elements in the NR/PP TPVs. By comparing the regions of brighter contrast in these images, it is clearly the ATH fillers were agglomerated into larger particles as more ATH fillers were incorporated into the TPVs. Therefore, the observations obtained from TEM and EDX-SEM techniques indicated the poor dispersion of ATH in the TPVs with increasing addition level of ATH. It should also be noted that the small bright spots observed in case of the unfilled TPV (**Figure 3(A)**) was due to computational artifact and they were not related with the distribution of aluminium in the NR/PP TPV. The reason was also confirmed by the inspection of a typical EDX spectrum of the unfilled TPV obtained by mapping of aluminium (Al) element (data not shown), in which the X-ray peaks at 0.25 keV, referring to carbon (C) element and the peaks at 2.2, 9.7 and 11.5 keV, assigning to gold (Au) element were observed, however, the X-ray peak at 1.5 keV, corresponding to the Al element was not found. This indicated that the white spots in the EDX image of the unfilled TPV was not also related to C and Au elements, but they were possibly from computational artifact.

Mechanical properties of ATH filled NR/PP TPVs

Figure 4 show stress-strain curves of the NR/PP TPVs with different ATH contents and their parent materials (phenolic resin crosslinked NR and PP). Variation of mechanical properties as a function of ATH content is shown in **Figure 5**. From **Figure 4(A)**, it is seen that all the TPVs had specific stress-strain behavior, which exhibited a combination of PP and NR characteristics (**Figure 4(B)**) that they were prepared from. The tensile stress at any given elongation was increased on increased addition of ATH filler from 20 PHP up to 120 PHP. According to the TEM observations (**Figure 2**), it was proved that the structure of the 60/40 NR/PP blend did not change or improve upon addition of ATH. Therefore, the increase in stress level was largely attributed to the ATH addition. Since the rigidity of inorganic filler is generally much higher than the polymer [27]. Thus, the increased incorporation of ATH into the NR/PP blends caused the increase of stress level at any given applied strain and also hardness of the blends

(Figure 5 (D)) due to higher proportion of the rigid ATH filler. However, the tensile strength appeared to decrease with a progressive reduction in breaking strain as the ATH content was increased (Figures 5(A) - (B)). The decrease in both properties with more addition of ATH was owing to greater filler-filler interaction, generating many of the large ATH agglomerates (Figures 2 - 3), which served as stress concentration region or weak interfacial adhesion between ATH and NR/PP blend matrix [27].

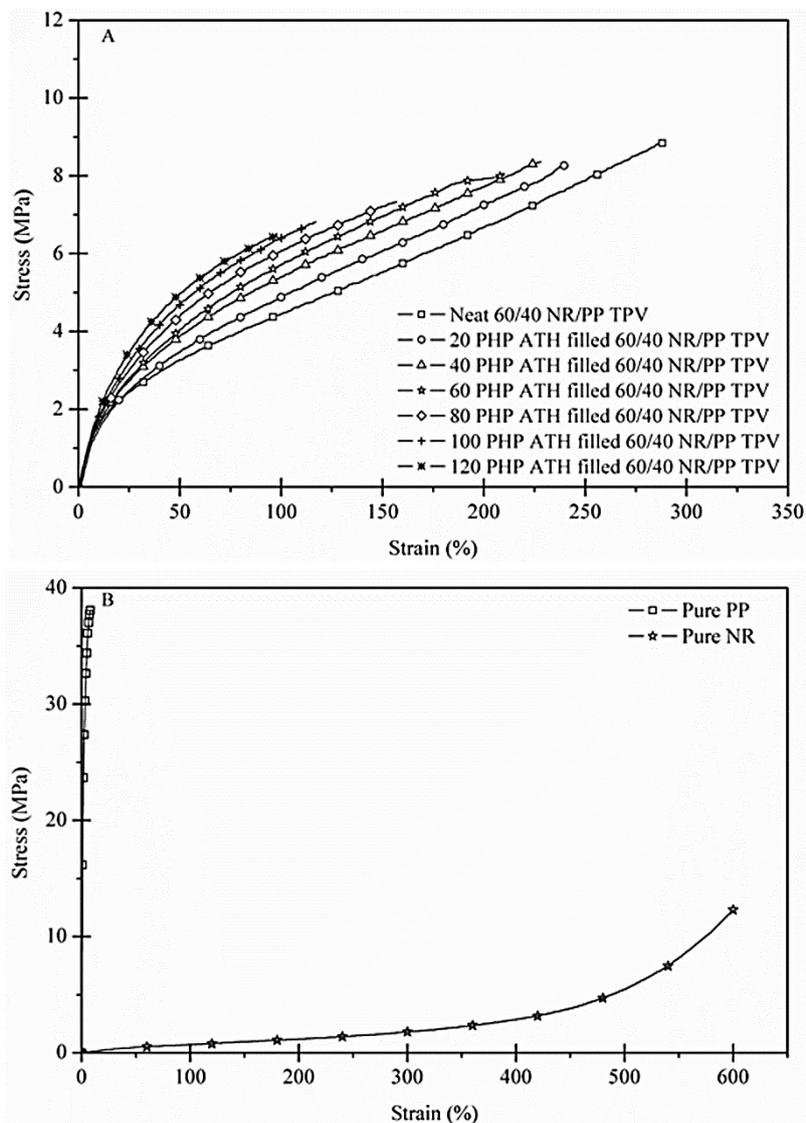


Figure 4 Typical stress-strain curves of (A) 60/40 NR/PP TPVs containing various ATH contents and (B) reference PP and phenolic resin crosslinked NR.

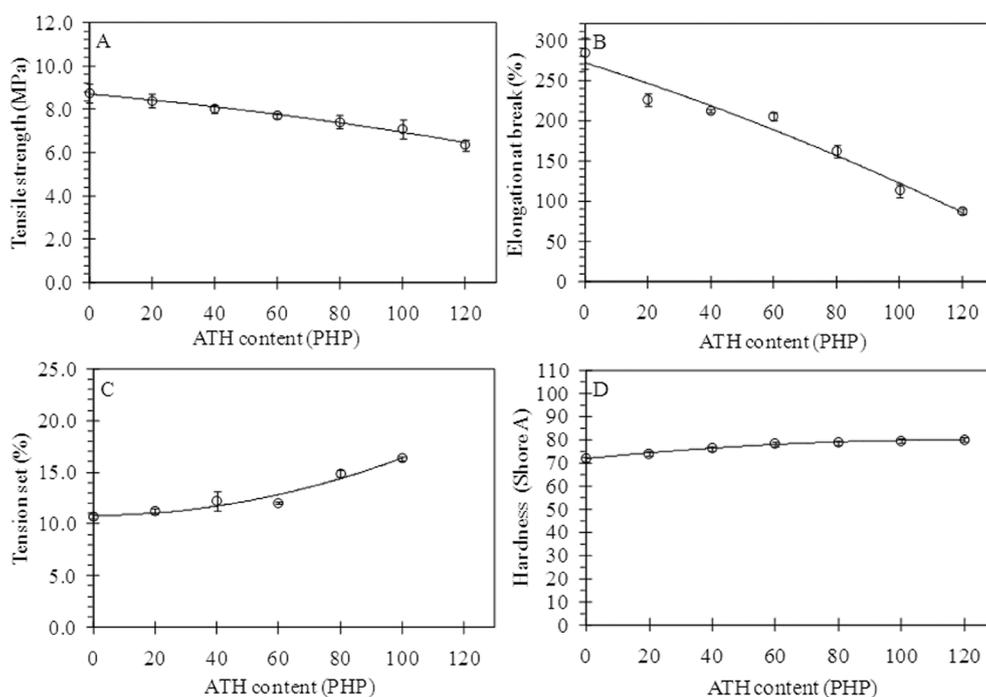


Figure 5 Effect of ATH content on (A) tensile strength, (B) elongation at break, (C) tension set and (D) hardness (shore A) of 60/40 NR/PP TPVs.

To assess flexibility or elasticity of the various ATH filled TPVs, the tension set at 100 % strain was measured. Tension set at 100 % is normally useful indication of elasticity for comparing elastic recovery of TPV material. From **Figure 5(C)**, it is seen that the tension set was gradually increased with increasing ATH content, implying that the TPV materials exhibited less elastic recovery. At the ATH content of 120 PHP, the tension set was not be able to measure because the sample could not be stretched upto 100 % elongation. In this sample, the maximum elongation at break was found to be about 87 ± 3 %.

Regarding to TPV criteria, it has been well accepted that the ultimate elongations greater than 100 % and tension set at 100 % less than 50 % are required to classify the material as an elastomer [8,28,29]. Therefore, from the above results, it suggested that the incorporation of ATH equally or less than 100 PHP showed good elastomeric properties according to the TPV criteria.

Thermal stability of ATH filled NR/PP TPVs

Study on degradation of TPV in an oxygen environment under heating is practically important. Thermo-oxidative degradation can provide the significant information on how the material behaves under more realistic atmosphere conditions. Hence, the effect of ATH on thermo-oxidative stability of the TPVs was investigated by TGA analysis, and the results are shown in **Figure 6**.

Figure 6 shows typical TGA and corresponding derivative thermogravimetric (DTG) thermograms of TPVs with various ATH contents in oxidative condition. Parameters such as initial decomposition temperature defined as temperature at 5 % weight loss (T_{d5}), maximum decomposition temperature (T_{dmax}) and residual weight at 600 °C are listed in **Table 2**. From **Figure 6(A)**, the TGA scan of the neat 60/40 NR/PP TPV showed that the material degradation was heterogeneous. The weight loss in the low temperature region of 200 - 320 °C was likely to be the loss of paraffinic oil resided in the TPV, judging from the degradation profile of pure paraffinic oil, which began to decompose at temperature between

180 - 550 °C (**Figure 7(A)**) with maxima degradation temperature at around 326 °C as presented in **Figure 7(B)** and **Table 2**. At higher temperature region starting at 320 °C and ending at 400 °C, the weight loss was mainly due to the chain degradation of the NR ($T_{dmax} = 353$ °C), followed by the random chain scission of PP chain [30] at between 400 - 530 °C ($T_{dmax} = 437$ °C). In the presence of ATH, the TPVs also degraded in 3 distinct temperature regions. The low temperature region ranging from 195 - 335 °C appeared to be the overlap in oxidative decomposition between ATH (210 - 320 °C) (**Figure 7**) and the paraffinic oil, whereas the intermediate and high temperature regions were the degradation of NR and PP, respectively. From **Figure 6** and **Table 2**, it is also seen that the T_{d5} and T_{dmax} of the TPVs were not considerably changed when the ATH was added. On the other hand, the mass-loss rate of the NR and PP at their corresponding peak decomposition (**Figure 6(B)**) clearly reduced with increasing amount of ATH.

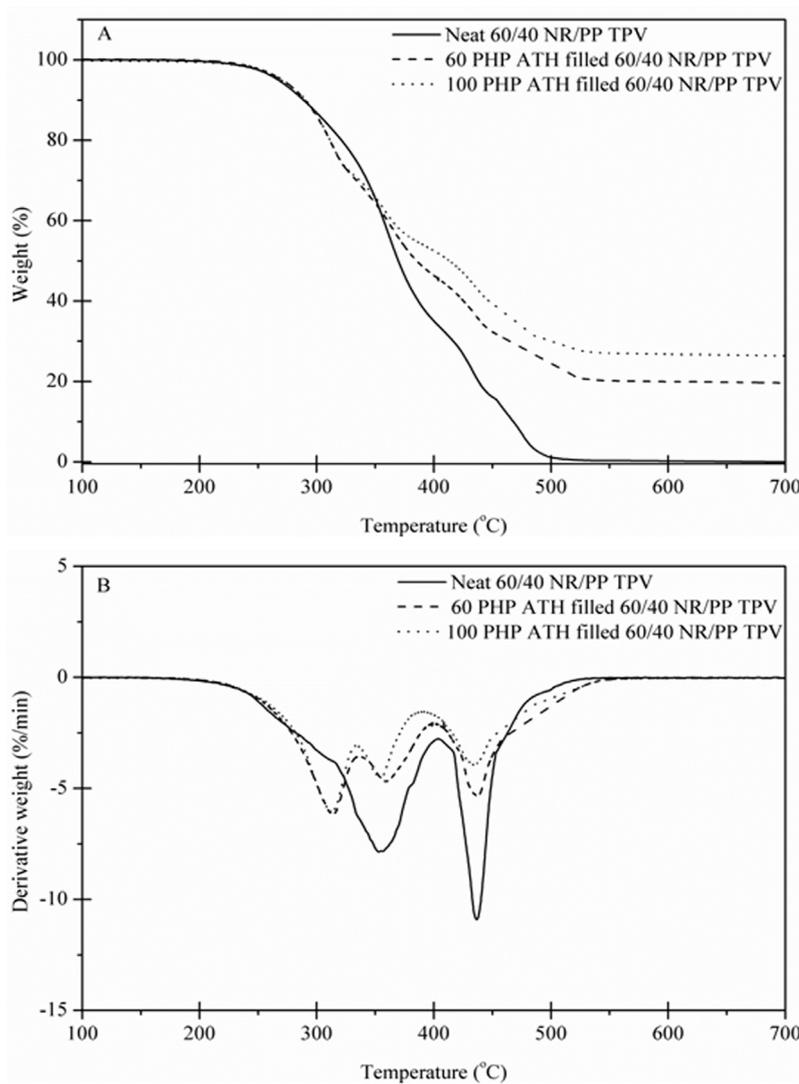


Figure 6 Comparison of (A) TGA curves and (B) DTG curves for 60/40 NR/PP TPVs containing various ATH contents.

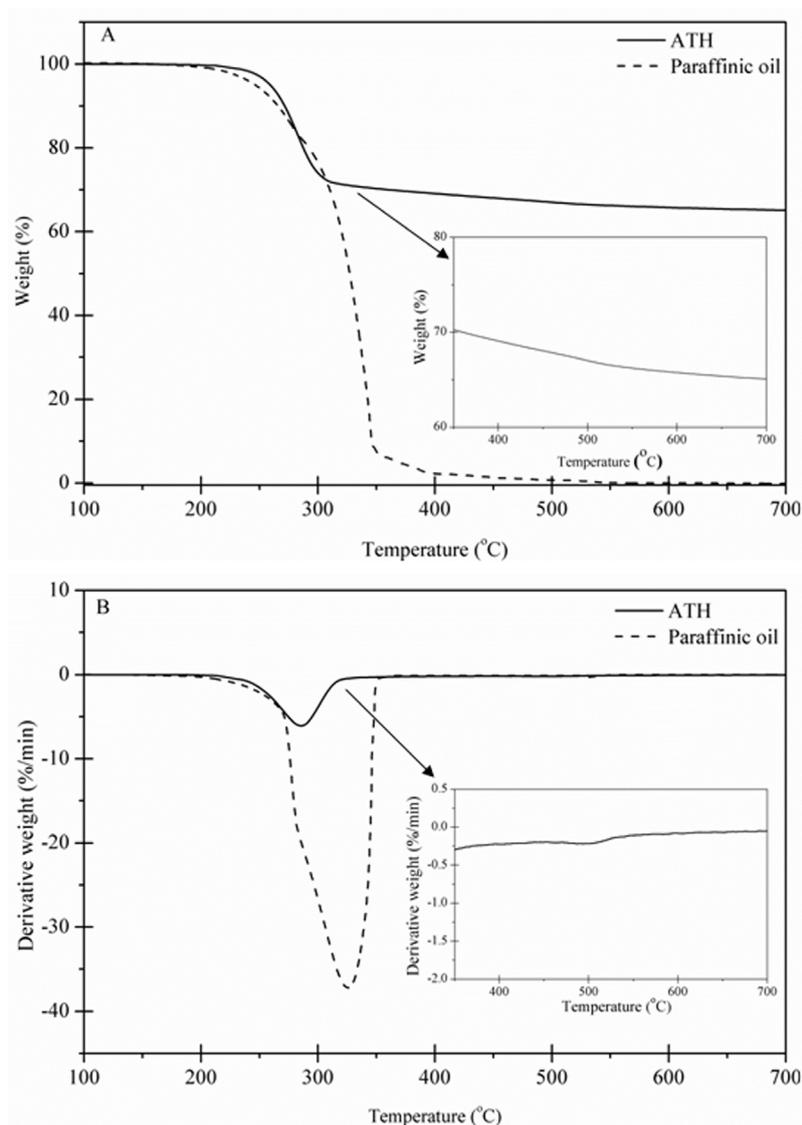


Figure 7 Typical profiles of (A) TGA curves and (B) DTG curves for reference ATH and paraffinic oil. Inserted plots in TGA and DTG curves are weight loss and derivative weight loss of ATH at the temperature region of 350 - 700 °C.

During the thermal-oxidative breakdown of the TPV at temperature between 320 - 400 °C, i.e., NR decomposition, the TGA curve of ATH shown in **Figure 7** suggested that most of ATH already decomposed to an intermediate mono-hydroxide, which was reported to be boehmite [AlO(OH)] [13,31]. Boehmite has a much higher thermal stability than NR, decomposing at about 400 - 590 °C [26] as shown in the inserted TGA profile for clarity. The formation of boehmite may protect the underlying material, leading to a retarded weight loss of the NR. Subsequently, in the final decomposition step of TPV, the dehydration of boehmite to alumina (Al₂O₃) [15,31] cooled down the material, which brought about the decrease in the process of oxidative degradation of PP, and thus reduction of released volatile products. In addition, the Al₂O₃ produced together with any carbonaceous char during thermo-oxidative degradation

could form effective insulating barrier [15], protecting the material against further thermo-oxidative decomposition, and lowering peak mass loss rate of PP. This then resulted in a higher amount of residue with increasing ATH content after TGA operation. The increasing trend in char residue also correlated well with a decreasing trend in mass loss rate of the PP (**Table 2**).

Table 2 Temperatures at onset of decomposition (T_{d5}), maximum decomposition (T_{dmax}) and residual weight for ATH, paraffinic oil, neat 60/40 NR/PP TPV and 60/40 NR/PP TPVs containing various ATH contents.

Materials	T_{d5} (°C)	T_{dmax} (°C)	Residual weight (%)
ATH	259	286	35.23
Paraffinic oil	247	326	0.00
60/40 NR/PP TPV	267	353, 437	0.00
60 PHP ATH filled 60/40 NR/PP TPVs	271	313, 359, 438	20.00
100 PHP ATH filled 60/40NR/PP TPVs	270	312, 353, 435	26.05

Fire retardant properties of ATH filled NR/PP TPVs

The LOI and UL94-V tests are widely used to determine the flame retardation of materials in order to screen flame retarded formulations of the polymer. The effect of ATH content on the LOI is shown in **Figure 8** and tabulated in **Table 3**. The results obtained from UL94-V test are also reported in **Table 3**.

From **Figure 8** and **Table 3**, it is seen that the LOI of the neat 60/40 NR/PP TPV was very low (16.7 %), indicating that the sample burned rapidly. However, the LOI values increased with increasing amount of ATH, indicating that the TPV was better flame retarded. At the addition amount of 60 - 80 PHP, the LOI values were above 21, meaning that the samples burned slowly. When the addition of ATH was greater than 80 PHP, the materials showed the LOI value over 26, suggesting that the blends exhibited self-extinguishing characteristic and were considered to be highly flame retardant [32,33]. In the NR/PP blends with flame retardant ATH, several modes of action could contribute to the increased LOI value. In the test, the ATH thermally degraded and water was released, which cooled the materials and dilute gas phase. This caused fewer amounts of volatiles (fuel) and oxygen in the flame area to support the combustion [20,22]. Furthermore, the formation of barrier in the condensed phase, due to pyrolysis of the TPV component, slowed down the decomposition process and fuel production, which also raised the flame resistance of the TPV materials [23]. From **Table 3**, it is also seen that the neat TPV and the ones with low ATH loading (20 - 40 PHP) did not pass the UL94-V test as classed no rating. When the addition of ATH was above 40 PHP, the flame resistance was enhanced as the results obtained from UL94-V improved from no rating to V-2 for the TPV containing 60 - 80 PHP ATH, to V-1 for the blend with 100 PHP ATH and to V-0 for the one with 120 PHP.

Table 3 LOI and UL94-V results of 60/40 NR/PP TPVs containing various ATH contents.

ATH content (PHP)	LOI	UL94-V
0	16.7	No rating, dripping of burning specimens
20	18.3	No rating, dripping of burning specimens
40	20.0	No rating, dripping of burning specimens
60	22.0	V-2, burning time less than 30 seconds with dripping of burning particles
80	25.0	V-2, burning time less than 30 seconds with dripping of burning particles
100	30.0	V-1, burning time less than 30 seconds with no dripping of burning particles
120	33.3	V-0, burning time less than 10 seconds with no dripping of burning particles

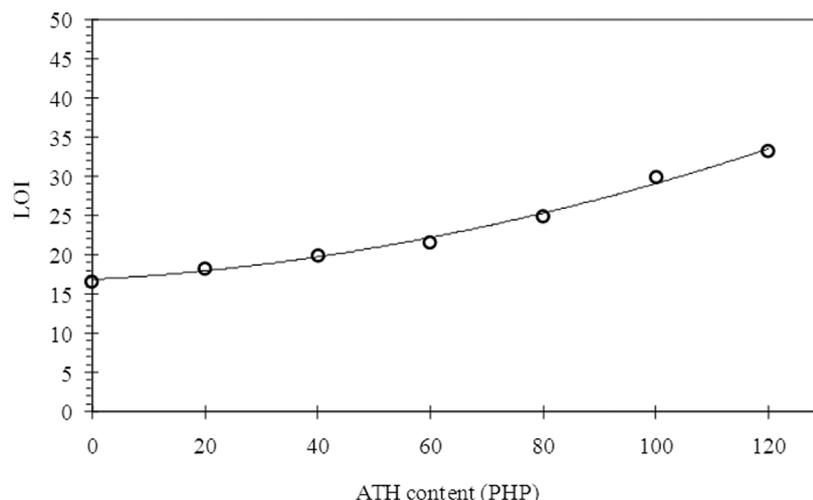


Figure 8 Effect of ATH content on LOI of 60/40 NR/PP TPVs.

Based on the discussion above, it is concluded that the strength, flexibility, decomposition process and flame retardant properties of the NR/PP TPVs showed a close relationship with the content of ATH. In comparison of different grades of TPVs within the context of this study, it was found that the 60/40 NR/PP blend with 100 PHP ATH passed criteria for flame retardant material (LOI value of 28 and UL94-V1 rating), while retaining the elastomeric properties required for the rubbery material.

Conclusions

TPVs obtained from blending NR, PP and ATH were prepared by melt mixing and crosslinking the component NR during the mixing process. The NR and PP were mixed in the composition of 60/40 %wt. The microscopic analyses by using TEM and EDX-SEM techniques showed that the 60/40 NR/PP TPVs with and without ATH had dispersed phase-like morphology and ATH was predominantly dispersed in NR phase. Increasing ATH content from 20 - 120 PHP, tensile strength and elongation at break decreased, whereas hardness and tension set slightly increased. TGA analysis showed that the addition of ATH was effective in resisting the mass-loss process of the 60/40 NR/PP blends. The LOI and UL94-V tests indicated that the flammability properties improved with increasing ATH content, and that the improvement was significant when the ATH at high content (≥ 100 PHP) was added to the 60/40 NR/PP TPVs. Regarding to the results obtained from this study, the suitable amount of ATH in the 60/40 NR/PP TPVs to achieve the required level of flame retardancy and good elastomeric properties was 100 PHP.

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References

- [1] WK Fisher. 1973, Thermoplastic Blend of Partially Cured Monoolefin Copolymer Rubber and Polyolefin Plastics, U.S. Patent 3,758,643.
- [2] AY Coran and R Patel. Rubber-thermoplastic compositions Part I: EPDM-polypropylene thermoplastic vulcanizates. *Rubber Chem. Tech.* 1980; **53**, 141-50.

- [3] MV Duin and AV Machado. EPDM-based thermoplastic vulcanizates: Crosslinking chemistry and dynamic vulcanisation along the extruder axis. *Polym. Degrad. Stab.* 2008; **90**, 340-5.
- [4] S Varghese, R Alex and B Kuriakose. Natural rubber-isotactic polypropylene thermoplastic blends. *J. Appl. Polym. Sci.* 2004; **92**, 2063-8.
- [5] C Nakason, P Wannavilai and A Kaesaman. Thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends: Effect of compatibilizers and reactive blending. *J. Appl. Polym. Sci.* 2006; **100**, 4729-40.
- [6] FR Passador, GJA Rojas and LA Pessan. Thermoplastic elastomers based on natural rubber/polypropylene blends: Effect of blend ratios and dynamic vulcanization on rheological, thermal, mechanical, and morphological properties. *J. Macromol. Sci. Part B: Phys.* 2013; **52**, 1142-57.
- [7] M Jarntong, Z Peng, N Lopattananon and C Nakason. Influence of incorporation sequence of silica nanoparticles on morphology, crystallization behavior, mechanical properties, and thermal resistance of melt blended thermoplastic natural rubber. *Polym. Compos.* 2012; **33**, 1911-20.
- [8] N Lopattananon, S Tanglakwaraskul, A Kaesaman, M Seadan and T Sakai. Effect of nanoclay addition on morphology and elastomeric properties of dynamically vulcanized natural rubber/polypropylene nanocomposites. *Int. Polym. Proc.* 2014; **29**, 332-41.
- [9] A Masa, H Saito, T Sakai, A Kaesaman and N Lopattananon. Morphological evolution and mechanical property enhancement of natural rubber/polypropylene blend through compatibilization by nanoclay. *J. Appl. Polym. Sci.* 2017; **134**, 44574.
- [10] AB Morgan and JW Gilman. An overview of flame retardancy of polymeric materials: application, technology, and future directions. *Fire Mater.* 2013; **37**, 259-79.
- [11] Y Zhu, M Otsubo, C Honda and A Ohno. Suppression effect of ATH filler on the erosion of filled silicone rubber exposed to dry band arc discharge. *Polym. Test.* 2005; **24**, 393-9.
- [12] M Sabet, A Hasssan and CT Ratnam. Flammability and thermal characterization of aluminium hydroxide filled with LDPE. *Intern. Polym. Proc.* 2013; **28**, 393-7.
- [13] P Hornby. *Fire Retardant Fillers*. In: CA Wilkie and AB Morgan (eds.). *Fire Retardancy of Polymeric Materials*. 2nd ed. CRC Press, New York, 2010, p. 163-85.
- [14] JM Cogen, TS Lin and PD Whaley. *Material Design for Fire Safety in Wire and Cable Applications*. In: CA Wilkie and AB Morgan (eds.). *Fire Retardancy of Polymeric Materials*, 2nd ed. CRC Press, New York, 2010, p. 783-808.
- [15] A Laachachi and JML Cuesta. *Flame Retardant Polymer Nanocomposites with Alumina as Filler*. In: V Mittal (ed.). *Thermally Stable and Flame Retardant Polymer Nanocomposites*. Cambridge University Press, New York, 2011, p. 314-31.
- [16] C Canaud, LLY Visconte and RCR Nunes. Mechanical and flammability properties of ATH-filled EPDM compositions. *Macromol. Mater. Eng.* 2001; **286**, 377-81.
- [17] X Zhang, F Guo, J Chen, G Wang and H Liu. Investigation of interfacial modification for flame retardant ethylene vinyl acetate copolymer/alumina trihydrate nanocomposites. *Polym. Degrad. Stab.* 2005; **87**, 411-8.
- [18] J Liang and Y Zhang. A study of the flame-retardant properties of polypropylene/Al(OH)₃/Mg(OH)₂ composites. *Polym. Int.* 2010; **59**, 539-42.
- [19] RH Farzad, A Hassan, MAM Piah and M Jawaid. Electrical and flammability properties of alumina trihydrate filled polypropylene/ethylene propylene diene monomer compositions as insulators in cable applications. *Polym. Eng. Sci.* 2014; **54**, 493-8.
- [20] R Sonnier, A Viretto, L Dummazert, M Longerry, S Buonomo, B Gallard, C Longuet, F Cavodeau, R Lamy and A Freitag. Fire retardant benefits of combining aluminum hydroxide and silica in ethylene-vinyl acetate copolymer (EVA). *Polym. Degrad. Stab.* 2016; **128**, 228-36.
- [21] Y Wang, L Zhang, Y Yang and X Cai. Synergistic flame retardant effects and mechanisms of aluminum diethylphosphinate (AlPi) in combination with aluminumtrihydrate (ATH) in UPR. *J. Therm. Anal. Calorim.* 2016; **125**, 839-48.
- [22] N Lopattananon, A Walong, A Kaesaman and M Seadan. Effect of MAH-g-PP on performance of ATH filled NR/PP thermoplastic vulcanizates. *J. Rubber Res.* 2016; **19**, 243-60.

- [23] P Khalili, KY Tshai, D Hui and I Kong. Synergistic of ammonium polyphosphate and alumina trihydrate as fire retardants for natural fiber reinforced epoxy composite. *Compos. Part B* 2017; **114**, 101-10.
- [24] C Nakason, P Wannavilai and A Kaesaman. Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends. *Polym. Test.* 2006; **25**, 34-41.
- [25] G Martin, C Barres, P Sonntag, N Garois and P Cassagnau. Morphology development in thermoplastic vulcanizates (TPV): Dispersion mechanisms of a pre-crosslinked EPDM phase. *Eur. Polym. J.* 2009; **45**, 3257-68.
- [26] S Abdou-Sabet, RC Puydak and CP Rader. Dynamically vulcanized thermoplastic elastomers. *Rubber Chem. Tech.* 1996; **69**, 476-94.
- [27] SY Fu, XQ Feng, B Lauke and YM Mai. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Compos. Part B* 2008; **39**, 933-61.
- [28] S Abdou-Sabet. *Thermoplastic Vulcanizates*. In: DR Paul and CB Bucknall (eds.). *Polymer Blends*, Vol. 2: Performance. A Wiley-Interscience Publication, New York, 2000. p. 517-55.
- [29] M Maiti, A Bandyopadhyay and AK Bhowmick. Preparation and characterization of nanocomposites based on thermoplastic elastomers from rubber-plastic blends. *J. Appl. Polym. Sci.* 2006; **99**, 1645-56.
- [30] JD Peterson, S Vyazovkin and CA Wight. Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene). *Macromol. Chem. Phys.* 2001; **202**, 775-84.
- [31] N Isitman and C Kaynak. Tailored flame retardancy via nanofiller dispersion state: Synergistic action between a conventional flame-retardant and nanoclay in high-impact polystyrene. *Polym. Degrad. Stab.* 2010; **95**, 1759-68.
- [32] AR Horrocks, M Tunc and D Price. The burning behaviour of textiles and its assessment by oxygen-index methods. *Text. Prog.* 1989; **18**, 1-186.
- [33] YL Liu, YC Chiu and TY Chen. Phosphorous-containing polyacryloxydiphenyl-silanes with high flame retardance arising from a phosphorous-siicon synergistic effect. *Polym. Int.* 2003; **52**, 1256-61.