

Thermal properties and morphologies for polymer blends comprising of epoxidized natural rubber and semicrystalline thermoplastic

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ABSTRACT

Thermal properties and morphologies of epoxidized natural rubber (ENR)-based blends are discussed. Poly(ethylene terephthalate) (PET), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(ethylene oxide) (PEO) were blended with ENR as the second component. The two glass transition temperatures that correspond to the neat constituents in the ENR blends reflect immiscibility of the ENR with the second component. Rate of crystallization of PET and PEO remains constant when mass fraction of ENR (W_{ENR}) ≤ 0.4 , whereas the rate of crystallization becomes slower when $W_{\text{ENR}} \geq 0.5$. The entrapment of the ENR amorphous region either intra or/and interspherulitically at higher content of ENR for the PET or PEO in the blends has caused the reduction in the rate of crystallization for the crystallizable component. For PHBV and its blends, fine intraspherulitic dispersion of ENR in PHBV can be observed when the $W_{\text{ENR}} \geq 0.2$. Decreasing of the rate of isothermal crystallization of PHBV is detected with increasing ENR content.

Keywords: Epoxidized natural rubber, Poly(ethylene terephthalate), Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), Poly(ethylene oxide)

1.0 INTRODUCTION

Blending of polymers is an economic alternative and popular industrial practice as compared to that of direct synthesis of new materials to achieve physical properties. Blends of elastomer/thermoplastic have been studied extensively [1-7]. For amorphous /semicrystalline immiscible polymer blends, one may observe minor influence of the amorphous constituent on the properties of the crystallizable constituents. The liquid-liquid demixing and liquid-solid phase separation offer variety of morphological patterns [8].

Epoxidized natural rubber (ENR) is the derivative of natural rubber (NR) with the replacement of some double bonds in the isoprene units by epoxy groups [9]. The presence of oxirane group in ENR was found to be effective in inducing specific interaction with the second polymer [10] or melt reactions with the second polymer can be observed at sufficiently high temperatures [11, 12]. ENR with 50 mol% of epoxy content is blended with poly(ethylene terephthalate) (PET), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) with 12 mol% of hydroxyvalerate content (PHBV) and poly(ethylene oxide) (PEO), respectively. PET, PHBV and PEO are thermoplastic polymers and display relatively high crystallinity. PET, a synthetic polyester, is an engineering polymer and it widely used as fibers, bottles and packaging materials. PHBV is a naturally occurring, biodegradable aliphatic polyester. Lastly, PEO is synthetic biodegradable polyether and it has been widely used for medical applications.

In elastomer/thermoplastic blends where the crystalline constituent is in excess, this component crystallizes out from the melt comprising a dispersion of ENR domains. The main target here is to study the influence of the ENR dispersion on the isothermal crystallization behavior as well as on the morphologies of the crystalline constituents.

2.0 EXPERIMENTAL

2.1 Preparation of the Blends

Characteristics of polymers are listed in Table 1. All the polymers were purified before further use. Thin films of the ENR/PHBV and ENR/PEO blends were prepared by solution casting method where chloroform (Fisher Scientific, UK) is the mutual solvent. However, blends of ENR/PET were prepared via precipitation method using phenol (Fisher Scientific, UK)/1,2-dichloroethane (Fisher Scientific, UK) in the ratio of 2:3 as mutual solvent and methanol (Fisher Scientific, UK) as the nonsolvent. All samples were dried at 50°C under vacuum for 48 hours. Compositions of the blends ranged from 100/0 to 0/100 in steps of 10 wt%.

2.2 Differential Scanning Calorimetry

Perkin-Elmer DSC 7 (Shelton, US) was used to study the crystallization behavior and TA Q200 (Delaware, US) was used to study the glass transition temperature of the blends. Both of the DSCs were calibrated with indium standard and nitrogen atmosphere was purged throughout the analysis. The samples were exposed to different thermal histories:

- I. Isothermal crystallization. Samples were annealed at annealing temperature (T_a), ($T_a=280, 175$ and 80 °C for blends of PET, PHBV and PEO, respectively. This annealing temperature is strictly followed for other thermal histories) for 1 min, followed by cooling with a rate of 20 °C min^{-1} to the respective crystallization temperature (T_c) and held until complete crystallization.
- II. Glass transition temperature. Samples were annealed at T_a for 1 min followed by quenched cooling to -50 °C for ENR/PET and ENR/PHBV blends or -90 °C for ENR/PEO blends and held there for 1 min. Afterwards, samples were reheated up to T_a with a rate of 20 °C

min^{-1} for ENR/PET and ENR/PEO blends or $10\text{ }^{\circ}\text{C min}^{-1}$ for ENR/PHBV blends (the second heating run).

2.3 Polarizing Optical Microscopy

Morphologies of blends were studied using Leica Q Win Software (Cambridge, UK) (for ENR/PET and ENR/PEO blends) or Image-Pro Express (for ENR/PHBV blends), which was attached to the Nikon microscope (Yokohama, Japan) equipped with a Linkam heating/cooling unit (Linkam TM 600/s) (Surrey, UK).

Samples were annealed at T_a for 1 min, followed by cooling with a rate of $20\text{ }^{\circ}\text{C min}^{-1}$ to the selected T_c and held until complete crystallization. Micrograph was captured at the selected T_c after 60 min.

Table 1: Characteristics of the blends constituents

Constituents	ENR with 50 mol% epoxy groups	PET	PHBV with 12 mol% HV	PEO
$M_n^a / \text{kg mol}^{-1}$	-	18	-	300
$M_w^b / \text{kg mol}^{-1}$	700	-	238	-
$M_n^c / \text{kg mol}^{-1}$	200	-	109	-
Supplier	Rubber Research Institute (Sungai Buloh, Malaysia)	Aldrich Chemical Co. (St. Louis, MO, US)		

^a Viscosity-average molecular weight provided by the supplier.

^b Weight-average of molecular weight as estimated in this work by gel permeation chromatography (GPC)

^c Number-average molecular weight as estimated in this work by GPC.

3.0 RESULTS AND DISCUSSION

3.1 Glass Transition Temperatures

Quantities T_g were taken from the second heating runs after thermal procedure II at temperature, which characterizes half of the delta heat capacity of the DSC heat flow curve. The values of T_g of the ENR blends are summarized in Table 2, which corresponds to that of the neat constituents, were found for blends of ENR/second component from 70/30 to 30/70. The two values of the T_g in the ENR blends reflect immiscibility of the ENR with PET, PHBV as well as PEO.

Table 2: Glass transition temperatures (T_g) of ENR blends measured according to thermal procedure II during reheating cycle

Blends	T_g of ENR / °C	T_g of the semicrystalline polymer / °C
ENR	-20	
ENR/PEO 70/30 to 30/70	-18 ± 1	-54 ± 2
PEO		-54
ENR/PHBV 70/30 to 30/70	-20 ± 1	-1 ± 1
PHBV		0
ENR/PET 70/30 to 30/70	-19 ± 1	79 ± 2
PET		81

3.1.1 Kinetics of Isothermal Crystallization of Crystallizable Component in ENR Blends

Isothermal crystallization experiments were carried out according to thermal procedure I, as described in the Experimental part. The overall crystallization rate can be monitored by thermal analysis through the evolution of heat of crystallization by DSC. The rate of crystallization of the crystallizable component in ENR blends is simply characterized by the reciprocal half time $[(t_{0.5})^{-1}]$. Half time of crystallization is defined as time taken for half of the crystallinity to develop in a sample. Results for neat crystallizable component may

serve as reference for evaluation of crystallization of crystallizable component in ENR blends. The rates of crystallization $[(t_{0.5})^{-1}]$ of neat PET, PHBV and PEO as well as their corresponding 50/50 ENR blends decrease exponentially with decreasing undercoolings [equilibrium melting temperature (T_m°) – isothermal crystallization temperature (T_c)] or in other words with ascending T_c as shown in Figure 1. It means that half times of neat semicrystalline polymers as well as crystallizable component in ENR blends increase with increasing T_c . T_m° for PET, PHBV, PEO are 270, 195, 84 °C, respectively [1-3].

As expected for immiscible blends, the rate of crystallization $[(t_{0.5})^{-1}]$ of PET and PEO at $T_c = const$ does not change markedly with blend composition at least in the range where crystallizable component is in excess ($W_{ENR} \leq 0.4$) (c.f. Figure 2). The amorphous constituent should have minor influence on the rate of crystallization as long as the crystallizable component is in excess and as long as the two constituents are largely separated. Hence, the rate of crystallization should be independent of blend composition under these conditions. Decreasing rates of crystallization PET and PEO with ascending content of ENR ($W_{ENR} > 0.4$) are observed, which may be due to the influence of borderlines that reduces slightly the rate. When the weight fraction of PET and PEO is less than 0.4, the rate of crystallization becomes so low that no crystallization can be detected reliably by DSC analysis. Decreasing rates of crystallization of PHBV with ascending content of ENR is observed ($W_{PHBV} \geq 0.3$) (c.f. Figure 2). When the weight fraction of PHBV is less than 0.3, the rate of crystallization is not detected by DSC analysis.

3.1.2 Blend Morphologies

Figure 3 shows selected examples of PET spherulite morphologies that developed in ENR blends at $T_c = 224$ °C. Small spherulites of PET as well as PET in blends are observed. Co-continuous phase is observed for 50/50 blends [13]. At $T_c = 224$ °C, the viscosity of ENR is relatively low (T_g of ENR is -19 °C). During the spherulite growth of the crystallizable matrix, small domains of the ENR may be rejected easily by the spherulitic growth front to the amorphous interspherulitic zone as shown in the ENR/PET 20/80 blends in Figure 3. When the two constituents are largely separated, the amorphous constituent (ENR) should have minor influence on the rate of crystallization of PET as long as the content of PET in the blends is in excess. This is in good agreement with the results shown in the kinetics of isothermal crystallization.

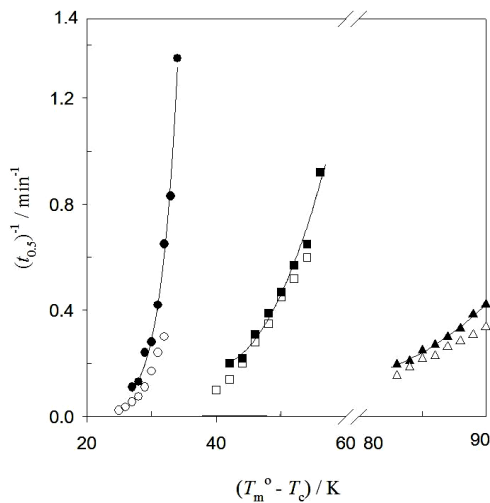


Figure 1: Reciprocal of half-time of isothermal crystallization versus undercoolings
 ■ – PET, ▲ – PHBV, and ● – PEO. An opened marker corresponds to the respective 50/50 ENR blends

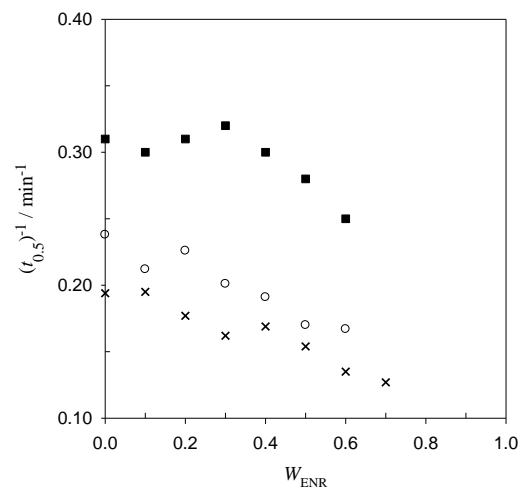
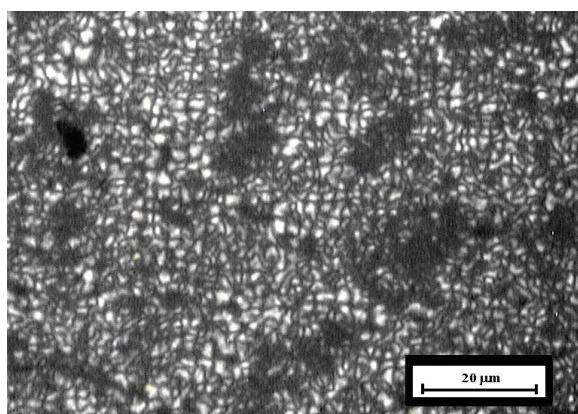


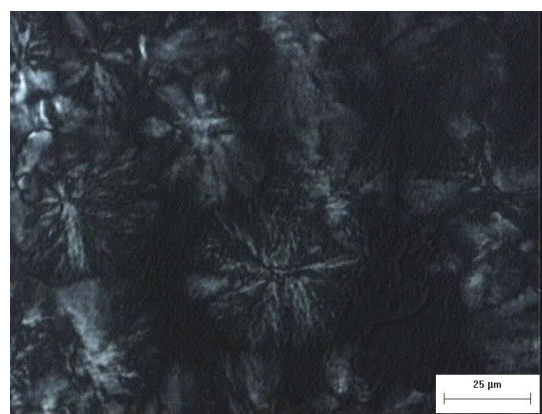
Figure 2: Reciprocal of half time after isothermal crystallization as a function of W_{ENR}
 ■ – PET at isothermal crystallization temperature (T_c) = 224 °C, × - PHBV at $T_c = 112$ °C, and ○ – PEO at $T_c = 49$ °C

Volume-filling spherulites grow in ENR/PHBV 0/100 to 30/70 blends at $T_c = 120$ °C. When the $W_{\text{ENR}} \geq 0.2$, fine intraspherulitic dispersion of ENR in PHBV can be observed (c.f. Figure 3). This has led to decrease in rate of crystallization with ascending ENR content since the growing front of PHBV cannot reject ENR efficiently. The entrapment of the amorphous ENR intraspherulitically is more pronounced with large size of the amorphous domains at higher content of ENR. It is in agreement with that of the decreasing of rate of isothermal crystallization $(t_{0.5})^{-1}$ (c.f. Kinetics of isothermal crystallization).

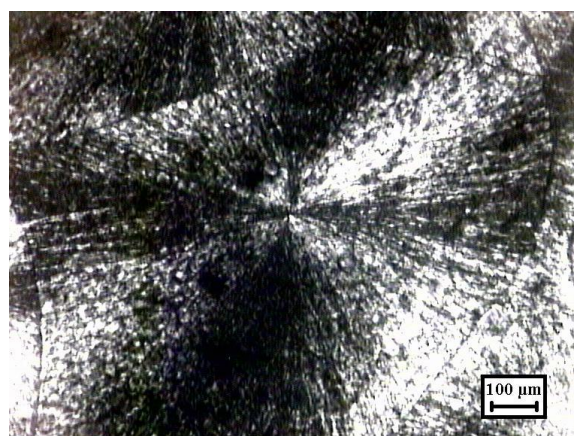
Volume-filling spherulites can be observed in ENR/PEO 0/100 to 40/60 blends at $T_c = 49$ °C. Neat PEO and blends with excess of PEO content exhibit fibrillar fine texture of the spherulites. At $W_{\text{ENR}} = 0.2 - 0.3$, intraspherulitic entrapment of ENR amorphous domains is not observed. The rejection of ENR amorphous region out from the PEO spherulites is more efficient in these blends up to $W_{\text{ENR}} = 0.4$ (c.f. Figure 3). However, at higher content of ENR ($W_{\text{ENR}} > 0.4$), ejection of ENR out from the spherulite growth front of PEO becomes difficult [14]. The intraspherulitic and the interspherulitic entrapment of the ENR amorphous region can be observed. This has caused reduction in the rate of crystallization of PEO at higher content of ENR. ENR has minor influence on the rate of crystallization as long as the crystallizable component is in excess (c.f. Kinetics of isothermal crystallization).



ENR/PET 20/80 at $T_c = 224$ °C



ENR/PHBV 20/80 at $T_c = 120$ °C



ENR/PEO 50/50 at $T_c = 49$ °C

Figure 3: Morphology for semicrystalline polymer in blends with ENR. Micrographs were taken after annealing at selected T_c for 60 min

4.0 CONCLUSION

Thermal properties and morphologies of ENR-based blends are discussed. PET, PHBV and PEO were selected to be blended with ENR as the second component. The two glass transition temperatures that correspond to the neat constituents in the ENR blends reflect immiscibility of the ENR with PET, PHBV as well as PEO. Rate of crystallization of PET and PEO remains constant when $W_{\text{ENR}} \leq 0.4$, whereas the rate of crystallization becomes slower when $W_{\text{ENR}} \geq 0.5$. The entrapments of the ENR amorphous region either intra or/and

interspherulitically at higher content of ENR for the PET or PEO in the blends has caused the reduction in the rate of crystallization for the crystallizable component. For PHBV and its blends, fine intraspherulitic dispersion of ENR in PHBV can be observed when the $W_{\text{ENR}} \geq 0.2$. Decreasing of rate of isothermal crystallization of PHBV is detected with increasing content of ENR.

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