

Engineering and Applied Science Research

https://www.tci-thaijo.org/index.php/easr/index

Published by the Faculty of Engineering, Khon Kaen University, Thailand

Natural rubber to replace acrylonitrile butadiene styrene in polycarbonate blends and composites

Patiparn Boonruam¹, Settakorn Uppasen¹, Soipatta Soisuwan¹, Christian Antonio² and Piyachat Wattanachai^{*1}

¹⁾Department of Chemical Engineering, Faculty of Engineering, Burapha University, Chonburi 20131, Thailand ²⁾JKMRC, University of Queensland, Brisbane 4068, Australia

Received 11 August 2020 Revised 5 October 2020 Accepted 14 October 2020

Abstract

In the challenging prospect of developing "green" materials, the present research studied the possibility to replace acrylonitrile butadiene styrene (ABS) which is a petroleum based, synthetic rubber in polycarbonate (PC) blends with natural rubber (NR) for thermoplastic elastomers (TPEs) applications. An acrylic based impact modifier and talc were included in order to investigate the correlation between phase morphology and mechanical and thermal properties of the blends and composites. A simple technique of two roll mills were performed to obtain the blend and composite pellets which later on were processed into test specimens using an injection molding technique. As NR is outstanding in terms of toughness, when blending with PC a significant improvement of Izod impact strength was advantageous even with a low amount of NR at 5% w/w. In opposite, the drawback of NR incorporated PC was a drastic reduction in ductility which was shown by 75% decrease in the percent elongation to break. As the NR contents increased, the phase heterogeneity was more pronounced and resulted in lowering most properties. However, a better homogeneity of the blend using an impact modifier did not show any property enhancement besides the impact strength. Scanning electron microscopy (SEM) study suggested that talc was more miscible in NR than in PC and hence tended to improve properties when added into a blend with a high NR content. With an inadequate NR amount, talc dispersed in the polymer matrix and only elastic modulus and Vicat softening point were enhanced due to the stiffness and heat resistant properties of talc. Mechanical and thermal properties, in general, of the PC/NR/talc and PC/ABS/talc were comparable, suggesting the possibility to replace ABS with NR. In addition, the reproducibility of the tests was observed, implying the efficiency of the two roll mills technique for blend and composite preparation.

Keywords: Polycarbonate, Acrylonitrile Butadiene Styrene (ABS), Natural rubber, Polymer blends, Polymer composites

1. Introduction

Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) blends, alloys, and composites have continuously been developed to serve various industrial demands and many of them have been commercialized for half a century [1, 2]. This is due to the fact that PC possesses outstanding characteristics including high strength, high toughness, good thermal stability, low moisture absorption, and good optical clarity while ABS contributes to low temperature toughness, notch insensitivity, processability, and low cost. PC/ABS blends have been found commercially available in a wide variety of industries, particularly in computer, electrical and electronics, and automotive. Properties of the blends were found to be dependent on several factors, such as PC molecular weight, the composition ratio, and percent rubber in ABS. Even though the mechanical properties of the PC/ABS blends were a result from additive effects of the two components, the properties did not always follow the additive law and there were other factors influencing the properties, morphological structure in particular [1, 3-7]. While tensile strength and elastic modulus of the blends decreased monotonically and closed to the additive law with increasing the ABS contents simply due to the rubber characteristic of the ABS, the ductility and impact strength were more complicated and a consequence of the combined effect of the materials behaviors and the blend compatibility. The PC chains themselves are packed tightly and hence producing steric hindrance to the rotation of the chains. When ABS is blended into PC, the chain packing becomes more lose allowing the chain mobility and hence lowering the tensile properties. On the other hand, the influence of the blend ratio on the ductility was more complicated. A drastic drop in elongation at break when up to 40% by weight of ABS were added into the PC matrix was because PC has been known to be very tough material and its percent elongation is a few time higher than that of ABS ranges of 40-80% w/w and increased slightly as the % ABS is higher than 80%. Impact strength is one of important properties of PC and it was found that impact strength decreased with increase in ABS contents [1, 7].

As the partial miscibility of the PC/ABS blends was recognized, numerous researches have been focusing on searching for compatibilizers or compatibilization techniques in order to improve the miscibility of the two polymers [8-11]. Reactive compatibilization using block or graft copolymers is common as it was found to be most effective. Maleic anhydride grafted polypropylene could improve the miscibility between PC and ABS, resulting in a significant increase in both the tensile ductility and impact strength [12]. As the epoxy resin was added at 2 phr, those properties further improved. However, as the ABS contents were higher than 40% w/w, the two compatibilizers

were ineffective. Balakrishnan et al. [10] reported that maleic anhydride grafted ABS was more miscible in PC than the unmodified ABS, giving rise in blend viscosity as well as notched impact strength. Amine-functional styrene-acrylonitrile (SAN) was also used as a reactive compatibilizer as the SAN was miscible to the SAN copolymer matrix of ABS while amine group reacted with PC at the carbonate linkage [11, 13]. While others concentrated on various types of compatibilizer, Aid et al. [8] disclosed that instead of using a classical technique of a twinscrew extruder to blend PC and ABS, a solution techniques in which both polymer was dissolved in tetrahydrofuran (THF) and agitated for 24 hours before drying for another 24 hours resulted in a better miscibility. In addition, some reinforcing materials such as talc and montmorillonite clay were found not to only improve mechanical properties by their inherent properties, but also by improve the PC and ABS compatibility [9, 14].

While ABS is a synthetic rubber derived from petroleum and petrochemicals, natural rubber (NR) of course is a natural product from Hevea Brasiliensis and hence considered as a "green" material. NR in raw form has outstanding toughness and when vulcanized, it imparts high elasticity, tensile strength and resistance to abrasion. One of the current uses of NR has been in the field of thermoplastic elastomers (TPEs) (also called thermoplastic natural rubber, TPNR) due to their elastic recovery as well as processability. Nakason et al. [15] compared the effects of sulfur, peroxide, and a combination of the two curing systems on the epoxidized natural rubber/polypropylene (ENR/PP) blends and found that peroxide-curing system provided the worst mechanical properties albeit the finest rubber particle sizes. This was due to the fact that the peroxide caused PP degradation. The mixed curing system obtained the best ENR/PP properties as both S-S linkages from sulfur curing and C-C linkages from peroxide curing were available. This contradicts the conclusion made by Punnarak et al. [16] that sulfur system provided the best properties of reclaimed tire rubber and high density polyethylene blends. Yuan et al. [17] reported that a high crosslink density of polylactic/natural rubber (PLA/NR) blends using phenolic resin as a curing agent was due to severe PLA degradation, generating a large number of free radicals that could crosslink with NR. However, as the PLA molecular weight largely decreased, mechanical properties and thermal stability of the blends were sacrificed. It was clearly shown that TPNR using cured rubber in the form of recycled rubber exhibited better mechanical properties than those of uncured natural rubber, as the presence of crosslinking in the rubber matrix imparts the blends' elasticity [16, 18]. Tensile strength and Young's modulus decreased while elongation and impact strength increased, as the rubber contents in TPEs increased due to the reduction in rigidity associate to the thermoplastic chains [17-21]. While the majority of TPE studies concentrated on conventional vulcanization systems, such as sulfur, peroxides, and phenolic resins, Mondal et al. [22] developed the PP/NR curing technique using Electron Induced Reactive Processing (EIReP). It was found that providing the PP degradation during the processing was prevented, the success of TPE vulcanization was achieved, changing the morphology from a co-continuous phase to a dispersed phase of rubber particles in PP matrix. However, a high absorbed electron dose could cause the reduction in PP molecular weight and branches, resulting in detriment of the properties.

As most polymer blends are thermodynamically incompatible, the enhancement in interactions between thermoplastic and NR leading to a better miscibility has been attempted. Vulcanization is one of the techniques that alter the co-continuous phase of the TPE to a fine dispersion of crosslinked rubber phase in a continuous matrix of PP [23]. The miscibility improvement can also be carried out by a chemical modification as well as incorporation of a compatibilizer. Without vulcanization, Taksapattanakul et al. [23] detected finer domains of continuous phase of PP and hydrogenated NR compared to the microstructure of PP/NR blends. Epoxidized NR offered the polarity so that it has been used to blend with polar thermoplastics and a better interaction between the polymers resulted in superior properties [15, 21, 24, 25]. Grafting is a typical technique in homogenizing polymer blends and NR-g-poly (methyl methacrylate) and maleic anhydride-g-NR are commonly used in TPNR. Benmesli & Riahi [26] disclosed that maleic anhydride-g-PP decreased the degree of crystallinity of PP as its melting temperature (T_m) decreased while a glass transition temperature (Tg) was unchanged. However, when blended with maleic anhydride-g-NR, a single Tg of the blend was detected and increased by 5°C, revealing a better compatibilized system. Not only does the compatibilizer has been a principal compound including in TPEs, but it also acts as the reinforcing materials due to some drawbacks of rubber, low resistance to tear and abrasion, in particular [27, 28]. Natural fibers have some advantages, for example, they are low cost, environmentally friendly, and readily available compared to other synthetic fibers. However, wood fibers are susceptible to moisture and can affect the mechanical properties of the TPE composites. Even though Cosnita et al. [29] suggested that the addition of calcium oxide (CaO) in rubber/polyethylene terephthalate/high density polyethylene/wood composites improved water resistance of the composites, a large amount of CaO could cause particle agglomeration, acting as barriers to stress transmission from the matrix to the wood fibers. Similar results were reported when rice husk ash and leaf fibers were used as reinforcing materials [24, 30]. The study by Tangudom et al. [31] indicated that the synergistic, antagonistic, or additive effects of TPE composites depended greatly on the interaction of the fillers and the polymer matrix as well.

To our knowledge, the replacement of ABS with NR in the PC/ABS blends and composites has not been carried out. This paper hence focused on the possibility to replace ABS with NR without detrimental and possibly improving the blend/composite properties. The unvulcanized NR was used in the study as to prevent a chance for PC degradation as well as keep the process simple. In addition, the effects of NR content, the addition of compatibilizer in a form of impact modifier and reinforcing material, and the amount of reinforcing material on mechanical and thermal properties were investigated and related to the morphology.

2. Materials and methods

2.1 Materials

Polycarbonate resin PC24XX was manufactured by a collaborating company whose identity cannot be disclosed. The molecular weight of the polymer was approximately 24,000 and considered as relatively low molecular weight and hence, it was normally used to blend with other PC grades for various applications. A Standard Thai Rubber STR 5L (manufactured from rubber latex) having Tg of -60°C was purchased from Thai Hua Rubber Public Co. Ltd., Thailand. ABS powder (with 60% w/w rubber content) having Tg of around 100°C, an acrylic based impact modifier of Tg of -41°C, a thermal stabilizer, as well as talc, of density of 0.96 g/ml and whiteness index of 96.87, used in this study followed the collaborating company's formulation and hence supplied by the company as well.

2.2 Polymer blends and composites preparation

All ingredients were weighed according to the formulation shown in Table 1. Please note that the initials in the sample coding designated whether the sample was blend (B), alloy (A), or composite (C). The numbers followed the initials was weight percent of the natural rubber. For the composites, the weight percent of talc was indicated as TX while C5-ref was the reference sample composing of 5% w/w ABS. It can be noted

Sample code	Composition (% w/w)					
	PC 24XX	NR STR 5L	ABS	Impact modifier	Talc	Heat stabilizer
PC	99.9	-	-	-	-	0.1
B5	94.9	5.0	-	-	-	0.1
B10	89.9	10.0	-	-	-	0.1
B15	84.9	15.0	-	-	-	0.1
A15	82.9	15.0	-	2.0	-	0.1
C5-ref	89.9	-	5.0	-	5.0	0.1
C5-T2.5	92.4	5.0	-	-	2.5	0.1
C5-T5	89.9	5.0	-	-	5.0	0.1
C5-T7.5	87.4	5.0	-	-	7.5	0.1
C15-T5	79.9	15.0	-	-	5.0	0.1

that a fixed concentration of 0.1% w/w of the thermal stabilizer was included in every samples. Due to the capacity limit of a two roll mill, 250 g of the blends and composites could be prepared per batch. Polycarbonate was molten on a NAL RM 100 two roll mill (NA-Rongchai Engineering, Thailand) which was set at 250°C. Once the PC was completely melt, NR was quickly added and mixed for about 5 minutes until the sample became homogeneous. Other ingredients, as applicable, were subsequently included and blended for another 2 minutes before the sample was taken out and left to be cool down. The sample was then ground into small pieces of 8 mm diameter using a NAC 5 plastic grinding machine (NA-Rongchai Engineering, Thailand). The same procedures were repeated several batches until a total of at least 2 kg of each sample was obtained in order to complete all the characterization. The ground sample was air dried in a Heraeus UT6200 (Germany) circulation air oven set at 90±5°C for 4 hours to eliminate any moisture and now ready for melt volume rate (MVR) and glass transition temperature (Tg) evaluations. In order to study the tensile properties as well as the microstructure using a SEM technique, the type 1A dumbbell specimens according to the International Standards Organization (ISO) 527-1 standard with a thickness of 4 mm were prepared using a 370C 2000-800 Arburg injection molding machine. For the Izod impact and Vicat softening experiments, the type 1A specimens measuring 80 x 10 x 4 mm were prepared by the injection molding machine.

2.3 Material characterization

2.3.1 Tensile test

The specimens obtained from injection molding were conditioned for 24 hours at 23°C with 50% relative humidity (RH) prior to the tensile test. Zwick-Roell Z010TH (Germany) tensile testing machine was used according to ISO 527-1 with an elongation rate of 50 mm/min. For each sample, at least five specimens were undertaken the test in order to study the reproducibility and obtain average values and standard deviations of the results.

2.3.2 Izod impact test

Prior to the Izod impact test, 12 specimens per sample prepared by injection molding were notched using a ZNO 2010 Zwick Notching Machine. The notch radius is 0.25 mm and the depth under the V notch of the specimen is 8 mm. The notched specimens were kept in a controlled environment of 23°C with 50% RH for at least 30 minutes before performing the test. The Izod impact test was carried out using a HIT 5.5P Zwick Pendulum Impact Tester equipped with a 2.75 Joule hammer.

2.3.3 Vicat softening

The injection samples with the size of 80 x 10 x 4 mm were used for Vicat softening measurements according to ISO 306 Method B120 using a Coesfeld Vicat/HDT IC6+, Germany. A cylindrical indenter of 3 mm long with 1.000 ± 0.015 mm² cross-sectional area was used with a 50 N weight load. The sample was heated at a rate of 120° C/hr by an integrated cooling.

2.3.4 Differential scanning calorimetry (DSC)

10-15 mg of the ground and oven dried sample were put in the 40 μ L aluminum crucible. The pan was heated at a heating rate of 10°C/min from 25-300°C under nitrogen blanket. The measurement was carried out using a Mettler DSC 823e.

2.3.5 Flow property

6-10 g of the ground samples were heated to $105\pm3^{\circ}$ C for 7 min using a SartoriusTM MA150Q-000230V1 Infrared Moisture Analyzer to remove any moisture. After that, they were put in a chamber of an Aflow extrusion plastometer, Zwick, Germany, which was set at 240±3°C for the MVR test according to ISO 1133 Method B. The die orifice had a size of 2.095±0.005 mm inside diameter and 8.000±0.025 mm long.

2.3.6 Scanning electron microscopy (SEM)

Surface morphology of cross-sectional areas of the composites which were microtomed using a glass knife was evaluated by SEM analysis using a Quanta 200 FEG operated at 15 kV. A Polaron Range Model SC 7620 Ion Sputter Coater was used for gold sputtering.

3. Results and discussions

3.1 Tensile properties

PC has been known as a very strong material, having an elastic modulus and tensile strength of approximately 2,100 and 20 MPa for this study as shown in Figures 1 and 2, respectively. When a small amount of 5% w/w NR was added into PC, the tensile modulus and strength were barely changed. However, as the NR compositions in the blends increased in the range of 5-15% w/w, both properties progressively decreased following the additivity law in the same way as PC/ABS blends [1, 4-6]. It was found that the blend elastic modulus decreased around 10% for every 5% w/w of NR were added. Interestingly, when an impact modifier which is an acrylic based polymer was included into the blend (A15) to obtain a better the PC/NR miscibility as seen in SEM images which will be discussed later in Section 3.6, the tensile properties were slightly worsen. This might be due to the fact that the amount of PC in A15 were 83% w/w which was



Figure 1 Elastic modulus of PC/NR blends, alloy, and composites at various composition



Figure 2 Tensile strength of PC/NR blends, alloy, and composites at various composition

slightly lower than 85% w/w PC in B15. Tjong & Meng [12] also reported that comparable tensile modulus and strength of the PC/ABS blends with and without using an epoxy resin as a compatibilizer in the range of concentration of 0.5-2 phr even though the blend morphology was more homogeneous with the incorporation of the compatibilizer. While the elastic modulus increased up to 10-30% depending on the amount of talc added when talc was used as a reinforcing material in the PC/NR composites, 2-4% decrease in the composite tensile strength were observed, suggesting that talc plays an important role in plastic's stiffness but not strength. Sung et al. [9] concluded that talc caused PC degradation and hence the reason for a decrease in tensile and impact strength of PC/ABS/talc composites. When compared PC/NR composite (C5-T5) with PC/ABS composite (C5-ref) at the same composition, the tensile modulus and strength of the two composites were comparable.

While elastic modulus and tensile strength of PC were slightly affected by the small addition of NR (B5), a drastic decrease in ultimate elongation, as shown in Figure 3, was observed to the findings by Deanin & Chu [3] and Laing & Gupta [6] with their PC/ABS blends, with all types of ABS used, i.e. easy processing, heat resistant, and high impact ABS. This is due to the fact that NR and butadiene rubber in ABS acted as centers of stress concentration, causing the premature failure. The percent elongation further depreciated as the amount of NR increased. The more homogenous phases of the alloy included the acrylic based impact modifier (A15) and the composite included the talc (C15-T5) possessed approximately 26% and 50% lower in ductility, respectively, than the blend without the impact modifier and talc (B15). This is because the amounts of PC, which is highly ductile, in B15, A15, and C15-T5 were 85, 83, and 80 %w/w, respectively. There are two reasons for the lower ductility of the PC/NR composites compared to the PC/NR blends; 1) the slightly less amount of PC and 2) the stiffer characteristics of the composites. Similar to the results of tensile



Figure 3 Elongation at break of PC/NR blends, alloy, and composites at various composition

strength, talc contents in the range of 2.5-7.5 %w/w barely affected percent elongation at break of the composites. The results showed that with the same compositions PC/ABS composite (C5-ref) was 4 times more ductile than PC/NR composite (C5-T5) as there was no any vulcanizing agent included into the composites.

3.2 Izod impact strength

Generally, impact strength is an outstanding property of both PC and ABS though the impact strength of PC could be twice as much as that of ABS [4, 6]. Previous studies reported the dependency of impact strength of PC/ABS blends on the amount and type of ABS [2-3, 32]. When ABS was incorporated into PC, notched Izod impact strength was dropped, in general, due to the lower impact strength of ABS compared to that of PC. Interestingly, as illustrated in Figure 4 when a small amount of NR at 5% w/w was added into PC, impact strength of the blend was improved to approximately 2.3 times of that of pure PC, due to superior impact properties of NR. As the amount of NR composition increased to 15% w/w, the Izod impact strength decreased proportionally to the NR content but was still 1.7 times higher than that of pure PC. Approximately 15% decrease in impact strength of every increase in 5% w/w NR were observed. These findings are in accordance with the results of Desa et al. [33] that found an introduction of NR into PLA/multiwalled carbon nanotubes contributed to significant improvement in impact strength and ductility of the nanocomposite. In addition, the low values of standard deviation of the blends found in both tensile and impact testes suggested the effectiveness of mixing technique as well as an adequate compatibility between PC and NR in a macroscopic scale. As one can expect, the addition of only small amount of an impact modifier (2% w/w) in A15, significant enhancement in impact strength was observed. When talc was added into PC/NR blends, however, the effects on impact strength depended on the NR contents. With the high amount of NR at 15% w/w, the impact strength of the composite (C15-T5) increased 50% compared to that of the blend (B15). This is because talc can dissolve in the NR phase resulting in homogeneous structure of the composite (see Figure 8(d)) while the PC/NR blend was heterogeneous (see Figure 8(b)). In contrast, with a low NR content of 5% w/w in the composite (C5-T5), there was not enough NR for talc to dissolve and hence talc particles were remained in the polymer matrix as seen in Figure 8(e) causing the impact strength to decrease approximately 25-30% as compared to the blend B5. Varying the amount of talc in the range of 2.5-7.5% w/w did not alter the impact strength of the composites. As the impact properties of NR is considerably greater than that of ABS, the impact strength of the PC/NR/talc composite (C5-T5) was twice as much of that of PC/ABS/talc composite (C5-ref).



Figure 4 Izod impact strength of PC/NR blends, alloy, and composites at various composition



Figure 5 Vicat softening point of PC/NR blends, alloy, and composites at various composition

3.3 Vicat softening point

Figure 5 illustrated that Vicat softening point of PC/NR blends in the range of NR 0-15% w/w seemed to follow the additive rule. The Vicat softening point of pure PC was 148.5°C and decreased up to almost 20°C when 15% w/w NR was added. Other research studies also reported a softening point reduction when NR was incorporated in a thermoplastic elastomer [34] as well as when ABS was added into PC [3, 5]. Incorporating a slight amount of an acrylic based impact modifier further decreased the softening point down 5.5°C, because of a slightly less amount of the PC. Similar to the results of Izod impact strength, the effects of talc on the Vicat softening point depended on the amount of NR. The composite of high amount of NR (C15-T5) had a lower softening point by 5°C compared to the blend (B15). This is because the composite was more homogeneous than the blend and hence the rubber properties could be revealed. Oppositely, with the low NR content of 5%, the Vicat softening point of the composites increased by 5°C compared to the blend as talc resists to heat and usually used for shrinkage and thermal expansion reduction for polymer composites. There was no difference in Vicat softening point of the PC/NR/talc composites with the concentration of talc between 2.5-7.5% w/w. As the Vicat softening point of ABS (~100°C) and NR (~90°C) are comparable, the Vicat softening points of the two composites (C5-ref and C5-T5) were not distinguishable.

3.4 Glass transition temperature

 T_g of PC, ABS, and NR are approximately 145, 100, and -60°C, respectively. The results of T_g of PC/NR blends in Figure 6 were followed the results of Vicat softening point. An introduction of a small amount of NR at 5% w/w remarkably decreased T_g by 7°C; however, further addition of NR in step of



Figure 6 Glass transition temperature of PC/NR blends, alloy, and composites at various composition

5% w/w up to 15% w/w only decreased Tg gradually around $2.5^{\circ}C$ for each step. The reduction of T_g in PC rich phase in PC/ABS blends and the enhancement of $T_{\rm g}$ in ABS rich phase was previously reported [8, 9, 12, 35]. As the Tg of PC/NR blends behaved in the same way as that of PC/ABS blends, it can be concluded that PC and NR are partial miscible as are the PC and ABS. The incorporation of an impact modifier (A15) also lowered the blend's Tg. Tjong & Meng [12] demonstrated that when a compatibilizer was included in PC/ABS blends, Tg in PC rich phase further decreased. The effects of talc on Tg of the PC/NR/talc composites, however, were different from the effects on the Vicat softening point. As talc possesses a heat resistance property, Tg of the PC/NR/talc composites was higher when NR composition was at 15% w/w. These findings, however, opposed the results on PC/ABS/talc composites reported by Sung et al. [9] who found that talc lowered T_g of the PC rich phase as talc caused the PC degradation. In our study, there was no indication of degradation of PC due to the addition of talc and we believed that the improvement of Tg suggested that talc was more miscible in NR than in PC. As a result, when an enough (high) amount of NR existed, talc could completely dissolve in NR resulting in a more homogenous PC/NR/talc composite. Surprisingly, with the low NR content of 5% w/w talc did not show any effect on the Tg of the composites. This might be due to the fact that there was not enough NR for talc to dissolve and hence talc particles remained in the PC matrix as shown in SEM images (Figure 8 (e)). Because of a higher Tg of ABS, PC/ABS composite (C5-ref) showed a higher T_g than that of PC/NR composite (C5-T5).

3.5 Melt volume rate (MVR)

Melt flow rate (MFI) or melt volume rate (MVR) is generally used in polymer industries as an indirect method to measure of polymer molecular weight, viscosity, as well as processability. One of the main reason for adding ABS into PC is to ease the processability as PC has a high glass transition temperature of around 145°C and must be processed at a temperature higher than 155°C. Deanin & Chu [3] found whether or not ABS can improve melt processability of PC depended entirely on the grade of ABS. With the high impact ABS which contained a high percentage of rubber, MVR of the blends were lower than that of the pure PC. This was the case for PC/NR blends as well as can be seen from the results in Figure 7. As the 5-10% w/w NR was incorporated in PC, MVR decreased to lower than that of pure PC. However, it is interesting that MVR increased as the NR contents increased and at 15% w/w NR, MVR of the blend was actually higher than that of the pure PC. Deanin & Chu [3] also disclosed that the MVRs of PC/ABS initially decreased as the amount of ABS increased, but as the amount of ABS became higher than 50%, the MVRs started to increase and then decreased again at 90% ABS. Many research works reported that the viscosity of the PC/ABS blends did not follow the rule of mixtures; however, the addition of ABS in PC improved the processability of PC



Figure 7 Melt volume rate of PC/NR blends, alloy, and composites at various composition

[6, 10, 35]. Maleic anhydride grafted ABS (MABS) was found to be more miscible to PC than normal ABS, resulting in well dispersion of MABS in PC matrix which gave rise in the blend viscosity compared to PC/ABS blends [10]. In our study, an acrylic based impact modified (A15) did not alter the MVR of the PC/NR blend (B15) even though the morphology study suggested a better miscibility of the two components. When talc was added into the PC/NR blends, MVR of the composite with 15% w/w NR increased while MVRs of the composites with 5% w/w NR at all the talc compositions were comparable to that of the blend. This was contradicted to the results of Sung et al. [9] who reported the decrease of viscosity of PC/talc composites as talc contents increased and concluded that talc was a cause of PC degradation. A slightly higher MVR of the PC/ABS/talc composite than that of PC/NR/talc composition was observed.

3.6 Microstructures

Morphology of the blends, alloy, and composites was very beneficial for understanding the mechanical properties as well as thermal properties. Figures 8 (a) and 8 (b) demonstrated that NR particles were well dispersed as elongated nodules in PC matrix and as the NR content increased, the immiscibility was more pronounced and the particles were more round, indicating an increase in interfacial tension between the two phases. This explained the deteriorated mechanical and thermal properties of the blends with 10 and 15% w/w NR concentrations. Cocontinuous phase of TPEs was detected as the amount of rubber in NR or ABS increase higher than 40% w/w in polyolefin [18, 20, 22, 36], leading to better mechanical properties. As an acrylic based impact modifier was included in the blend of PC/NR at a ratio of 85/15, the blend became co-continuous phase shown in Figure 8 (c), implying that the impact modifier was compatible to both phases. However, surprisingly besides the impact strength, other properties barely affected. The slightly depreciation in most properties when the impact modifier was added was due to a slightly lower PC content in the blend (83% w/w) compared to that without the impact modifier (85% w/w). As talc was incorporated into the PC/NR blend at the 85/15 ratio, the morphology of this composite became co-continuous phase with some dispersed talc particles as seen in Figure 8 (d). It might be concluded that talc dissolved better in NR and in addition to that, it abetted the two phases to be more miscible. It appeared that the acrylic impact modifier and talc had similar roles in blend because the mechanical properties of the A15 and C15-T5 were comparable except thermal properties. Since talc has an excellent heat resistance and functionality as lubricant, the blend C15-T5 had, in general, slightly better higher Vicat softening point, T_g , and MVR. Figure 8 (e) shows the morphology of the PC/NR/talc composite at a NR content of 5% w/w. It was obvious that talc dissolved better in the NR phase as more talc particles were dispersed with some agglomerates in the PC/NR matrix compared to the composite with a high amount of NR at 15% w/w (Figure 8 (d)). The matrix of this composite was more homogenous than the PC/NR blend (B5 in Figure 8 (a)) with some smaller, elongated rubber particles appearance. The microstructure of the PC/ABS/talc composite in Figure 8 (f) was identical to that of PC/NR/talc composite in Figure 8 (e), and hence, it can be concluded that talc well dissolved in polybutadiene rubber phase of ABS while styrene acrylonitrile (SAN) was miscible with PC phase.



Figure 8 SEM Images of PC/NR blends, PC/NR/impact modifier alloy, PC/NR/talc composite, and PC/ABS/talc composite: (a) B5, (b) B15, (c) A15, (d) C15-T5, (e) C5-T5, and (f) C5-ref







Figure 8 (continued) SEM Images of PC/NR blends, PC/NR/impact modifier alloy, PC/NR/talc composite, and PC/ABS/talc composite: (a) B5, (b) B15, (c) A15, (d) C15-T5, (e) C5-T5, and (f) C5-ref

4. Conclusions

Morphology as well as the mechanical and thermal properties have proven that unvulcanized NR showed a potential for ABS replacement. At a rubber content of 5% w/w, tensile properties of the PC/NR/talc composites were comparable to those of PC/ABS/talc. As the NR was uncured, its toughness was superior albeit low ductility. Despite a significant lower T_g of NR compared to ABS, T_g of the two composites were similar. MVR results suggested that the processing conditions would be unaffected if the NR was to replace ABS. SEM study suggested that talc was more miscible in NR and hence incorporating talc into the PC/NR blends resulted in improvement of properties especially with high NR contents. Surprisingly, albeit more compatible between PC and NR, the addition of an acrylic impact modifier barely altered the blend's properties except the impact strength. One of the crucial findings was that the reproducibility of the tests implied the efficiency of a two mill rolls technique to produce PC/NR blends and composites.

5. Acknowledgements

This projected is financially supported by the Faculty of Engineering, Burapha University under the grant no. WJR. 1/2559.

6. References

- Suarez H, Barlow JW, Paul DR. Mechanical properties of ABS/polycarbonate blends. J Appl Polymer Sci. 1984;29(11):3253-9.
- [2] Wu JS, Shen SC, Chang FC. Effect of rubber content in acrylonitrile-butadiene-styrene and additional rubber on the polymer blends of polycarbonate and acrylonitrile-butadiene-styrene. Polymer J. 1994;26(1):33-42.
- [3] Deanin RD, Chu CW. Polyblends of polycarbonate with ABS. J Elastomers Plast. 1986;18(1):42-9.
- [4] Hassan A, Jwu WY. Mechanical properties of high impact Abs/Pc blends - effect of blend ratio. Simposium Polimer Kebangsaan Ke-V; 2005 Aug 23-24; Hotel Resident, Uniten. Materials Science; 2005. p 65-76.
- [5] Krache R, Debah I. Some mechanical and thermal properties of PC/ABS blends. Mater Sci Appl. 2011;2(5):404-10.
- [6] Liang R, Gupta R. Processing and characterization of recycled PC/ABS blends with high recycle content. ANTEC. 2002;3:2948-52.
- [7] Raj MM. Studies on mechanical properties of PC-ABS blends. J Appl Sci Eng Res. 2014;3(2):512-8.
- [8] Aid S, Eddhahak A, Ortega Z, Froelich D, Tcharkhtchi A. Experimental study of the miscibility of ABS/PC polymer blends and investigation of the processing effect. J Appl Polymer Sci. 2017;134(25).
- [9] Sung YT, Fasulo PD, Rodgers WR, Yoo YT, Yoo Y, Paul DR. Properties of polycarbonate/acrylonitrile-butadienestyrene/talc composites. J Appl Polymer Sci. 2012;124(2):1020-30.
- [10] Balakrishnan S, Neelakantan NR, Saheb DN, Jog, JP. Rheological and morphological behaviour of blends of polycarbonate with unmodified and maleic anhydride grafted ABS. Polymer. 1998;39(23):5765-71.
- [11] Wildes G, Keskkula H, Paul DR. Fracture characterization of PC/ABS blends: effect of reactive compatibilization, ABS type and rubber concentration. Polymer. 1999;40(25):7089-107.
- [12] Tjong SC, Meng YZ. Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly (acrylonitrile-butadi styrene) blends. Eur Polymer J. 2000;36(1):123-9.
- [13] Wildes GS, Harada T, Keskkula H, Paul DR, Janarthanan V, Padwa AR. Synthesis and characterization of an aminefunctional SAN for the compatibilization of PC/ABS blends. Polymer. 1999;40(11):3069-82.
- [14] Merijs R, Zicans J, Ivanova T, Berzina R, Saldabola R, Maksimovs R. The effect of introduction of montmorillonite clay (MMT) on the elastic properties of polycarbonate (PC) composition with acrylonitrilebutadiene styrene (ABS). Compos Struct. 2015;134:950-6.

- [15] Nakason C, Wannavilai P, Kaesaman A. Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends. Polymer Test. 2006;25(1):34-41.
- [16] Punnarak P, Tantayanon S, Tangpasuthadol V. Dynamic vulcanization of reclaimed tire rubber and high density polyethylene blends. Polymer Degrad Stabil. 2006;91:3456-62.
- [17] Yuan D, Chen K, Xu C, Chen Z, Chen Y. Crosslinked bicontinuous biobased PLA/NR blends via dynamic vulcanization using different curing systems. Carbohydr Polymer. 2014;113:438-45.
- [18] Ismail H, Suryadiansyah. Thermoplastic elastomers based on polypropylene/natural rubber and polypropylene /recycle rubber blends. Polymer Test. 2002;21(4):389-95.
- [19] Mahapram S, Poompradub S. Preparation of natural rubber (NR) latex/low density polyethylene (LDPE) blown film and its properties. Polymer Test. 2011;30(7):716-25.
- [20] Sae-Oui P, Sirisinha C, Sa-nguanthammarong P, Thaptong P. Properties and recyclability of thermoplastic elastomer prepared from natural rubber powder (NRP) and high density polyethylene (HDPE). Polymer Test. 2010;29(3):346-51.
- [21] Mohamad N, Zainol NS, Rahim FF, Maulod HEA, Rahim TA, Shamsuri SR, et al. Mechanical and morphological properties of polypropylene/epoxidized natural rubber blends at various mixing ratio. Procedia Eng. 2013;68:439-45.
- [22] Mondal M, Gohs U, Wagenknecht U, Heinrich G. Polypropylene/natural rubber thermoplastic vulcanizates by eco-friendly and sustainable electron induced reactive processing. Radiat Phys Chem. 2013;88:74-81.
- [23] Taksapattanakul K, Tulyapitak T, Phinyocheep P, Ruamcharoen P, Ruamcharoen J, Lagarde F, et al. Raman investigation of thermoplastic vulcanizates based on hydrogenated natural rubber/polypropylene blends. Polymer Test. 2017;57:107-14.
- [24] Hashim F, Ismail H, Rusli, A. Comparison of properties of ethylene vinyl acetate/natural rubber/mengkuang leaf fibre (EVA/NR/MLF) and ethylene vinyl acetate/epoxidized natural rubber/mengkuang leaf fibre (EVA/ENR-50/MLF) thermoplastic elastomer composites. Polymer Test. 2017;61:1-7.

- [25] Mascia L, Su R, Clarke J, Lou Y, Mele E. Fibres from blends of epoxidized natural rubber and polylactic acid by the electrospinning process: Compatibilization and surface texture. Eur Polymer J. 2017;87:241-54.
- [26] Benmesli S, Riahi F. Dynamic mechanical and thermal properties of a chemically modified polypropylene/natural rubber thermoplastic elastomer blend. Polymer Test. 2014;36:54-61.
- [27] Liu X, Liu H, Wang D, Wang E, Liu W, Yao K, Chen N. Metallic glass-strengthened thermoplastic elastomer composites. Physica E Low Dimens Syst Nanostruct. 2017;90:37-41.
- [28] Smitthipong W, Suethao S, Shah D, Vollrath F. Interesting green elastomeric composites: Silk textile reinforced natural rubber. Polymer Test. 2016;55:17-24.
- [29] Cosnita M, Cazan C, Duta A. The influence of inorganic additive on the water stability and mechanical properties of recycled rubber, polyethylene terephthalate, high density polyethylene and wood composites. J Clean Prod. 2017;165:630-6.
- [30] Ismail H, Nizam JM, Abdul KHPS. The effect of a compatibilizer on the mechanical properties and mass swell of white rice husk ash filled natural rubber/linear low density polyethylene blends. Polymer Test. 2011;20(2):125-33.
- [31] Tangudom P, Thongsang S, Sombatsompop N. Cure and mechanical properties and abrasive wear behavior of natural rubber, styrene-butadiene rubber and their blends reinforced with silica hybrid fillers. Mater Des. 2014;53(Supplement C):856-64.
- [32] Inberg JPF, Gaymans RJ. Co-continuous polycarbonate /ABS blends. Polymer. 2002;43(8):2425-34.
- [33] Desa MSZM, Hassan A, Arsad A. The effect of natural rubber toughening on mechanical properties of poly(lactic acid)/ multiwalled carbon nanotube nanocomposite. Adv Mater Res. 2013;747:639-42.
- [34] Norzalia S, Surani B, Ahmad FMY. Properties of rubbermodified polypropylene impact blends. J Elastom Plast. 1994;26(2):183-204.
- [35] Wu JS, Shen SC, Chang FC. Effect of polycarbonate molecular weight on polymer blends of polycarbonate and ABS. J Appl Polymer Sci. 1993;50(8):1379-89.
- [36] Fang QZ, Wang TJ, Li HM. Large tensile deformation behavior of PC/ABS alloy. Polymer. 2006;47(14):5174-81.