J. Rubb. Res., **17(2)**, 80–95

Effect of Rubber Composition on Foaming and Properties of EVA/NR/PP Thermoplastic Vulcanisates (TPVs)

NATINEE LOPATTANANON*#, NUTTIDA WANGPRADIT*, CHAROEN NAKASON* AND AZIZON KAESAMAN*

Thermoplastic vulcanisate (TPV) foams made of ethylene vinyl acetate (EVA), natural rubber (NR) and polypropylene (PP) were prepared via *dynamic vulcanisation and subsequently foamed using a single screw extrusion process. EVA and NR were blended at different compositions by keeping proportion of the rubber part (EVA/NR blend) to PP at 60/40 %wt. Azodicarbonamide was used as a chemical blowing agent. Scanning electron microscopic study was performed to evaluate the foaming behaviour of TPVs and morphology of unfoamed TPVs. Blending EVA alone with PP resulted in low cell density and large cell diameter. However, the cell density increased and cell diameter decreased significantly upon partial replacement of EVA with NR. The bulk density of EVA/NR/PP foams was found to be independent of blend composition. Tensile strength and elongation at break were improved with increased NR content, but these two properties were reduced after heat ageing. Thermogravimetric analysis indicated that thermal stability of the TPV foams was not affected as more EVA in the component rubber was replaced with NR. The present study suggested that the production of light weight and good thermal resistant EVA/NR/PP TPV foams with improved cell structure and strength was obtained with the partial replacement of EVA by 12 %wt NR.*

Keywords: Natural rubber; ethylene vinyl acetate; polypropylene; thermoplastic vulcanisate; foam

Ethylene vinyl acetate copolymer (EVA) is one of the popularly used polymers for production of foam due to its balanced combination of properties such as resistance to chemicals, UV radiation, resistance to abrasion, flexibility and rubberiness[1–3]. However, the EVA foam has certain inherent weaknesses, *i.e*., low tear strength, low compression set and low rebound resilience, which limit its potential use in some applications of rubber foams. Additionally, the EVA has low melt strength and cannot withstand the pressure acting on cell walls during the expansion, leading to collapse of gas bubbles and loss of foaming gas[1], thus resulting in a non-uniform cell structure and poor properties of EVA foam products. As

*Center of Excellence in Natural Rubber Technology (CoE-NR), Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, 94000 Thailand.
Corresponding author (e-mail: lnatinee@bunga.pn.psu.ac.th)

the EVA foams present a series of problems, it is necessary to improve their properties to meet the end product specifications and requirements for rubber foams. It was reported that one of the simple and effective approaches often applied to change the properties of EVA foams is mixing EVA with other rubbers that exhibit good mechanical properties and high elasticity[4] and/or filler[5].

NR, a natural polymer, has very high tensile strength, good flexibility, low compression set, high resilience and good resistance to tearing and abrasion. Many attractive properties of NR make it suitable for blending with EVA to modify the foam properties. In the previous study of Kim *et al.*[4], it was shown that a great improvement in tear strength and rebound resilience of EVA foams was obtained by introducing just 10 – 30 p.h.r. NR.

To promote final properties of rubber foams, the crosslinking of rubber foam is normally introduced for better control over nucleation and formation of cells with uniform size[6]. However, the crosslinked rubber and scrap or defective parts generated along the foaming process are not processable. Consequently, the use of rubber foam in many applications results in a growing volume of foam waste and environmental problems.

Thermoplastic vulcanisates (TPVs) are a special class of rubber/plastic blends developed by Fisher[7] as well as Coran and Patel[8]. They are produced by a process of crosslinking the rubber phase during melt mixing with thermoplastics. The resulting morphology consists of a cured rubber phase dispersed within the continuous plastic mixture[9]. This particular morphology combines the benefits of vulcanised rubber with the processing ease of thermoplastics. These properties also make TPV recyclable. The major advantage of TPV is increased usage in automotive application, wires/cables, soft-touch materials, *etc*. As for thermoplastic elastomers, the interest in developing TPV foam products has been a focus of research studies[10–14]. The first attempt to foaming commercial grade TPVs based on ethylene-propylene-diene monomer (EDPM)/ polypropylene (PP) blends was carried out by Dutta and Cakmak[10]. Kiatkamjornwong *et al.*[11], studied the foaming behaviour of natural rubber/polyethylene (PE) blends. Their results indicated that the cellular structure dramatically affected the mechanical properties of the foamed NR/PE blends, which was in turn controlled by foam processing variables such as heating time, blowing agent content, crosslinking agent content and rubber to plastic blend composition. The processing condition dependent morphological effects were also presented for foaming EDPM/PP TPVs[12], waste ground tyre rubber powder (WGRT)/PP[13] and thermoplastic elastomer based on styrene-ethylene-butylene-styrene block copolymer (SEBS)/polystyrene blend[14].

In this study, we attempted to develop TPV foam prepared from EVA/NR/PP ternary blend. The EVA and NR were blended at different EVA/NR blend compositions. The EVA/NR blends were later mixed with PP at a fixed rubber to plastic ratio of 60:40 %wt. The dynamic vulcanisation and foaming of EVA/NR/PP blends were carried out by using a single-screw extruder. The cellular structure, tensile properties, ageing properties and thermal stability of the EVA/NR/PP TPV foams and morphology of the unfoamed EVA/ NR/PP TPVs were studied.

EXPERIMENTAL

Materials

NR ribbed smoked sheet (RSS3), having a density of 0.92 g/cm^3 and Mooney viscosity (ML 1+4 (100ºC)) of 76, was locally obtained from the Rubber Farmer Organisation of

Khokpho-Maelarn (Pattani, Thailand). Ethylene vinyl acetate (EVA) with a vinyl acetate content of 28% and melt flow index of 20 g/10 min (190ºC/2.16 kg) was purchased from POLENE Co., Ltd. (Thailand). This material had a density of 0.96 g/cm^3, Mooney viscosity [ML 1+4 (100ºC)] of 16 and melting temperature of 70ºC. Polypropylene (PP) (Moplen HP553R) with melt flow rate of 22 g/10 min at 230ºC and density of 0.90 g/cm^3 was supplied by HMC Polymers (Bangkok, Thailand). The melting temperature of PP was at 145 – 151ºC. Azodicarbonamide (ADC, Grade Cellcom-AC300F) supplied by Innovation Co. Ltd., (Thailand) was used as foaming agent. This material had a decomposition temperature of 201 – 208ºC and a gas yield of 215 – 225 mL/g. Zinc oxide (ZnO, Univentures Public Co. Ltd., Thailand) and stearic acid (Imperial Chemical Co. Ltd., Thailand) were used as kicker to lower the decomposition temperature of the foaming agent. Dicumyl peroxide (DCP, Wuzhou International Co. Ltd., China) was used as a curing agent for vulcanisation of EVA and NR. Trimethylol propane trimethylacrylate (TMPTMA) (Behn Meyer Chemical Co. Ltd., China) was used as a co-curing agent. 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (Flexsys, US) was used as an antioxidant. Ultra-blend^{TM}6000 (Perfarmance Additives Sdn. Bhd., Malaysia) was used as a blend homogeniser. Ultra-blend^{TM}6000 is the mixture of light coloured, aliphatic hydrocarbon resins. Ultra-lube^{TM}220 (Perfarmance Additives Sdn. Bhd., Malaysia) was used as a processing aid. It is a high molecular weight, aliphatic fatty acid ester. Paraffinic oil (White oil grade A no. 15, China Petrochemical International Co. Ltd., China) was used as a plasticiser to reduce the viscosity difference of EVA/NR blend and as processing aid to promote filler dispersion. Commercial grade china clay (Kij Paiboon Chemical Ltd., Thailand) was used as filler. Commercial china clay used was principally composed of hydrated aluminosilicate ($Al_2O_3.2SiO_2.2H_2O$).

Fabrication of EVA/NR/PP TPV Foams

EVA pellets and NR (EVA/NR composition: 60/0, 48/12, 36/24, 24/36, 12/48, 0/60 %wt) were firstly melt-mixed in an internal mixer at a temperature of 70ºC and rotor speed of 60 r.p.m. and the additives were added in the following order: Ultra-blend^{TM}6000, TMQ, Ultra-lube^{TM}220, paraffinic oil and clay. The mixture ingredients are shown in *Table 1*. The obtained EVA/NR blends were then mixed with PP at 180ºC and 60 r.p.m. in the internal mixer and added with ZnO (3.0 part by weight, p.b.w.) and stearic acid (1.0 p.b.w.). The composition of rubber (EVA/NR mixture) and PP was kept at 60/40 %wt. Finally, ADC (5 p.b.w.), DCP (0.7 p.b.w.) and TMPTMA (4 p.b.w.) were added to EVA/NR/PP blends on the two-roll mill at 100ºC. The compounds of EVA/NR/PP blends were cut into pellets. The blend pellets were extruded using a single-screw extruder (L/D = 25/1) equipped with a slit die ($12^w \times 20^l$ mm^2). The extruder barrel was heated in three zones (160, 170, 180ºC) from the feed to die zone. The screw speed was 30 r.p.m. Foaming of EVA/NR/PP blends included simultaneous decomposition of ADC and crosslinking of polymer during extrusion, followed by expansion at die exit. The extruded strips of foamed TPV were cooled using cold water. The TPV foam specimens were cut from the extruded strips and dried in an oven at 50ºC for 24 hours. These samples were kept in a desiccator prior to characterisation.

Characterisation of EVA/NR/PP TPV Foams

The tensile test was performed on a Hounsfield tensometer model H10KS (Hounsfield Test Equipment Co. Ltd. UK), according to *ASTM D412-98a*[15]. The dumb-bell shaped test specimens were cut from foamed TPV. The specimens were stretched at

TABLE 1. COMPOUNDING FORMULATION OF EVA/NR RUBBER BLENDS

Ingredients	Quantities (Parts per hundred of rubber, p.h.r.)
EVA/NR rubber blend	100
Ultra-blend^{TM}6000	2
TMQ	3
Ultra-lube^{TM}220	3
Paraffinic oil	80
China clay	40

room temperature (25 ± 2ºC) with an extension rate of 500 ± 50 mm/min. The average tensile properties for each cellular TPV sample were determined from five specimens.

Heat ageing properties were studied according to *ASTM D573-04*[16]. The dumbbell test pieces were heated at 100ºC in an oven for 22 hours. These samples were then conditioned at room temperature for 16 h prior to mechanical testing at room temperature.

Density of the foamed EVA/NR/PP TPVs was determined by mean of mass : volume ratio of the samples according to *ASTM D1622-93*[17].

The thermal stability for the foamed blends was studied using a thermogravimetric analyzer (TGA 7, STA 6000, Perkin Elmer, USA). The TGA analysis was operated under inert atmosphere of N_2 at a flow rate of 20 mL/min. The samples (8 – 12 mg) were heated from 0ºC – 800ºC at the rate of 10ºC/min.

The structures of the unfoamed and foamed TPVs were examined using a scanning electron microscope (SEM, FEI Quanta 400 FEG, Netherland). The unfoamed TPVs were cryogenically cracked in liquid nitrogen, followed by treatment in boiling xylene for 20 min to dissolve the uncrosslinked rubber and PP over the fractured surfaces. For the foamed TPVs, the samples were immersed in liquid nitrogen and razor cut. The samples were then sputter-coated with a thin layer of gold to avoid electrical charging during examination. The average cell diameter (d) was determined by measuring the maximum diameter of each cell and cell density (N_f), or the number of cells per unit volume, was calculated from *Equation 1*[18].

$$N_f = \left(\frac{nM^2}{A}\right)^{3/2} \quad \ldots 1$$

where n is the number of cells on the SEM photomicrograph, M is the magnification factor and A is the area of the micrograph (cm^2).

RESULTS AND DISCUSSION

Structure of EVA/NR/PP TPV Foams

Figure 1 shows the SEM images of the cellular structure of the unaged EVA/NR/PP TPVs with different EVA/NR compositions. Generally, it is seen that the cured EVA/NR/PP blends had a closed cell structure. The foam made of 60/0/40 EVA/NR/PP blend showed more or less spherical cells together with less cells and larger cell diameter than that of 0/60/40 EVA/NR/PP blend

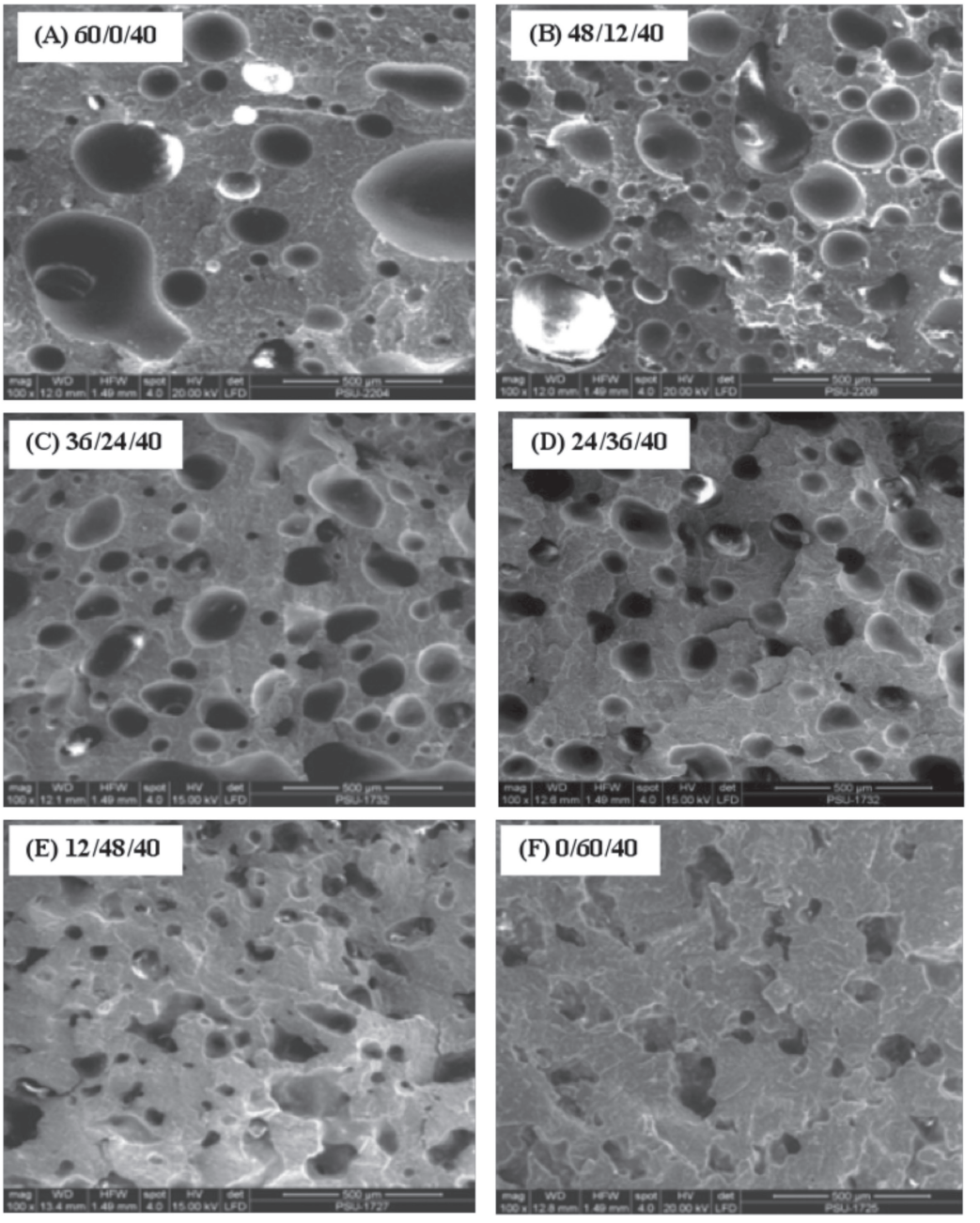

Figure 1. SEM photomicrographs representing cell structure of EVA/NR/PP TPV foams before thermal ageing at different EVA/NR rubber blend compositions.

(*Figures 2* and *3*). The differences in cell density and cell diameter between these two blends are due to changing in the component rubber, which could be mainly connected with the variation in rubber properties such as rubber viscosity and solubility of foaming gas in each blend component.

In the previous study[5], it was proved that the gas bubble was mainly generated in the EVA phase rather than NR phase for the peroxide cured EVA/NR blend, foamed by using azodicarbonamide as blowing agent. Comparing the TPV foam containing only NR in the rubber phase, the nucleation of gas cells in the TPV with EVA alone was expected to be greater because of its comparatively higher foamability. However, the Mooney viscosity, as a measure of rubber viscosity, for the EVA [ML 1+4(100ºC) = 16] was much lower than that of the NR [ML 1+4(100ºC) = 76], meaning that the mixture of EVA and PP also had greater ability to flow or lower melt viscosity. This implied that the melt strength of EVA/PP blend material present in the cell wall at processing temperature was insufficient to withstand the gas pressure acting on the cell wall as the nucleated bubbles continued to grow. The cell walls would eventually rupture and coalesce to form bigger cells and thereby the numbers of gas cells was reduced accordingly. When the small amount of natural rubber (12 %wt) was added into the rubber phase of the TPV foam, the cell density increased significantly and the cell diameter decreased (*Figures 2* and *3*). The introduction of natural rubber may cause stiffer cell walls, which suppressed cell growth and breaking of the cell during the foaming stage, resulting in an increase in cell density, smaller cell diameter together with increased uniformity in cell diameter distribution (*Figures 1* to *3*). However, as the added content of NR was increased above 12 %wt, the cell density and cell diameter of the EVA/NR/PP blends were not significantly different within experimental error (*Figures 2* and *3*).

The above results suggest that both cell density and cell diameter of the EVA/NR/PP TPV foams were not strongly influenced by EVA/NR compositions and the improved morphology of the EVA/NR/PP foam *i.e.*, increased cell density and decreased cell diameter, was only attained when small amounts of natural rubber (12 %wt) was added.

Density of EVA/NR/PP TPV Foams

Figure 4 shows the variation of foam density of EVA/NR/PP TPV with different NR contents. The final foam density is generally controlled by two competitive processes in the cell formation, *i.e.*, cell nucleation, cell growth and coalescence[19]. As can be seen from *Figure 4*, the foaming of EVA/PP binary blend-based TPV gave rise to lower bulk density when compared with that of NR/PP blend-based one with the same rubber to plastic composition. Although the cell density of the foamed EVA/PP TPV was lower than that of the NR/PP TPV foam, the cell diameter of the EVA/PP blend-based TPV foam was about twice over that of the NR/PP TPV foam. So, the lower foam density of EVA/PP blends was mainly due to the large cell size. However, the introduction of NR at levels between 12 – 48 %wt into the TPV foams did not give a noticeable change in foam density because their cell density and cell diameter (*Figures 2* and *3*) were comparable.

Tensile Properties of EVA/NR/PP TPV Foams

Figure 5 shows the variation of tensile strength and elongation at break of the EVA/NR/PP TPV foams with increasing NR content before and after heat ageing. It is well accepted that the mechanical properties of the foam polymers are sensitive to the nature of solid phase, cell structure and foam density[11,20–21].

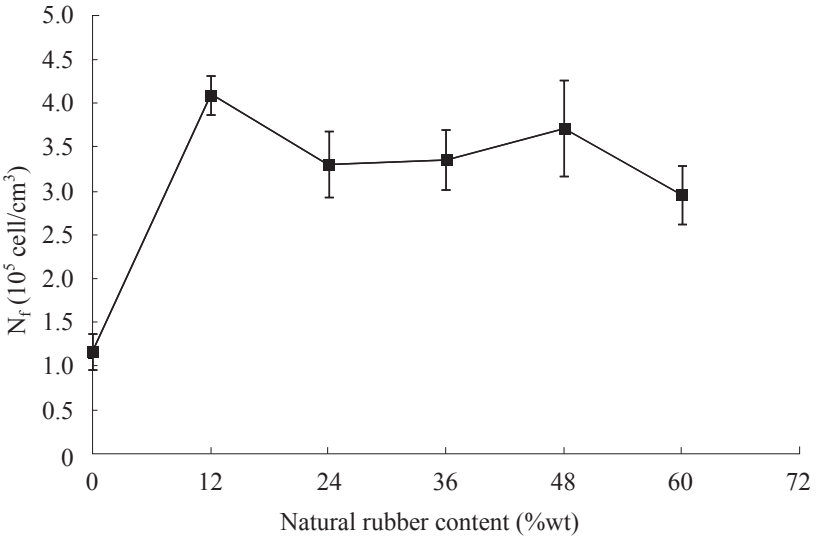

Figure 2. Cell density (N_f) of EVA/NR/PP TPV foams before thermal ageing at different NR contents.

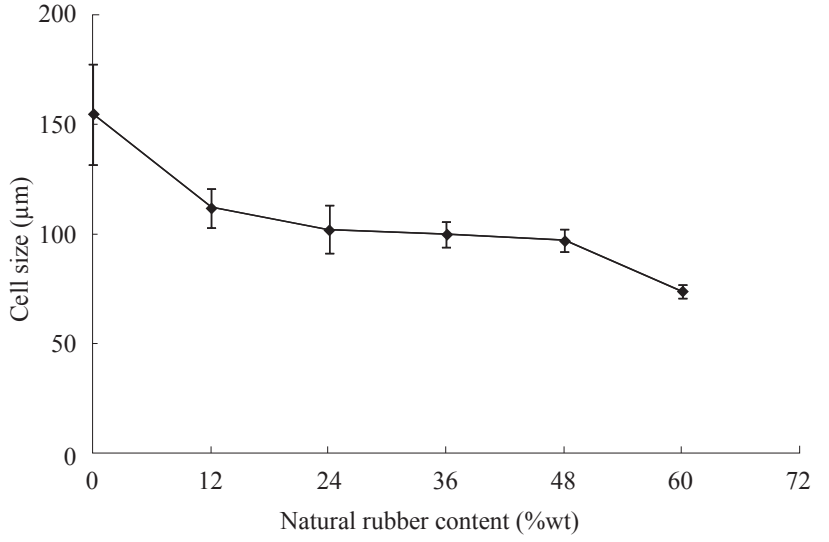

Figure 3. Cell size of EVA/NR/PP TPV foams before thermal ageing at different NR contents.

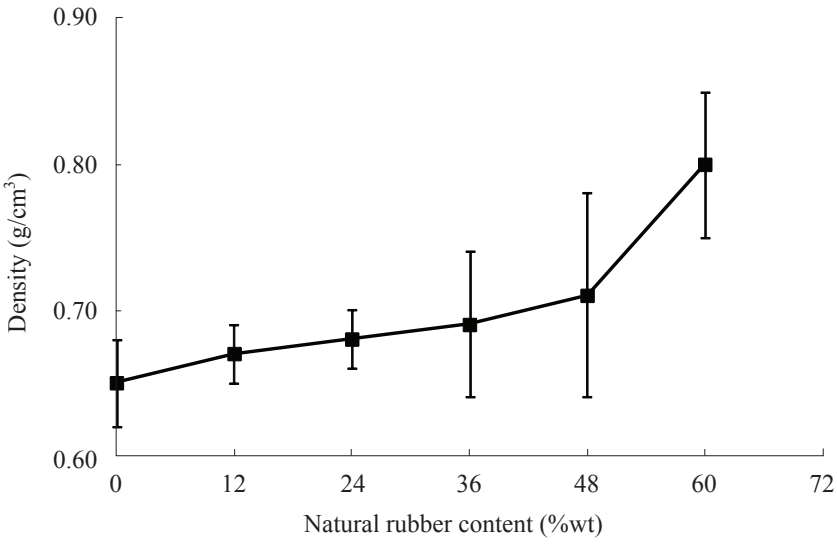

Figure 4. Density of EVA/NR/PP TPV foams of EVA/NR/PP TPV foams before thermal ageing at different NR contents.

The tensile strength and elongation at break of the dynamically cured EVA/NR/PP blends generally increased as more NR was added into the blends. Regarding SEM observations of TPV morphology for the different blends which will be discussed later, the results show that crosslinking level of the blends increased with increasing NR content. Therefore, the foams with more crosslinked rubber would promote tensile properties. From *Figure 5*, it is also seen that both tensile strength and elongation at break of all the foamed EVA/NR/PP blend-based TPV were reduced due to oxidation and degradation of the blend components by heat ageing. The reduction in these two properties was likely evident with replacement of virgin EVA rubber with higher NR content because concentration of the unsaturated double bond available in the blends was increased. This unsaturated bond is the main attack site in the chain scission process during heat ageing[22]. The change in TPV properties as a result of material degradation is not only induced by the main chain scission, but also the change in original crosslink structure such as formation of crosslinking between rubber chains and scission of crosslink bond. However, it is well known that the C-C crosslink formed between chains in the peroxide curing system was thermally stable[23]. Thus, the random bond scission on the main chains of blend components reasonably caused the decrease in tensile properties after ageing. It is also interesting to note the observation of a large decrease in elongation at break for the EVA/PP blend-based foams on ageing. The apparent explanation for this observation was the change in crystalline part of the EVA phase after heat ageing. The ethylenic blocks of EVA may undergo segmental motion during heat ageing at 100ºC, leading to partial alignment of their molecular chains when cooling. As a result, the EVA/PP blend material became stiffer by the influence of crystalline part of the EVA and had a lower elongation at break after heat ageing.

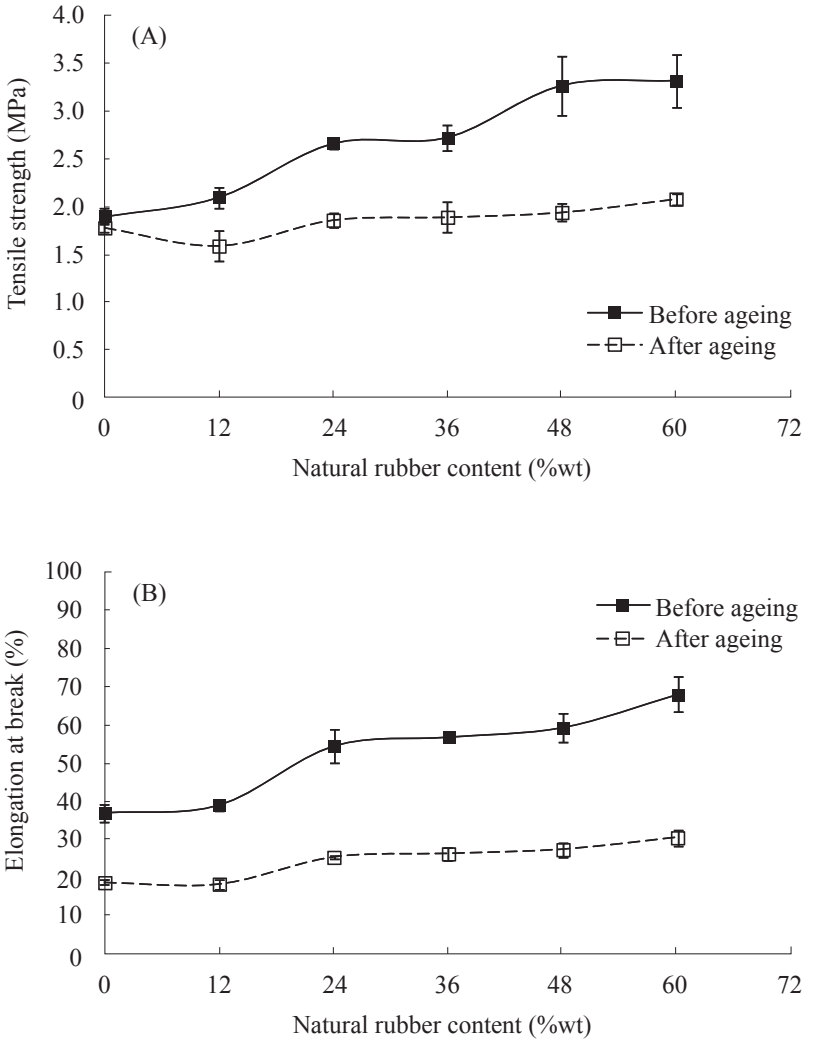

Figure 5. Tensile strength (A) and elongation at break (B) of EVA/NR/PP TPV foams before and after thermal ageing at different NR contents.

Thermal Stability of EVA/NR/PP TPV Foams

Figures 6 and *7* show the profiles of TGA weight loss and derivatives of thermogravimetry (DTG) plotted against temperature for reference materials such as pure and unfoamed EVA, NR and PP as well as the TPV foams with different blend ratios, respectively. From *Figure 6A*, the mass loss curve of EVA showed that the EVA decomposed by a two-step mechanism[24], with the loss of acetic acid of vinyl acetate groups at the first step (280 − 390ºC) and the random

chain scission of the polyethylene containing unsaturated polyenes at around 400 − 500ºC. The TGA analysis of the NR and PP represents a single step decomposition behaviour, where the weight loss was in a temperature range of 180 − 480ºC and 325 − 485ºC, respectively. The onset temperature of decomposition defined as temperature at which a mass loss of the material is 5% (T_{d5}) and maximum decomposition temperature (T_{dmax}) of the raw materials are determined and also given in *Table 2*. The onset degradation temperature indicates the thermal stability of the materials[25]. It is seen that the PP had higher onset degradation temperature than that of the EVA and NR, indicating better thermal stability. As can be seen from *Figures 7A* and *B*, the TPV foams having a large portion of EVA (48 – 60 %wt) as component rubber showed two degradation processes at low temperatures (150 − 380ºC) and high temperatures (380 − 500ºC), whereas ones containing higher amounts of NR (24 − 60 %wt) presented additional degradation process at intermediate temperatures (320 − 400ºC). From *Figure 7B*, it is clear that the mass loss rate at lower temperatures did not change with changing blend composition. The paraffinic oil (80 p.h.r.) was mixed with the EVA/NR blends (*Table 1*) and the TGA investigation of paraffinic oil (*Figure 6A*) suggested that this oil started to decompose at 140ºC and completely decomposed at 380ºC, as the acetic acid was eliminated over this temperature range. Thus, weight loss of the TPV foams at low temperatures was caused by the simultaneous decomposition of paraffinic oil and EVA. The weight loss at intermediate temperatures was related to NR degradation (*Figure 6A*) and the weight loss rate was increased in correspondence with the increase in the NR content (*Figure 7B*). The degradation at high temperatures corresponded with co-concurrence of PP pyrolysis and thermal degradation of polyethylene forming after deacetylation of EVA. In case of the foamed EVA/NR/PP TPVs, the T_{d5} was likely reduced with addition of NR, but the change in T_{d5} was slight even with the sample where the EVA was entirely replaced with NR (*Figure 7* and *Table 2*). This was due to similar levels of thermal stability (T_{d5}) for both EVA and NR. It is also seen that the T_{dmax} of the foamed TPVs was not influenced by blend composition and they were quite comparable to those of individual components (*Table 2*). Based on the TGA results, it is suggested that the partial replacement of EVA by low addition of NR (12 %wt) provided the most stable blend when compared with the other EVA/NR/PP TPV foams.

Morphology of EVA/NR/PP TPV

Since microscopy techniques have provided enough evidence to support the fact that blend morphology is one of the important factors affecting TPV performance, therefore morphology of TPV samples before foaming was characterised by the SEM technique. *Figure 8* shows SEM micrographs of the xylene extracted fractured surfaces for the unfoamed TPVs at different blend compositions. The surfaces of these TPVs showed a number of small spherical domains of crosslinked parts of different blended EVA/NR rubbers, which were left over after preferential dissolution of PP matrix in hot xylene. These observations indicated that all the blends showed a morphology that was typical to dispersed phase morphology. From *Figure 8*, it is obvious that the size of rubber particles was apparently similar (1 – 5 μm), but the number of rubber particles clearly differed among the blends. For instance, more rubber particles were seen together with higher incorporation of NR. In any dispersed phase system of TPV, the parameters related to rubber components that have been identified to influence the ultimate tensile strength and elongation of a TPV are its degree of crosslink and particle size together

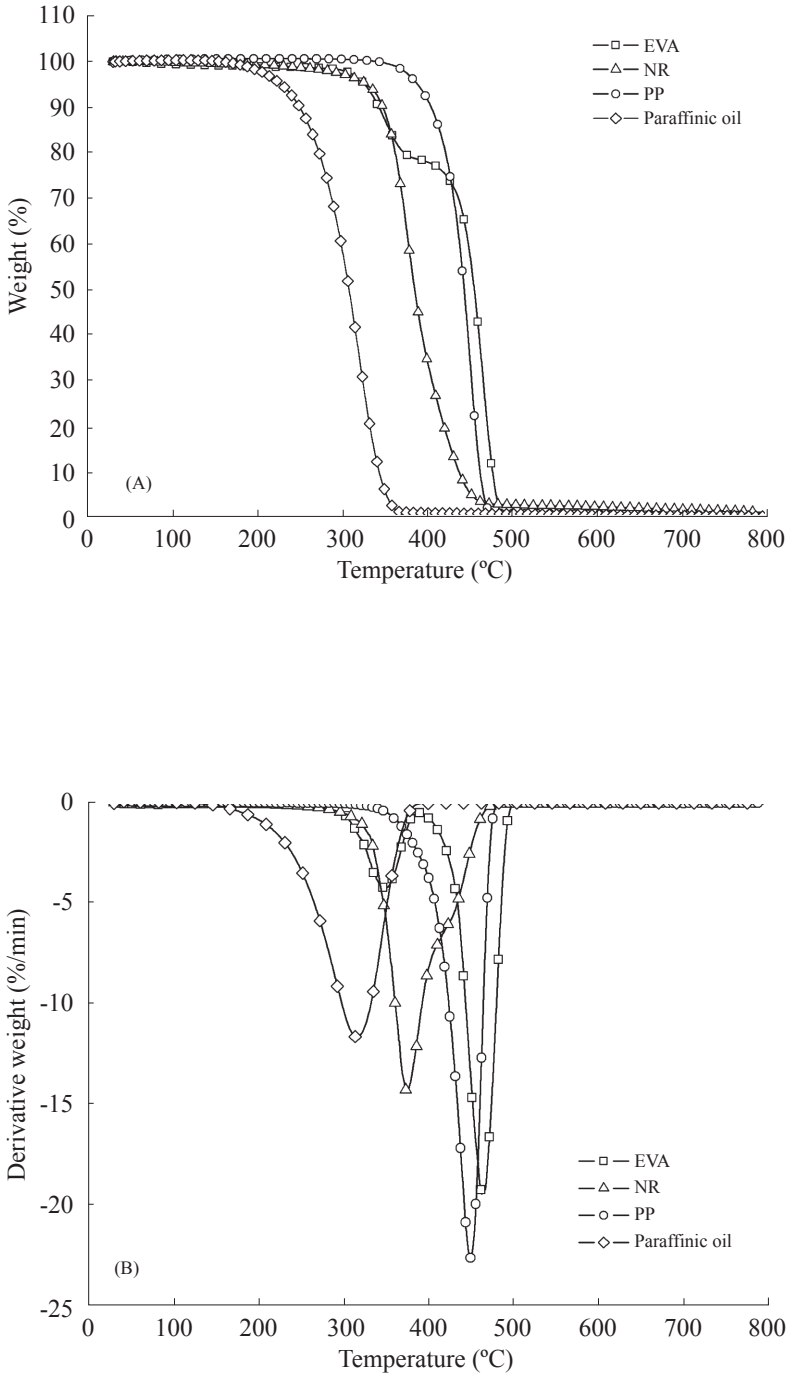

Figure 6. TGA (A) and DTG (B) curves of reference EVA, NR, PP and paraffinic oil.

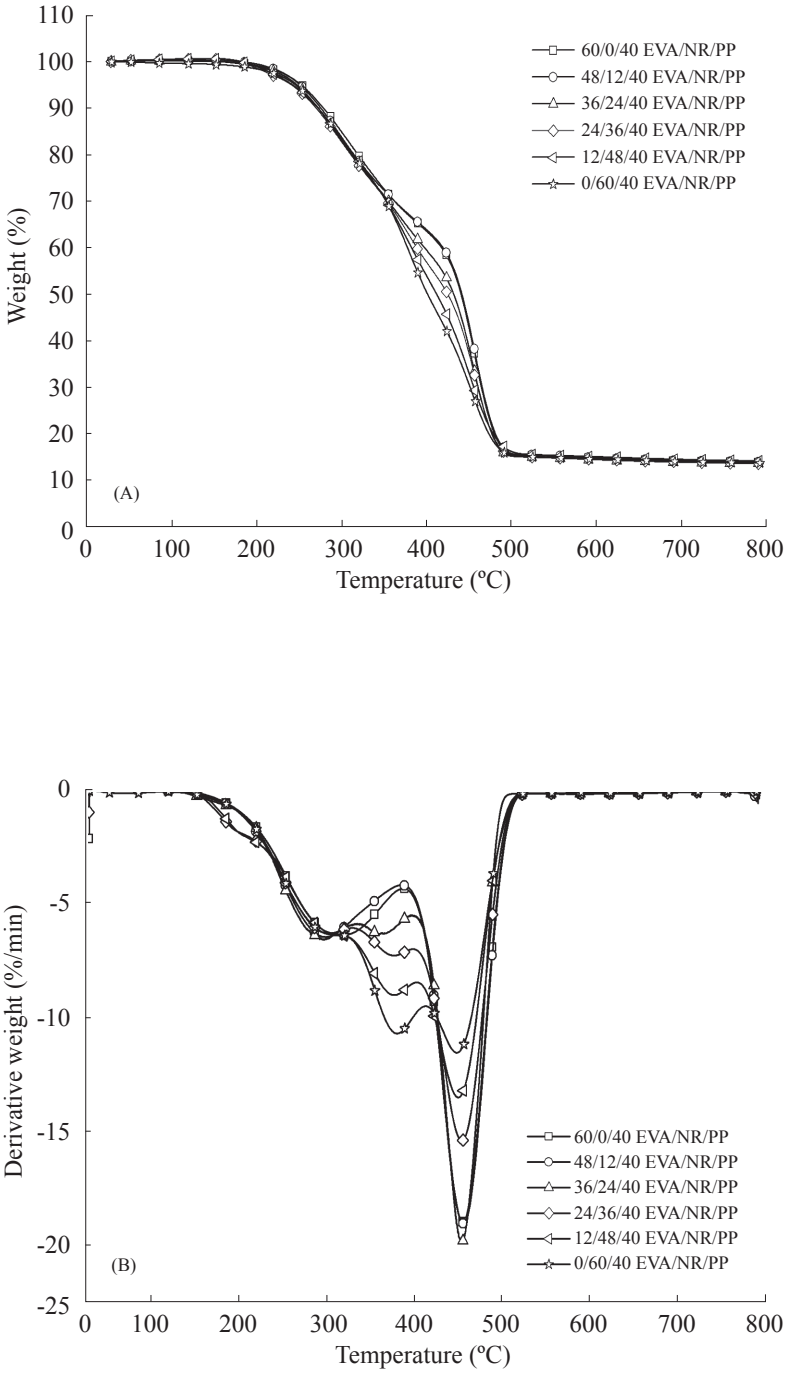

Figure 7. TGA (A) and DTG (B) curves of EVA/NR/PP TPV foams before thermal ageing at different EVA/NR rubber blend compositions.

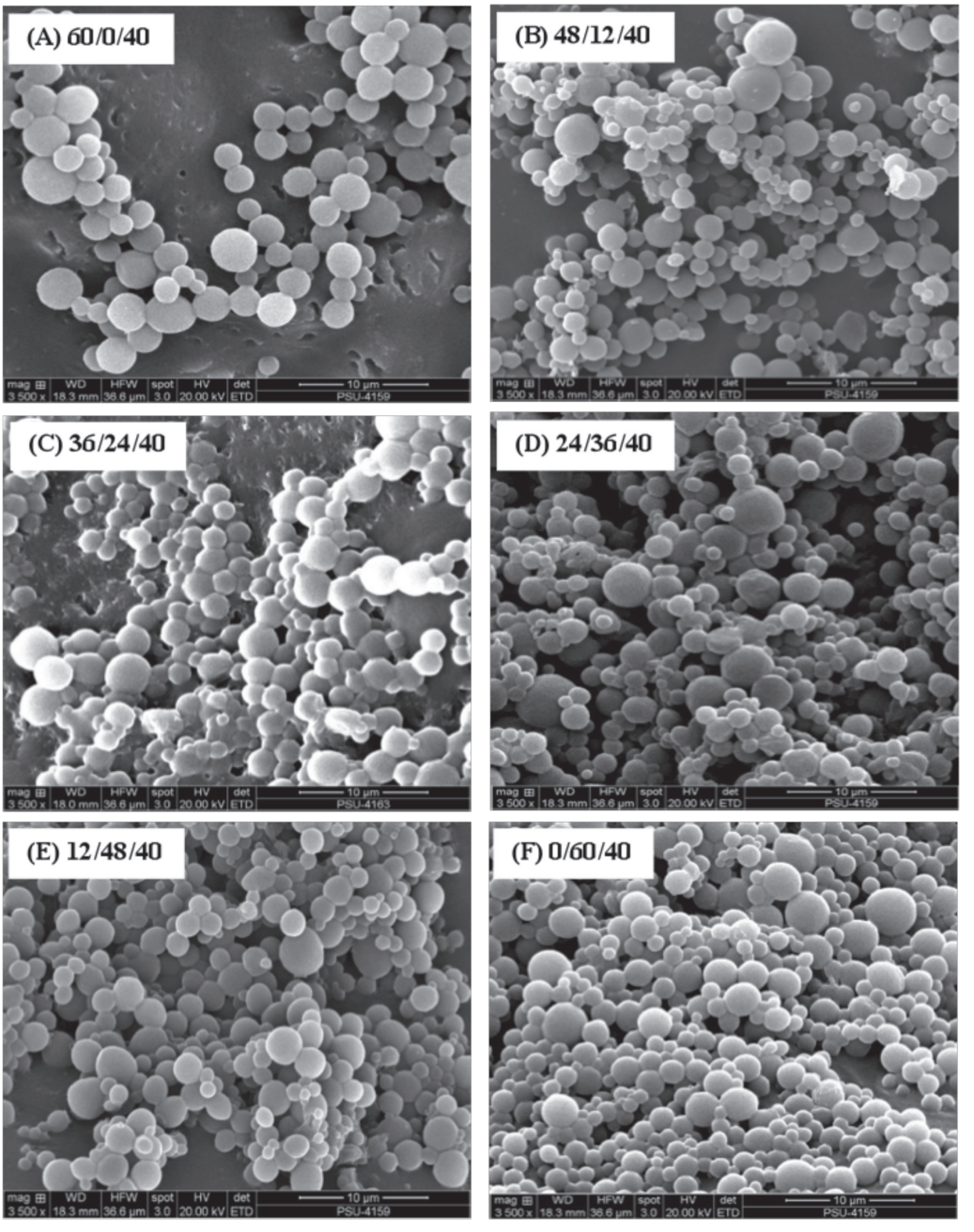

Figure 8. SEM photomicrographs representing morphology of unfoamed EVA/NR/PP TPVs at different EVA/NR rubber blend compositions.

TABLE 2. TEMPERATURES AT ONSET OF DECOMPOSITION (T_{d5}) AND MAXIMUM DECOMPOSITION (T_{dmax}) OF PURE EVA, PURE NR, PURE PP, PARAFFINIC OIL AND EVA/NR/PP TPV FOAMS

Materials	T_{d5} (ºC)	T_{dmax} (ºC)
EVA	326	347, 460
NR	328	375
PP	388	455
Paraffinic oil	228	310
60/0/40 EVA/NR/PP TPV foam	252	315, 455
48/12/40 EVA/NR/PP TPV foam	251	298, 455
36/24/40 EVA/NR/PP TPV foam	247	297, 364, 454
24/36/40 EVA/NR/PP TPV foam	240	299, 371, 454
12/48/40 EVA/NR/PP TPV foam	242	303, 371, 450
0/60/40 EVA/NR/PP TPV foam	246	303, 375, 450

with its distribution[26]. More observed number of rubber particles indicated a more stabilised structure of component rubber, introduced during dynamic vulcanisation, thereby promoting the tensile strength and elongation at break of ENR/NR/PP TPVs as previously shown in *Figure 5*.

CONCLUSIONS

Properties of TPV foams produced by dynamic vulcanisation and foaming of EVA/NR/PP ternary blends at different EVA/NR rubber blend compositions were characterised. The weight fraction of rubber to plastic was kept at 60/40 %wt. SEM results showed that the EVA/NR/PP foams had a closed cell structure. Foaming the TPV containing EVA as component rubber gave rise to lowest cell density and largest cell diameter. However, the cell density was greater and cell diameter became smaller when the component rubber in the TPV foams was combined with NR. For the TPV foams made with different EVA/NR blends, there was no noticeable difference in cell density and cell diameter. The bulk density of the EVA/NR/PP blend-based foams had not changed significantly as the EVA/NR blend composition was changed. The crosslinking level of rubber phase in the foamed EVA/NR/PP TPVs increased with increasing NR content. As a result, the tensile strength and elongation at break were promoted. It was also found that the tensile strength and elongation at break of ternary blend foams decreased after heat ageing and the decrease depended on the amount of NR. Thermal stability of the foamed TPVs was not affected by NR incorporation. According to this study, dynamic crosslinking and foaming EVA/NR/PP blends with 12 %wt addition of NR produced light weight and good heat resistant foamed materials with improved cellular structure and strength in comparison with the EVA/PP TPV foam.

ACKNOWLEDGEMENTS

We would like to acknowledge the Higher Education Research Promotion and National Research University Project of Thailand (SAT540523M), the Center of Excellence

in Natural Rubber Technology (CoE-NR) and the Graduate School, Prince of Songkla University, Thailand for financial support.

Date of receipt: September 2013
Date of acceptance: December 2013

REFERENCES

1. RIZVI, A., CHEN, N. AND PARK, C.B. (2001) Study on the Mechanical Properties of Crosslinked EVA Foams. *SPE-ANTEC Tech. Papers, Paper# PENG-11-2010-0462*, Boston, MA, May 1−4.

2. XU, Z.R., PARK, H.Y., KIM, H.Y. AND SEO, K.H. (2008) Effects of Modified MMT on Mechanical Properties of EVA/ MMT Nanocomposites and their Foams. *Macromol. Symp*., **264**, 18.

3. PARK, K.W., KIM, G.H. AND CHOWDHURY, S.R. (2008) Improvement of Compression Set Property of Ethylene Vinyl Acetate Copolymer/Ethylene-1-Butene Copolymer/ Organoclay Nanocomposite Foams. *Polym. Eng. Sci*., **48**, 1183.

4. KIM, M.S., PARK, C.C., CHOWDHURY, S.R. AND KIM, G.H. (2004) Physical Properties of Ethylene Vinyl Acetate Copolymer (EVA)/Natural Rubber (NR) Blend Based Foam. *J. Appl. Polym. Sci*., **94**, 2212.

5. LOPATTANANON, N., JULYANON, J., MASA, A., KAESAMAN, A., THONGPIN, C., SAKAI, T. "The Role of Nanofillers on NR/EVA/Clay Nanocomposite in Blending and Foaming", *J. Vinyl Addit. Techn*. (in press).

6. TAI, H.J. (2005) Bubble Size Distribution and Elastic Retraction in Crosslinked Metallocene Polyolefin Elastomer Foams. *J. Polym. Res*., **12**, 457.

7. FISHER, W.K. (1973) Thermoplastic Blend of Partially Cured Monoolefin Copolymer Rubber and Polyolefin Plastics, *U.S Patent no. 3758643*.

8. CORAN, A.Y. AND PATEL, R. (1980) Rubber-Thermoplastic Compositions. Part I. EPDM-Polypropylene Thermoplastic Vulcanizates. *Rubb. Chem. Technol.*, **53**, 141.

9. DUIN, M. V. AND MACHADO, A. V. (2008) EPDM-based Thermoplastic Vulcanisates: Crosslinking Chemistry and Dynamic Vulcanisation Along the Extruder Axis. *Polym. Degrad. Stabil*., **90**, 340.

10. DUTTA, A. AND CAKMAK, M. (1992) Influence of Composition and Processing History on The Cellular Morphology of The Foamed Olefinic Thermoplastic Elastomer. *Rubb. Chem. Technol*., **65**, 932.

11. KIATKAMJORNWONG, S., THINAKORN, S. AND TASAKORN, P. (2000) Foaming Conditions of High Density Polyethylene-Natural Rubber Blends. *Plast. Rubb. Compos*., **29**, 177.

12. KIM, S.G., PARK, C.B., KANG, B.S. AND SAIN, M. (2006) Foamability of Thermoplastic Vulcanizates (TPVs) with Carbon Dioxide and Nitrogen. *Cell. Polym*., **25**, 19.

13. ZHANG, Z.X., ZHANG, S.L., LEE, S.H., KANG, D.J., BANG, D.S. AND KIM, J.K. (2008) Microcellular Foams of Thermoplastic Vulcanizates (TPVs) Based on Waste Ground Rubber Tire Powder. *Mater. Lett*., **62**, 4396.

14. SHARUDIN, R.W. B. AND OHSHIMA, M. (2013) Preparation of Microcellular Thermoplastic Elastomer Foams from Polystyrene-b-Ethylene-Butylene-b-Polystyrene (SEBS) and Their Blends with Polystyrene. *J. Appl. Polym. Sci*., **128**, 2245.

15. Annual Book of ASTM D412-98a (2005) Standard Test Method for Vulcanized Rubber and Thermoplastic Elastomers-Tension. Section 9: Rubber, 09.01, 44–57.

16. Annual Book of ASTM D573-04 (2005) Standard Test Methods for Rubber Property-Deterioration in an Air Oven. Section 9: Rubber, 09.01. 124–129.

17. Annual Book of ASTM D1622-93 (1977) Standard Test Method for Apparent Density of Rigid Cellular Plastics. Section 8: Plastics, 08.01, 342–344.

18. KUMAR, V. AND SUH, N.P. (1990) A Process for Making Microcellular Thermoplastic Parts. *Polym. Eng. Sci*., **30**, 1323.

19. MITSUNAGA, M., ITO, Y., RAY, S.S., OKAMOTO, M. AND HIRONAKA, K. (2003) Intercalated Polycarbonate/Clay Nanocomposites: Nanostructure Control and Foam Processing. *Macromol. Mater. Eng*., **288**, 534.

20. KIM, D.W., PARK, K.W., CHOWDHURY, S.R. AND KIM, G.H. (2006) Effect of Compatibilizer and Silane Coupling Agent on Physical Properties of Ethylene Vinyl Acetate Copolymer/Ethylene-1-Butene Copolymer/clay Nanocomposite Foams. *J. Appl. Polym. Sci*., **102**, 3259.

21. XIN, Z.X., ZHANG, Z.X., PAL, K., KANG, D.J., LEE, S.H. AND KIM, J.K. (2009) Effects of Waste Ground Rubber Tire Powder (WGRT) and Chemical Blowing Agent Content on The Cell Morphology and Physicomechanical Properties of Injection-Molded Polypropylene/WGRT Foams. *J. Vinyl Addit. Technol*., **15**, 275.

22. CHEN, M., AO, N.J., LIAO, Y.Y., CHEN, Y. AND ZHOU, H.L. (2006) Thermooxidative Degradation of Natural Rubber/Clay Composite. *J. Appl. Polym. Sci*., **100**, 3809.

23. DLUZNESKI, P.R. (2001) Peroxide Vulcanization of Elastomers. *Rubb. Chem. Technol*., **74**, 451.

24. MCGARRY, K., ZILBERMAN, J., HULL, T.R. AND WOOLLEY, W.D. (2000) Decomposition and Combustion of EVA and LDPE Alone and When Fire Retarded with ATH. *Polym. Int*., **49**, 1193.

25. HANU, L.G., SIMON, G.P., CHENG, Y.B. (2006) Thermal Stability and Flammability of Silicone Polymer Composites. *Polym. Degrad. Stabil*., **91**, 1373–1379.

26. ELLUL, M.D., TSOU, A.H. AND HU, W. (2004) Crosslink Densities and Phase Morphologies in Thermoplastic Vulcanizates. *Polym*., **45**, 3351.