

# Miscibility of Polymer Blends Comprising Poly (Ethylene Oxide) - Epoxidized Natural Rubber

Mohd Azizi Nawawi, Sim Lai Har, and Chan Chin Han

**Abstract**—Miscibility of thermoplastic-elastomer blends comprising poly(ethylene oxide) (PEO) and epoxidized natural rubber with 25 mol% epoxide level (ENR-25) were studied by differential scanning calorimetry (DSC) and polarized optical microscope (POM), respectively. Two glass transition temperatures ( $T_g$ ), corresponding to those of neat PEO and ENR-25 are observed over the entire composition range. It reflects the immiscibility of the two constituents in the molten state. Hoffman-Weeks method was employed to determine the equilibrium melting temperatures ( $T_m^0$ ) for the PEO/ENR-25 blends. No systematic variations of  $T_m^0$  and equivalently the apparent melting temperature ( $T_m$ ) with ascending ENR-25 content for the blends are detected. However, quantities  $T_m$  increase with ascending isothermal crystallization temperature ( $T_c$ ). There is no melting transition of PEO in PEO/ENR-25 blends when the ENR-25 content in the blend > 50 wt%. Reciprocal half time ( $t_{1/2}^{-1}$ ) is applied to characterize the isothermal crystallization kinetics of the phase-separated blends. The rate of crystallization and equivalently the spherulite growth rate ( $G$ ) of PEO decreases with increasing  $T_c$  but exhibit no systematic variations with ascending ENR-25 content. No crystallization is observed for the blends when the PEO content is  $\leq 50$  and  $\leq 40$  wt% when analyzed using DSC and POM, respectively. The birefringence Maltese cross structure of PEO appears deformed with irregular border and coarse texture when the amount of ENR-25 in the blend  $\geq 40$  wt%.

**Index Terms**—Epoxidized natural rubber, glass transition temperature, isothermal crystallization, morphology

## I. INTRODUCTION

Great demand of polymer components and the high cost incur with polymer synthesis have induced extensive development in polymer blending both industrially and academically. Blending of polymers is a well-established way to produce a new material with properties somewhere between those two polymers mixed. It is a cost effective and economic approach to produce a new material with desired properties. The properties of polymer blends can be controlled by regulating blend morphology, blend compositions as well as processing condition [1]. After P. V. Wright's discovery of ionic conductivity in alkali metal salt complexes of poly(ethylene oxide) (PEO) in 1973 [2], PEO becomes the most common polymer being studied in polymer electrolyte field due to the fact that it has a low glass transition temperature ( $T_g$ ). PEO is a highly crystalline and water soluble thermoplastic which has a moderate tensile

modulus and possesses good mechanical and electrical properties [3]. High degree of crystallinity of PEO gives a negative impact on its ionic conductivity. It has been reported that PEO-based electrolytes show a very low ionic conductivity in the range of  $10^{-8}$  to  $10^{-4}$  at the temperature between 40 to 100 °C [4]. The idea of blending epoxidized natural rubber (ENR) with PEO may solve the brittleness problem and therefore promoting enhancement of ionic conductivity of the system. However, the compatibility between the two polymers is the main factor that determines the properties of the blends.

## II. EXPERIMENTAL

### A. Material

Poly(ethylene oxide) with viscosity-average molecular weight ( $M_v = 300\,000$ , Aldrich) and epoxidized natural rubber with 25 mol% epoxide level (ENR-25) supplied by Rubber Research Institute of Malaysia (RRIM) were used after purification processes.

### B. Preparation of Blends

The thin films of PEO/ENR-25 blends were prepared via solution casting method. 2% (w/w) stock solutions of the two parent polymers (PEO and ENR-25) were prepared in tetrahydrofuran (THF). Different weights of the two polymer stock solutions were measured and mixed to give PEO/ENR-25 blends of compositions ranging from 100/0 to 0/100 in steps of 10% (w/w). The mixture was stirred at 50 °C for 48 hours before casting from THF onto Teflon dish. The solvent was allowed to evaporate slowly overnight at room temperature. The free standing films were further dried under vacuum at 50 °C for 48 hours to remove residual solvent.

## III. RESULTS AND DISCUSSION

### A. Glass Transition Temperature

Determination of  $T_g$  by DSC is commonly practiced in the investigation of phase behaviour of polymer blends. The PEO/ENR-25 blends were exposed to specific thermal procedure in order to estimate the glass transition temperature ( $T_g$ ). The  $T_g$ s of the PEO/ENR-25 blends are summarized in Fig. 1. Two distinct  $T_g$  values corresponding to the two neat constituents for all blend compositions are observed. This suggests that the two polymers, PEO and ENR-25 are phase-separated in the amorphous phase under the experimental condition imposed. Furthermore, we observe that the  $T_g$ s of PEO and ENR-25 in the PEO/ENR-25

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blends are relatively constant throughout the entire composition range.

### B. Melting Temperature

Melting temperature ( $T_m$ ) of PEO in the blends with ENR-25 was extracted from the reheating cycle after isothermal crystallization for  $5t_{1/2}$  carried out at  $T_c = 46^\circ\text{C}$  to  $T_c = 52^\circ\text{C}$  using the DSC.  $T_c = 49^\circ\text{C}$  is chosen as the reference temperature to study the melting behavior of PEO/ENR blends, because PEO in all the blend compositions investigated is able to crystallize at an appreciable rate. Fig. 2 shows the DSC traces of the reheating cycle for three selected blend compositions of PEO/ENR-25 after isothermal crystallization at  $T_c = 49^\circ\text{C}$ . All the blends display broadened endothermic peaks above  $67^\circ\text{C}$  except neat PEO which exhibits a sharp endothermic peak at  $67^\circ\text{C}$ .

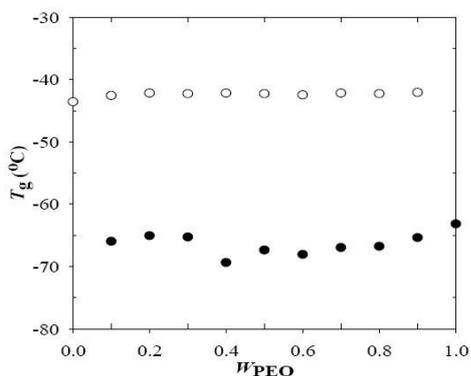


Fig. 1.  $T_g$  as a function of  $W_{PEO}$  for the blends of PEO/ENR-25. (○)  $T_g$  of PEO (●)  $T_g$  of ENR-25

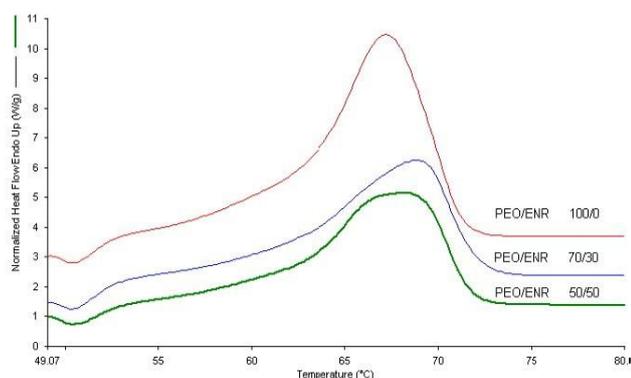


Fig. 2. DSC traces of reheating cycles after exposing PEO/ENR-25 samples to the thermal treatment at  $T_c = 49^\circ\text{C}$ .

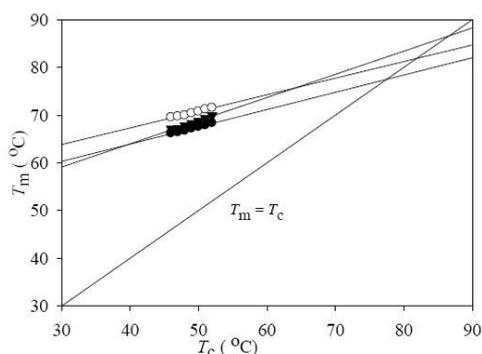


Fig. 3. Hoffman-Weeks plots for PEO in PEO/ENR-25 blends. (●) 50/50; (▲) 80/20; (○) 100/0.

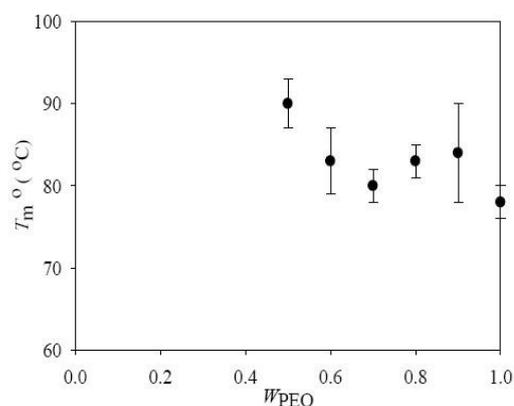


Fig. 4.  $T_m^\circ$  as a function of  $W_{PEO}$  for PEO/ENR-25 blends.

The equilibrium melting temperature ( $T_m^\circ$ ) of PEO for the PEO/ENR-25 blend was estimated after the Hoffman-Weeks method [5]. Linear plots of  $T_m$  versus  $T_c$ , to a good approximation for each blend, is extrapolated to intersect with the theoretical curve  $T_m = T_c$ . The point of intersection yields the  $T_m^\circ$ . Fig. 3 depicts that extrapolation of the linear regression of the experimental data  $T_m$  against  $T_c$  to intersect with the theoretical curve  $T_m = T_c$  gives  $T_m^\circ$  for selected blends. Fig. 4 shows the variations of  $T_m^\circ$  as a function of weight fraction of PEO in PEO/ENR-25 blends. No systematic variations of  $T_m^\circ$  with descending weight fraction of PEO are observed. The inconsistent variation in  $T_m^\circ$  of PEO in the PEO/ENR-25 blends correlates with the existence of two  $T_g$ s for the blends, thus, reflects the immiscibility of the two polymers.

### C. Kinetics of Isothermal Crystallization of PEO

Perkin Elmer DSC-7 calibrated with indium standard has been used for the analysis of samples under nitrogen atmosphere. Sample was heated to  $80^\circ\text{C}$  at a rate of  $20\text{ K min}^{-1}$  and annealed for 1 minute before cooling at a rate of  $20\text{ K min}^{-1}$  to the respective crystallization temperature ( $T_c$ ), ranging from  $46^\circ\text{C}$  –  $52^\circ\text{C}$ . The sample was held at a particular  $T_c$  until complete crystallization. The half time of crystallization ( $t_{1/2}$ ) was determined at constant  $T_c$ . Fig. 5 shows the crystallization rate versus weight fraction of PEO at  $T_c = 49^\circ\text{C}$ . No systematic variation of crystallization of PEO is observed with ascending amorphous ENR-25 content suggesting that this system is immiscible. In addition, no crystallization of PEO is observed after isothermal crystallization at  $T_c = 49^\circ\text{C}$  when the content of ENR-25  $\geq 60\text{ wt } \%$  in the PEO/ENR-25 blends even after 3 hours of experimental analysis.

### D. Spherulite Growth Rates

Nikon Eclipse ME600D polarizing microscope equipped with Linkam TM600/s heating and cooling unit was used to study the growth rates and morphologies of blends. The radial growth rate,  $G$ , of PEO spherulites was determined by POM at three crystallization temperatures i.e.  $46^\circ\text{C}$ ,  $49^\circ\text{C}$  and  $52^\circ\text{C}$ . The sample was annealed above its melting temperature for 1 minute, followed by cooling with a rate of  $20\text{ K min}^{-1}$  to the respective  $T_c$  and held there until complete crystallization. Micrographs were captured at appropriate time intervals during the isothermal crystallization. No systematic variation on the growth rate of PEO spherulite

with decreasing  $W_{\text{PEO}}$  (see Fig. 6) indicates that system is heterogeneous on microscopic scale.

### E. Blend Morphologies

The phase structure and the morphology of a crystallizable blend depend strictly on the composition, chemical nature of the components and the interaction between the components [6]. Sample was annealed at 80 °C for 1 minute followed by cooling with a rate of 20 K min<sup>-1</sup> to 46 °C and held until complete crystallization. Micrographs were captured at  $T_c = 46$  °C for all blend compositions. The fine fibrillar texture of neat PEO becomes irregular and coarse when the amount of ENR-25 in the blend increases from 10-60 wt %. The irregularity and distortion of PEO spherulite at high ENR-25 content especially when ENR-25 content is  $\geq 40\%$  caused by the entrapment of ENR-25 in the amorphous region of the PEO spherulite. The entrapment of the ENR-25 hinders the mobility of the crystallizable material and the crystal growth front which explain the decrease in the spherulite growth rate from 60 wt% PEO to 40 wt% PEO shown in Fig. 6. The volume filled fibrous spherulites in neat PEO transforms into isolated spherulites dispersed in a continuous amorphous region seen as dark areas around the spherulite. This implies that there is interspherulitic segregation of ENR in the blend of PEO/ENR-25 at high content of ENR-25.

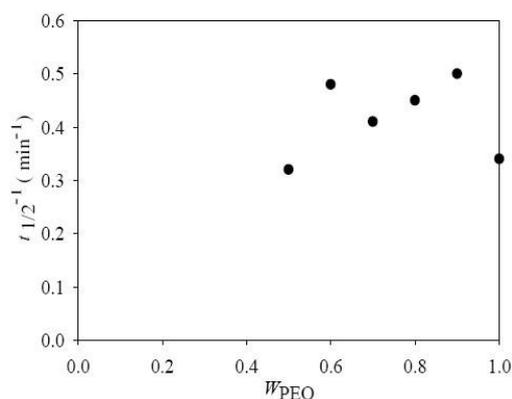


Fig. 5. Crystallization rate versus weight fraction of PEO in PEO/ENR-25 blends at  $T_c = 49$  °C.

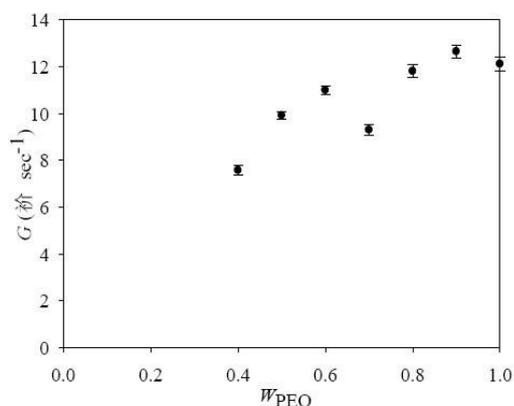
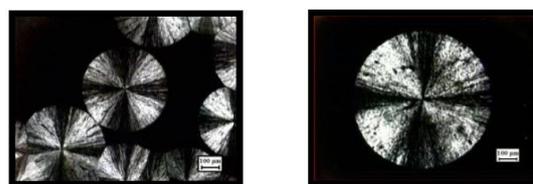


Fig. 6. The radial growth rate of PEO spherulites as a function of weight fraction of PEO in PEO/ENR blends at  $T_c = 46$  °C.



(a) PEO/ENR-25 100/0

(b) PEO/ENR-25 80/20



(c) PEO/ENR-25 60/40



(d) PEO/ENR-25 40/60

Fig. 7. Micrographs of PEO growing spherulites for the blends of PEO/ENR-25 at  $T_c = 46$  °C with magnification 10x. The bar corresponds to 100  $\mu\text{m}$ .

## IV. CONCLUSION

Crystallization, melting behavior and morphologies of binary blends PEO/ENR-25 have been studied. Two distinct  $T_g$ s, reflect the immiscibility of the two polymers. The  $T_m$  obtained after isothermal crystallization at the reference temperature,  $T_c = 49$  °C is relatively constant for all the blend compositions investigated. No systematic variation of  $T_m$  with ascending weight fraction of PEO is observed. No systematic variation of crystallization of PEO with ascending ENR-25 content, further confirming the immiscibility of the blends.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] M. M. Dumoulin, "Polymer blends handbook (ed. L. A. Utracki)," *Dordrecht: Kluwer Academic*, vol. 2, 2003.
- [2] D. E. Fenton, J. M. Parker, and P. V. Wright, "Complexes of alkali metal ions with poly (ethylene oxide)," *Polymer*, vol. 14, no. 11, pp. 589, 1973.
- [3] L. H. Sim, S. N. Gan, C. H. Chan, H. W. Kammer, and R. Yahya, "Compatibility and conductivity of LiClO<sub>4</sub> free and doped polyacrylate-poly (ethylene oxide) blends," *Materials Research Innovations*, vol. 13, no. 3, pp. 278-281, 2009.
- [4] A. M. Stephan, "Review on gel polymer electrolytes for lithium batteries," *European Polymer Journal*, vol. 42, pp. 21-42, 2006.
- [5] J. D. Hoffman and J. J. Weeks, "Melting process and the equilibrium melting temperature of polychloro trifluoro ethylene," *J. Res. Natl. Bur. Std.*, 1962. 66: p. 13-28.
- [6] G. Dreezen, Z. Fang, and G. Groeninckx, "Miscible binary blends of poly (ethylene oxide) and poly (ether sulphone). Part I: crystallization kinetics, morphology and thermal behavior," *Polymer*, vol. 40, vol. 21, pp. 5907-5917, 1999.