Mechanical Properties, Thermal Stability, Gas Permeability, and Phase Morphology in Natural Rubber/Bromobutyl Rubber Blends

N. Rattanasom,[1,2] S. Prasertsri,[3] K. Suchiva[2,3]

[1]Institute of Science and Technology for Research and Development, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand
[2]Centre for Rubber Research and Technology, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand
[3]Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

ABSTRACT: This work was performed to relate the morphological features and all important properties of the natural rubber (NR) and bromobutyl rubber (BIIR) blends containing hybrid fillers. The BIIR content was varied from 0 to 100 wt%. It is found that tensile and tear strength, hardness as well as resilience of blends tend to decrease with increasing BIIR loading. Regarding the blend morphology, phase inversion is observed when BIIR loading is >50 wt % where BIIR becomes a continuous phase. This result coincides with the marked improvement of thermal stability of the blends determined using thermogravimetric analysis and heat ageing method. Interestingly, that, the gas permeability of blends markedly reduces with an increase in BIIR loading up to 40 wt % when the relatively large elongated particles of BIIR dispersed phase is formed. The results indicate that the relatively large connected structure of the dispersed BIIR can act effectively as a gas barrier. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3985–3992, 2009

Key words: natural rubber; bromobutyl rubber; mechanical properties; gas permeability; phase morphology

INTRODUCTION

Blending of polymers is an interesting route for developing new polymeric materials with tailored properties and improvement of processing characteristics as well as reduction in product cost.[1–3] Although, some scientific progress has been made to comprehend the bulk behavior of multicomponent blend systems, renewed research to elucidate the relationship of their phase morphology and properties is still needed for better understanding of the blend characteristics.[4–9]

Natural rubber (NR) and its blend compounds have received much attention in the literature because of their superior performance in many applications. However, NR is highly susceptible to degradation, due to the presence of double bonds in the main chain. Therefore, several attempts have been made to improve this drawback of NR vulcanizates. Varkey et al.[6] studied the thermal stability of NR/styrene butadiene rubber (SBR) latex blends by thermogravimetric method and found that the thermal stability of the blends increases with increasing SBR content. Botros[10] showed that the 25/75 and 50/50 NR/ethylene propylene diene rubber blends possess the best resistance against thermal ageing and UV irradiation, respectively. Sae-oui et al.[11] also revealed that increasing the amount of chloroprene rubber (CR) in the silica-filled NR/CR blends helps to improve oil, thermal, and ozone resistance of the vulcanizates. Bromobutyl rubber (BIIR) has also been blended with NR to search for the benefits from each rubber. Lemieux and Killgoar[7] added low levels of BIIR (0–50 wt%) to NR and reported the increase of damping and thermal stability with increasing BIIR loading. On the other hand, Rodgers et al.[8] added high levels of BIIR (60–100 wt%) to NR to modify its final compound properties. They found the rise in gas barrier property with an increase in BIIR level from 60 to 100 wt %, whereas tensile strength and rebound resilience of the blends decrease. In addition, the statistical experimental design was applied to predict the effects of NR/BIIR blend ratios on the cure characteristic and physical properties of NR/BIIR blends.[9] The predicted results showed that the properties of the blends are dominated by the NR content. It can be seen that although some past studies have been made to study the properties of NR/BIIR blends, their phase

TABLE I
Ingredients and Formulations Used in the Present Study

Ingredient	Amount (phr)[a]	Grade/supplier
NR	Variable[b]	STR 5L/Yala Latex Industry, Thailand
BIIR	Variable[b]	BX2/ LANXESS, United States
Mixed fillers[c]	74	Thai Carbon Product, Thailand; Smurfit-Stone Container Enterprises, United States; and Tokuyama Siam Silica, Thailand
Zinc oxide (ZnO)	5	Commercial/Enery Product, Thailand
Stearic acid	0.5	Commercial/Enery Product, Thailand
Acc[d] (guanidine type)	0.7	Commercial/Chemmin, Thailand
Acc[d] (sulfenamide type)	0.8	Commercial/Chemmin, Thailand
Acc[d] (thiazole type)	1.6	Commercial/Chemmin, Thailand
Sulfur (S_8)	2.5	Commercial/Chemmin, Thailand

[a] Parts per hundred of rubber.
[b] Blend ratios of NR/BIIR are 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100.
[c] Mixture of carbon black (N330), calcined clay and silica (Tokusil® 233).
[d] Accelerator.

morphology that would deliver a better understanding of the blend characteristics has not been reported in the above publications. Though, Achalla et al.[12] examined the phase morphology of the unfilled NR/BIIR blends using Atomic Force Microscopy (AFM), the other properties of the blends were not determined. They found that BIIR is dispersed in NR when BIIR content is <50 wt % and NR BIIR is dispersed phase when BIIR content is >50 wt %. In addition, the co-continuous morphology is observed for 50/50 NR/BIIR blend. In this work, it is of our interest to systematically elucidate the relationship among mechanical properties, thermal stability, gas permeability, and the phase morphology of the filled NR/BIIR blends at various ratios. The phase morphology of the blends was examined using a scanning electron microscope. The thermal stability was studied both by means of heat ageing and thermogravimetric method. The results of reversion characteristic obtained from the rheometric curves and relating to thermal ageing resistance are also discussed in this article.

EXPERIMENTAL

Materials

Details of the ingredients and rubber formulations are shown in Table I. All mixing ingredients were used as received.

Preparation of NR/BIIR blends

The compound formulations using conventional vulcanization system are given in Table I. NR/BIIR blends were prepared using mixing procedures involving two stages. In the first stage, all ingredients except the curatives were mixed with rubbers in the internal mixer (Brabender Plasticorder R2000)

for 5.5 min with a fill factor of 0.7 at a set temperature of 50°C and a rotor speed of 50 rpm. In the second stage, the compounds were further mixed with the accelerators and sulfur using a two roll-mill (Labtech LRM150) at 40°C for 6 min. Finally, 10 end-roll passes were made before sheeting off.

Preparation and testing of rubber vulcanizates

All vulcanized sheets and specimens were prepared using hydraulic hot press (Wabash G 30H) at temperature of 150°C under pressure of 15 MPa. The optimum cure time (t_{c90}) was determined using moving die rheometer (MDR, TechPro MD+) at 150°C in accordance with ASTM D5289-95. Then, the vulcanized sheets and specimens were compression molded at 150°C using hydraulic hot press according to their respective t_{c90} from rheograph.

Hardness was measured using a Wallace Shore A durometer, according to ASTM D2240-97. The tensile properties and tear property were measured according to ASTM D412-98 and ASTM D624-00, respectively, by using a universal extensometer (Instron 5569 series) with 1 kN of load cell and the crosshead speed of 500 mm/min. Crescent test pieces were used for determining the tear strength. The values of tear and tensile properties were the average of 4–5 specimens.

The tensile specimens were aged at 100°C for 22 h in circulating air chamber for studying the thermal ageing resistance. The aged specimens were left at room temperature for at least 18 h before tensile testing. The tensile properties of aged specimens were determined in the same manner as the unaged specimens. Tensile strength retention was calculated using the eq. (1).

$$\text{Tensile retention } (\%) = (\text{TS}_{\text{after}}/\text{TS}_{\text{before}}) \times 100, \quad (1)$$

where TS_{before} and TS_{after} are tensile strength before and after thermal ageing, respectively.

Rebound resilience was determined by a Dunlop tripsometer (Toyoseiki 221). The resilience was calculated using eq. (2).

$$\% \, \text{Resilience} = [(1 - \cos \theta)/(1 - \cos 45)] \times 100, \quad (2)$$

where θ is the rebound angle.

Oxygen gas permeability of vulcanized membrane was measured using Illinois instrument (Model 8000), in accordance with ASTM D3985-02. The vulcanized sheets having thickness $\sim$ 0.30 mm and a permeation area of 169 cm^2 were prepared for testing. The measurement was carried out at 25°C, 0% relative humidity, and 1 atm pressure.

Blend morphology examination

The vulcanized blend samples were mounted on a microtome equipped with a cryostat and then microtomed to achieve a flat surface for morphology study. To facilitate identification of phases and to enhance morphological features, the microtomed samples were stained by osmium tetroxide (OsO$_4$) to generate phase contrast, and then sputtered with carbon to prevent charging on the surface before examining. The micrographs were taken on a scanning electron microscope (SEM, JEOL JSM-6301F) with 15 kV accelerating voltage.

Thermogravimatric analysis

A thermal stability of NR/BIIR blends was studied using thermogravimetric analyzer (TGA, TGA/ SDTA 851) with nonisothermal mode. Approximately 10 mg of vulcanized sample was heated from 40°C to 600°C at a heating rate of 20°C/min with a continuous N$_2$ flow at 60 mL/min. Thereafter, the purge atmosphere was automatically changed to O$_2$, and the sample was continuously heated up to 850°C. Sample weight and its rate of weight loss were continuously recorded as a function of temperature.

RESULTS AND DISCUSSION

Cure characteristics

Figure 1 shows cure curves of the compounds having different blend ratios. When BIIR content is increased, the retarding effect of BIIR on the curing is observed by the increased scorch time and cure time because BIIR has fewer double bonds than NR. The maximum torque (M_H) and torque difference (M_H-M_L) of the blends are found to obviously decrease with an increase in BIIR content. This is because BIIR is less reactive toward sulfur vulcanization than NR.[13,14] As a consequence, crosslink for-
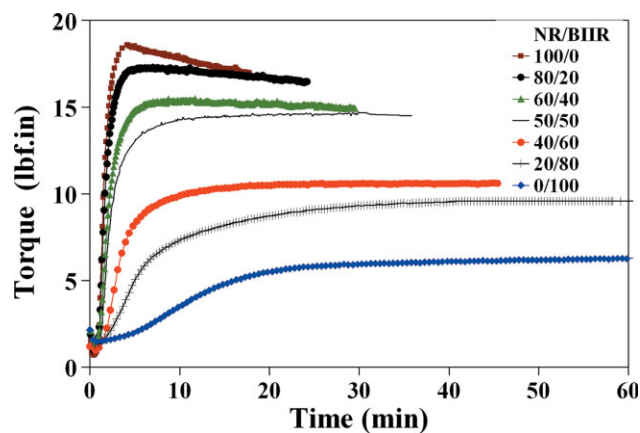

Figure 1 Cure curves of NR/BIIR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mation decreases when higher amount of BIIR is added. According to the reversion behavior, it is clearly observed in NR-rich blends and tends to decrease with increasing BIIR content. The reversion phenomenon is network loss due to oxidative thermal ageing under an applied oscillating shear that usually appears for NR cured with a conventional sulfur system.[14] Thus, the obtained results indicate that the resistance to thermal degradation of NR/ BIIR can be observed when the blends contain at least 50 wt % of BIIR.

Blends morphology

It is well known that immiscible polymer blends exhibit two phases shown as a continuous phase and a dispersed phase morphology, depending on the compositions. The phase morphology of various NR/BIIR blends obtained using scanning electron microscope (SEM) is given in Figure 2. The results reveal two-phase blend morphology where the stained NR appears as a bright and grey phase whereas the BIIR is seen as a dark phase. In addition, the dark phase progressively increases with increasing BIIR content. For 80/20 NR/BIIR blend [Fig. 2(a)], relatively small particles of BIIR dispersed phase are observed. Then, the relatively large connected particles of BIIR dispersed phase are clearly formed in 60/40 and 50/50 NR/BIIR blends, indicating the occurrence of phase coalescence [indicated by arrows in Fig. 2(b,c)]. It is likely that large connected structure of BIIR dispersed phase occurs, because there is an insufficient shear stress to break down the BIIR dispersed phase resulting from the too high viscosity of BIIR dispersed phase and/or the too low viscosity of the NR matrix. Therefore, NR is seen as the continuous phase in the blends, even in 50/50 NR/BIIR blend. To clarify the obtained results, the Mooney viscosity (ML (1+4)
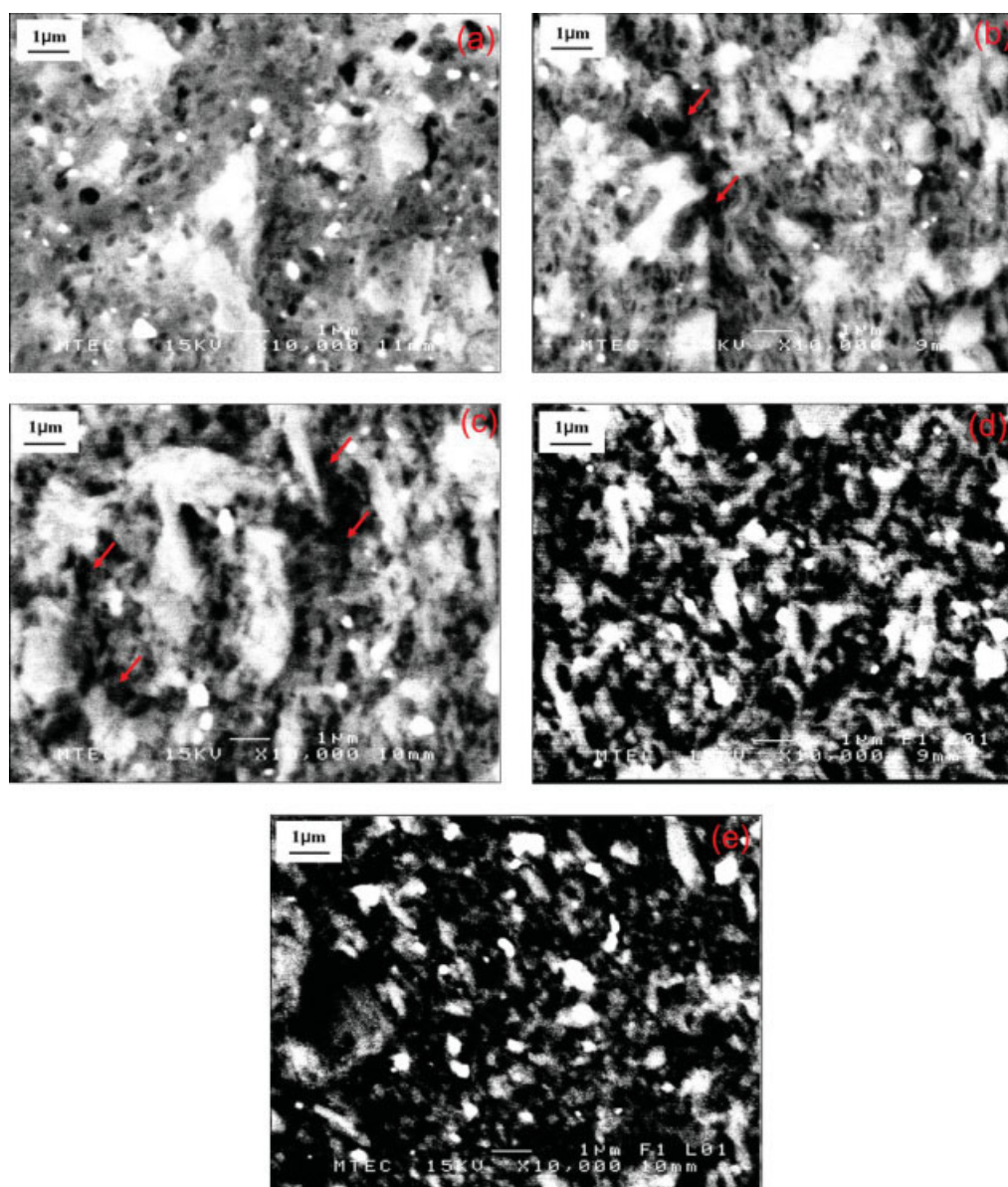
Figure 2 Scanning electron micrographs of NR/BIIR blends: (a) 80/20, (b) 60/40, (c) 50/50, (d) 40/60, and (e) 20/80. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

100°C) of raw materials and rubber compounds was determined. The viscosity of raw NR and BIIR is 83.4 and 78.2 Mooney units (MU), respectively. When NR and BIIR are compounded using the same formulation and mixing conditions, the viscosity of NR compound is found to be 22.6 MU while that of BIIR and 50/50 NR/BIIR compounds is 77.6 and 49.6 MU, respectively. It can be noticed that Mooney viscosity of 50/50 blend is about the average of Mooney viscosity of the NR and BIIR compounds. The results infer the higher break down of NR chains during mixing process and lead to a decrease in molecular weight compared with BIIR. As a result, NR readily flows and appears as a continuous phase in 50/50 NR/BIIR blend. However, Achalla

et al.[12] reported that the co-continuous morphology is observed for the unfilled 50/50 NR/BIIR blend using AFM. In Figure 2(d), SEM micrograph also reveals that the phase inversion takes place in 40/60 NR/BIIR blend where BIIR becomes the continuous phase, and NR is the dispersed phase. It is also found in BIIR-rich blends that the NR dispersed size depends on the blend compositions.

Mechanical properties and gas barrier property

Figure 3 illustrates the hardness and 100% modulus of the vulcanizates having various NR/BIIR ratios. When BIIR content in the blends is 0–30 wt%, both hardness and modulus of the vulcanizates is not
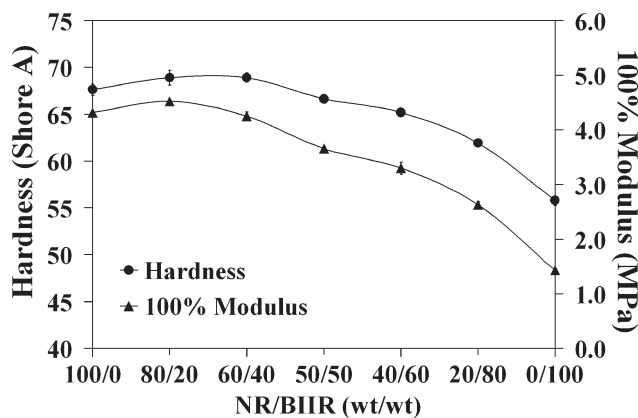
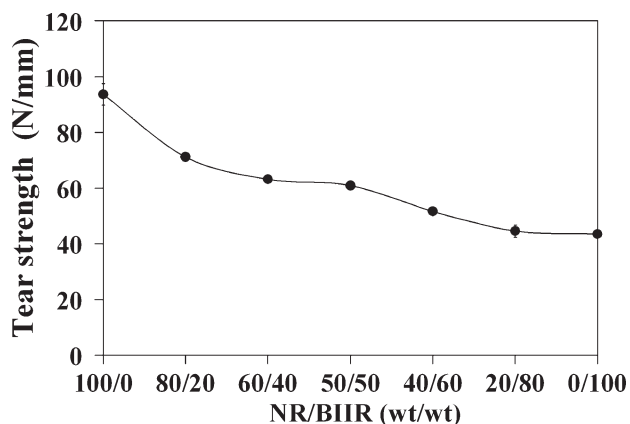**Figure 3** Hardness and 100% modulus of NR/BIIR blends.

Figure 5 Tear strength of NR/BIIR blends.

significantly different with changing BIIR content. When BIIR content is >40 wt %, hardness and modulus progressively decrease with increasing BIIR loading due to the decrease in crosslink density. Figure 4 shows the effect of blend ratio on the tensile strength and elongation at the break of the NR/BIIR vulcanizates. Tensile strength of the blends tends to decrease with increasing BIIR content, because the high tensile strength NR is diluted by the low-strength BIIR. Furthermore, the low cure compatibility between NR and BIIR may be another reason of the decrease in tensile strength. It is also found that the elongation at the break does not markedly change when BIIR content is increased until 90 wt %. This may be resulted from two competitive parameters, which are the decrease in crosslink density when BIIR content is high and the low cure compatibility between NR and BIIR. On the other hand, the neat BIIR vulcanizates shows the highest strain ability due to the lowest degree of crosslinking.

Tear strength of NR/BIIR blends is presented in Figure 5. The results show that tear strength tends to decrease when BIIR content is increased. The

same explanations as that for tensile strength could be applied. Increasing the BIIR content also lead to the decrease in resilience, as displayed in Figure 6. This result is attributed to the dilution effect. It is well established that BIIR having sterically hindered molecular structure requires high energy for molecular mobility and thus leads to high energy loss or damping.[13,15] In addition, the reduction in crosslink density when increasing BIIR content is another possible explanation for the decreased resilience.

The oxygen gas permeability of various NR/BIIR blends is illustrated in Figure 7. As can be seen, the permeability decreases with an increase in the amount of BIIR in the blend systems. Gas permeability rapidly decreases with an increase in BIIR loading up to 40 wt % where the relatively large elongated particles of BIIR dispersed phase is created. Then, the gas permeability slowly decreases with further increasing BIIR content despite. This result corresponds with the occurrence of the relatively larger elongated particles of BIIR dispersed phase and finally a continuous BIIR phase, as previously shown in Figure 2(c–e). Therefore, it seems
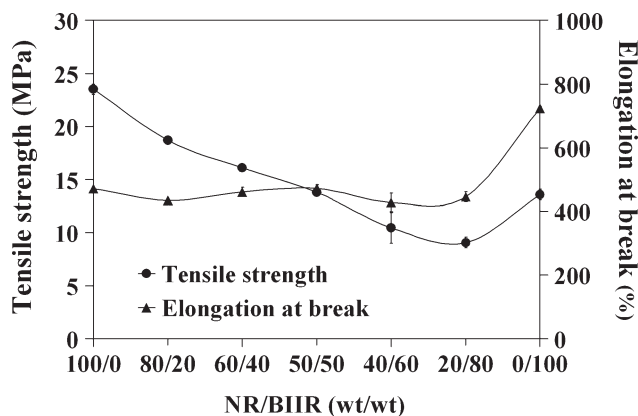

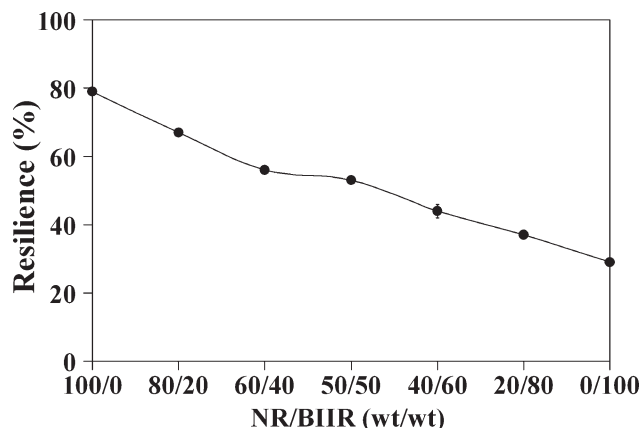**Figure 4** Tensile strength and elongation at the break of NR/BIIR blends.

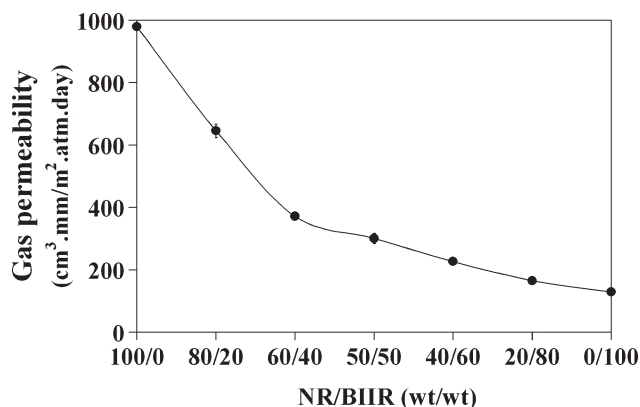**Figure 6** Resilience of NR/BIIR blends.

Figure 7 Gas permeability of NR/BIIR blends.

that the relatively large elongated particles of the dispersed BIIR can already act as a good gas barrier by causing the gas molecules to cover an even longer distance to pass around the BIIR domain.

Thermal ageing properties

Figure 8 shows the comparison of 100% modulus of the blends before and after thermal ageing. It can be seen that modulus after thermal ageing is higher than before thermal ageing. As a consequence, the elongation at the break of aged samples tends to decrease, as shown in Figure 9. The rise in modulus and reduction in elongation at the break of aged specimens over those of unaged specimens may be due to the formation of an additional crosslinks caused by postcuring effect.[16–18] Because of the post-curing effect, degree of crosslinking may exceed the optimum value of crosslink density and the network becomes too dense and causes the decrease in tensile strength (Fig. 10), whereas their moduli increase. Moreover, it can be noticed in Figures 8–10 that the trend of tensile properties as a function of blend ratios of aged specimens is similar to that of unaged specimens. Nevertheless, the magnitude of the
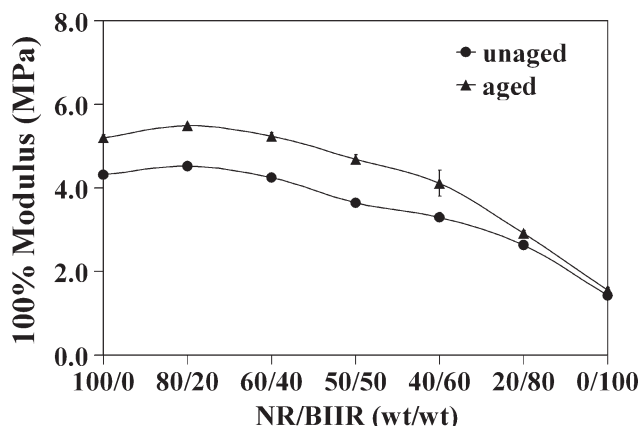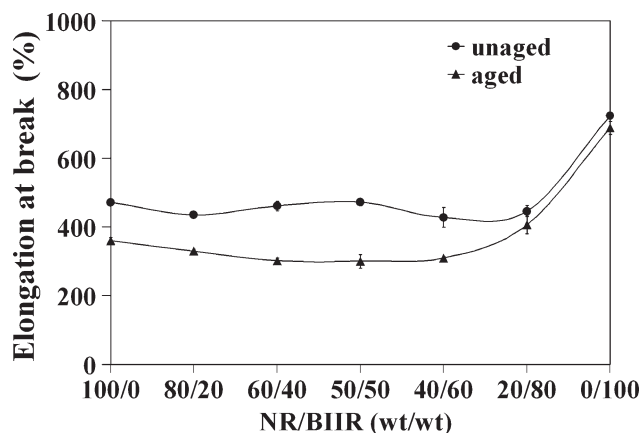

Figure 9 Elongation at the break of NR/BIIR blends before and after thermal ageing.

change in tensile properties after heat ageing depends on the blend ratio. Interestingly, the tensile properties of aged specimens shift closer to those corresponding unaged specimens when BIIR content in the blends is >50 wt % at which BIIR becomes the continuous phase as supported by the phase morphology shown in Figure 2.

Tensile retention of the blends having BIIR up to 50 wt % does not considerably differ, although the NR is diluted by BIIR at different amounts as illustrated in Figure 11. This is quite surprising. However, according to the blends morphology as previously shown in Figure 2(a–c), the NR as a low thermal ageing resistance is the continuous phase. Thus, it would dominate the thermal ageing properties of the blends. On the other hand, improvement of the tensile retention of 40/60 NR/BIIR blend is clearly observed and then it further increases with increasing BIIR content. These results correspond well with the phase morphology that BIIR is now a continuous phase and it exhibits a strong role in enhancing the thermal ageing resistance of blends.
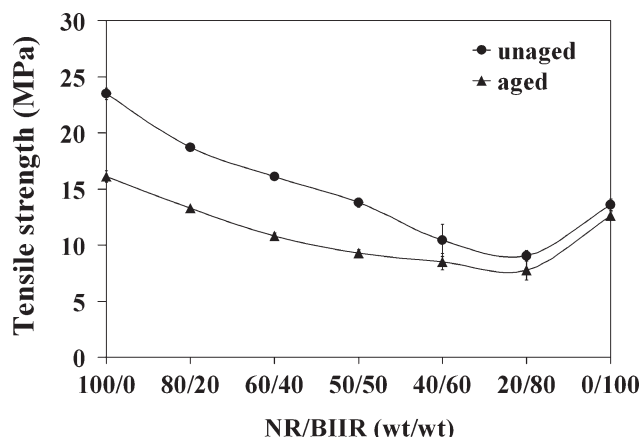

Figure 8 100% modulus of NR/BIIR blends before and after thermal ageing.

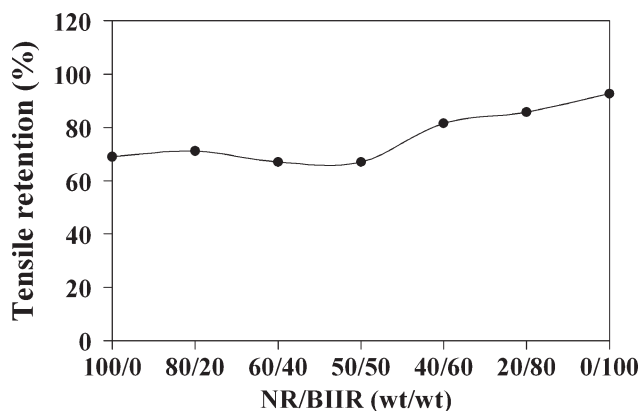**Figure 10** Tensile strength of NR/BIIR blends before and after thermal ageing.

Figure 11 Tensile retention of NR/BIIR blends.

Thermogravimetric analysis

TGA and its derivative (DTGA) curves of various NR/BIIR blends are shown in Figure 12. The results show that the first decomposition of the blends occurs in region 220–500°C under N$_2$ atmosphere and it corresponds to 54 wt % of low boiling point of rubber chemicals and elastomers. DTGA curves of blends show overlapping of the maximum decompo-
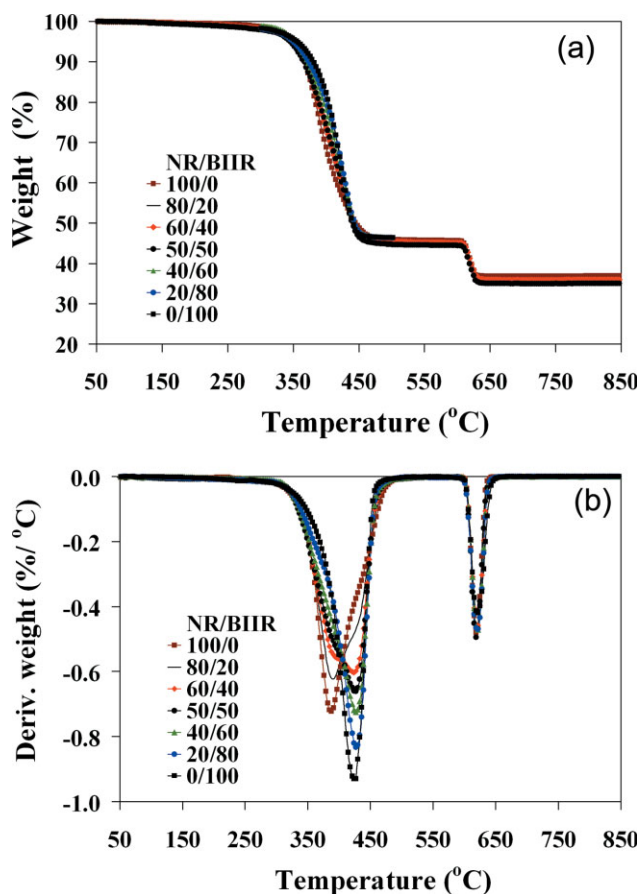
sition rate or the first DTGA peak T^1_{max} in the range of 320–480 °C depending on the blend compositions. The second DTGA peak T^2_{max} observed in O$_2$ atmosphere at about 628°C for all samples, is related to 9 wt % of carbon black. Finally, the residue weighed about 37 wt % corresponds mainly to the inorganic components such as silica and calcined clay.

To analyze the thermal stability of various NR/BIIR blends, the TGA and DTGA curves are enlarged at temperatures ranged from 300 to 500°C and they are shown in Figure 13. In addition, the temperature at 10% weight loss (T_{10}) and 30% weight loss (T_{30}) of the blends is determined and shown in Figure 14. It seems that the degradation temperature of the neat NR is less than the neat BIIR. This is because NR is a highly unsaturated elastomer, and thus it is more susceptible to thermal degradation. It also seems that the T^1_{max} of the blends shifts closer to that of the neat BIIR when BIIR content is increased. Besides, both T_{10} and T_{30} of the blends tend to increase with increasing BIIR content. The results imply that the delay of thermal degradation is greater for the blends having higher BIIR
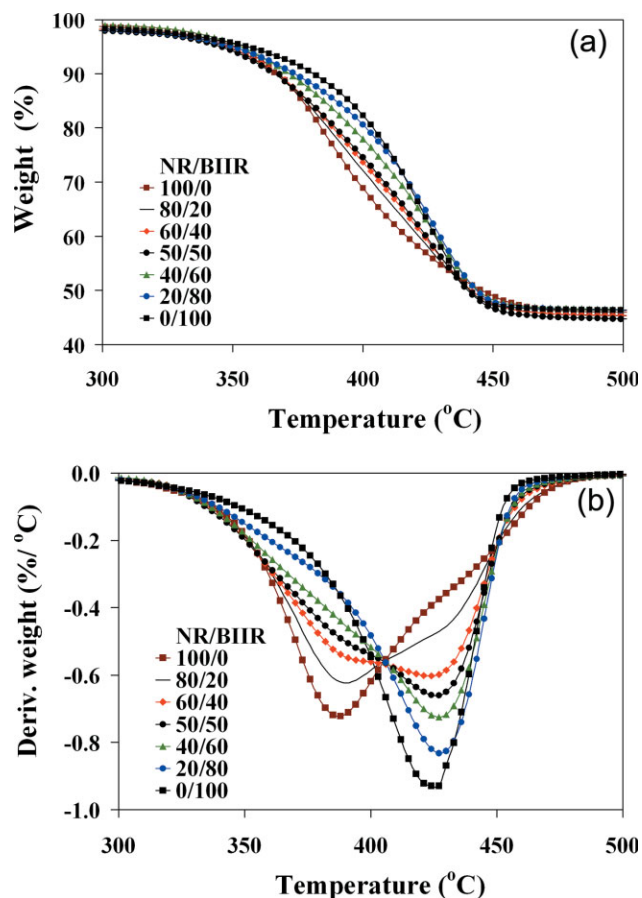

Figure 12 (a) TGA and (b) DTGA curves of NR/BIIR blends as a function of temperature (50–850°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 13 (a) TGA and (b) DTGA curves of NR/BIIR blends as a function of temperature (300–500°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
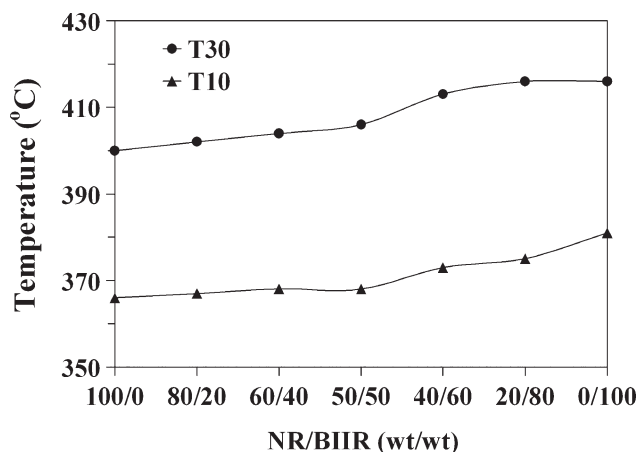
Figure 14 Variation of the temperature at 10% weight loss (T_{10}) and 30% weight loss (T_{30}) as a function of NR/BIIR blend ratios.

content. Furthermore, the magnitude of the increased thermal stability is obviously observed when the BIIR content in the blends is higher than 50 wt %. These results are also in good agreement with the tensile retention and blend morphology as discussed previously.

CONCLUSIONS

It can be concluded that thermal stability and gas permeability of the blends are strongly related with their phase morphologies. The results reveal that the cure reversion is clearly observed in NR-rich blends and tends to decrease with increasing BIIR content. Tensile strength, tear strength and rebound resilience of NR/BIIR blends tend to decrease with increasing BIIR content because the neat BIIR has lower strength and rebound resilience than NR. The reduction in strength of the blends is also believed to be caused by low cure compatibility between NR and BIIR, and the reduction in crosslink density when the BIIR content is increased. Interestingly, gas permeability is considerably reduced with an increase in BIIR content up to 40 wt % when the relatively large connected particles of BIIR dispersed phase is formed. It implies that the relatively large connected particles of the dispersed BIIR can act effectively as a gas barrier. Hence, the reduction rate of gas permeability declines when BIIR loading is

further increased. Besides, it is found that phase inversion where BIIR becomes the continuous phase and NR is the dispersed phase takes place in 40/60 NR/BIIR blend. This is coincident with the obvious increase in tensile retention and temperature at 10 and 30% weight loss (T_{10} and T_{30}) indicating the enhancement of the thermal stability of the blends when BIIR becomes a continuous phase.

References

1. Flokes, M. J.; Hope, P. S. Polymer Blends and Alloys; Chapman & Hill: London, 1993.
2. Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum Press: New York, 1976.
3. Tinker, A. J.; Jones, K. P. Blends of Natural Rubber-Novel Techniques for Blending With Specific Polymers; Chapman & Hill: London, 1998.
4. Poh, B. T.; Ismail, H.; Quah, E. H. Polym Test 2001, 20, 389.
5. Ismail, H.; Poh, B. T. Eur Polym J 2000, 36, 2403.
6. Varkey, J. T.; Augustine, S.; Thomas, S. Polym Plast Technol Eng 2000, 39, 415.
7. Lemieux, M. A.; Killgoar, O. C. Rubber Chem Technol 1984, 57, 792.
8. Rodgers, M. B.; Webb, R. N.; Wang, W. Rubber World 2006, 234, 36.
9. Lewis, C.; Buanpa, R.; Kiatkamjornwong, S. J Appl Polym Sci 2003, 90, 3059.
10. Botros, S. H. Polym Plast Technol Eng 2002, 41, 341.
11. Sae-Oui, P.; Sirisinha, C.; Hatthapanit, K. Express Polym Lett 2007, 1, 8.
12. Achalla, P.; Mccormick, J.; Hodge, T.; Moreland, C.; Esnault, P.; Karim, A.; Rageavan, D. J Polym Sci Part B: Polym Phys 2006, 44, 492.
13. Hofmann, W. Rubber Tecnology Handbook; Hanser Publishers: New York, 1989.
14. Roberts, A. D. Natural Rubber Science and Technology; Oxford University Press: Oxford, 1988.
15. Morton, M. Rubber Technology; Van Nostrand Plublisher: New York, 1973.
16. Rattanasom, N.; Saowapark, T.; Deeprasertkul, C. Polym Test 2007, 26, 369.
17. Chen, C. H.; Koenig, J. L.; Shelton, J. R.; Collins, E. A. Rubber Chem Technol 1982, 55, 103.
18. Rattanasom, N.; Poonsuk, A.; Makmoon, T. Polym Test 2005, 24, 728.