Korea-Australia Rheology Journal
Vol. 11, No. 3, September 1999 pp.219-223

Articles

Rheological anomalies of the poly(ethylene 2, 6-naphthalate) and poly(ethylene terephthalate) blends depending on the compositions

Hyang Mok Lee, Duck Jong Suh, Seung Bum Kil, O Ok Park* and Kwan Han Yoon*****
Center for Advanced Functional Polymers, Department of Chemical Engineering
Korea Advanced Institute of Science and Technology, 373-1, Kusong-dong
Yusong-gu, Taejon 305-701, Korea
****Department of Polymer Science and Engineering, Kumoh National*
University of Technology, 188 Shinpyung-dong, Kumi, Kyungbuk, 730-701, Korea
(Received May 20, 1999; final revision received July 10, 1999)

Abstract

The effects of the transreactions on the rheological properties have been found in the poly(ethylene 2, 6-naphthalate) (PEN) and poly (ethylene terephthalate) (PET) blends. The rheological properties were very much dependent on the blend compositions, which, in turn, were related to extent of the reactions. In particular, a blend with 50/50 wt% composition exhibits an unusual and remarkable decrease in complex viscosity and it may be related to the randomness of the copolymer structure through transreactions. It has been identified by investigating the extent of transreactions and block length of the copolymer from the (ethylene 2, 6-naphthalate) (EN) and (ethylene terephthalate) (ET) units from ^{1}H n.m.r. spectra.

Key words : transreaction, rheological properties, complex viscosity, poly(ethylene 2, 6-naphthalate), poly(ethylene terephthalate), block length

1. Introduction

Poly (ethylene 2,6-naphthalate) (PEN) has increasingly become a "polyester" of industrial and scientific importance because of its excellent thermal and mechanical properties. However, there remain still some problems to be resolved. Among them, high melt viscosity and high cost of PEN should be overcome for any realistic application. The former causes many difficulties in polymer processing and the latter does not allow a faster entry into the new markets as expected. In order to overcome such limitations, it would be interesting to blend the PEN with poly (ethylene terephthalate) (PET). The transreactions such as alcoholysis, acidolysis, and transesterification may occur between the ethylene moiety units of both the components of this blend. In this blend, the ability to tailor product properties for a particular performance and cost balance can be obtained by controlling the degree of transreaction, which is also associated with miscibility between the two polymers. Recently, some results about miscibility and transreactions in PEN/PET blends have been reported(Stewart, *et al.*, 1993). In the case of melt extrusion of the two polymers, the blending time and temperature mainly influenced the extent of reaction but blend composition and residual catalysts in the polyester did not.

It is well known that rheological measurements are useful to elucidate an occurrence of chemical reactions or phase changes during processing. However, such experiments are usually performed at high temperatures so that additional transreactions during the rheological measurement will affect the measured properties. We will examine the effects of transreactions on the rheological properties in the PEN/PET blends.

2. Experimental

PEN used in this work was prepared by the melt polycondensation of dimethyl naphthalate and ethylene glycol. Details about the preparation of PEN have been reported elsewhere(Yoon, *et al.*, 1994) and PET was kindly supplied by Kolon, Inc. The weight-averaged molecular weights of PEN and PET were 2.03×10^4 and 3.93×10^4 g/mol, respectively. Melt blending of the PET and the PEN was carried out using a Brabender single-screw extruder at 280°C with an L/D ratio of 25/1 and the average residence time of the polymers was about 2 min. Samples were blended in seven compositions ranging from 0 to 100 wt% of PEN in PET. The blends will be referred to as PEN10 and so forth, where the number denotes the weight percentage of PEN. The thermomechanical history of all the samples was kept identical.

*Corresponding author: oopark@sorak.kaist.ac.kr
**Current Address : LG Chem. Research Park, P.O.Box 61, Yusong, Taejon 305-380, Korea
© 1999 by The Korean Society of Rheology

For the effects of transreaction on the rheological property, a cone-and-plate rheometer (PHYSICA, Rheo Lab. MC 120) was used to investigate storage (G') and loss (G") modulus and complex viscosity (η^*) as a function of angular frequency (ω) in the oscillatory shear mode. The cone angle and the diameter of the plate were 0.1 rad and 50 mm, respectively. To avoid the effects of oxidative degradation on the rheological properties, nitrogen was purged continuously to the environmental chamber. The strain amplitude was maintained in the limited region so that all samples were linear viscoelastic and all data given below have been obtained at 280°C, at which both the components were in the molten state.

Differential scanning calorimetry (DSC) was used to characterize the thermal behavior of the blends. DSC measurements were carried out in a Dupont DSC cell equipped with a Dupont 2010 thermal analyst system. Samples were heated to 290°C at a heating rate 10°C/min under a nitrogen atmosphere.

To investigate the extent of transreaction between PEN and PET, ^{1}H n.m.r. spectra of the blends, which were taken from the sample just after finishing the rheological measurement were obtained by using a Bruker AMX-500 FT-NMR spectrometer (500 MHz).

3. Results and Discussion

Fig. 1 shows the results of the frequency sweep experiment at 280°C for both the components and their blends. Whole pools of samples have Newtonian behavior at the low frequency region and then exhibit a shear thinning behavior at the high frequency region. Over the entire range of frequency, PEN has a higher complex viscosity than PET. The viscosities of blends have an intermediate value those of between PEN and PET except PEN50. The viscosities of the blends increase with an increase in the percentage of PEN except PEN50. It is worthwhile to note that PEN50 has the lowest complex viscosity. In order to facilitate the comparison, the complex viscosities at a constant frequency ω=10 rad/s are presented as a function of the weight fraction of PEN in Fig. 2. It is apparently observed that the complex viscosity of PEN50 is put down unusually and remarkably low. These data indicate that there may be a significant effect of blend composition on the complex viscosity near the 50 wt% composition. In general, it is well known that extrusion of the blends of PEN and PET results in transreaction between the two polymers, which leads to production of random PEN-PET copolymers. Basically, PEN and PET are immiscible but phase transition gradually occurs from heterogeneous to homogeneous phase depending on the transreaction time as the reactions proceed during melt processing. According to the results reported by previous workers(Lee, *et al.*, 1997), the solution blends of PEN and PET show double

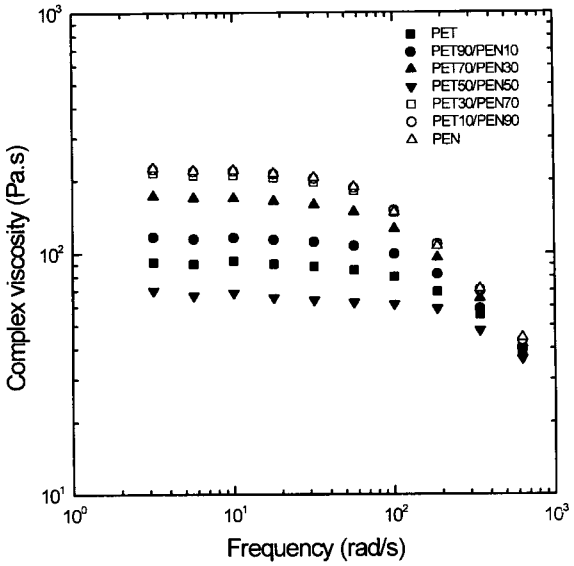

Fig. 1. Frequency sweep for PEN, PET and their blends at 280°C.

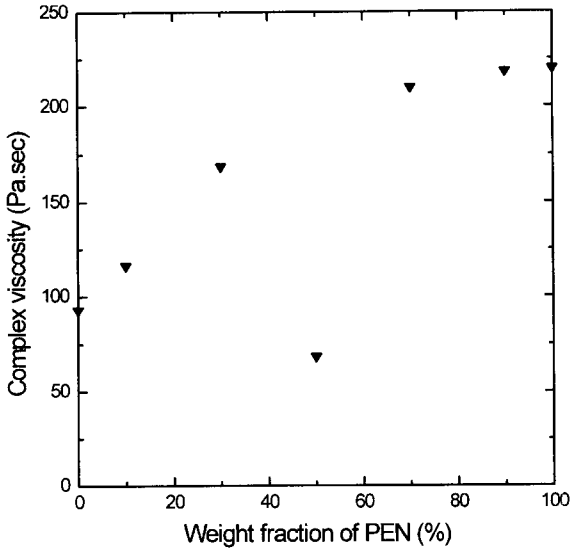

Fig. 2. Variation of the complex viscosity with weight fraction of PEN at constant angular frequency ω=10 rad/s.

glass transition temperatures, which indicate that they are immiscible without any reaction. However, thermal treatment at 280°C for 20 min or more gives a single glass transition temperature, which means that this blend becomes miscible.

In many cases, the rheological behavior of polymer blend serves as not only a key property in processing but also as an indicator in determining its miscibility. To investigate the effects of miscibility on the rheological property, we shall consider logarithmic plots of G'(ω) and G"(ω) as suggested by Chuang and Han(1984). They proposed that such plots would be sensitive to the morphological state or the degree of miscibility in the polymer blend system. Fur-

thermore, it has been demonstrated that the change of temperature does not affect these plots. If the polymer blends have the same miscibility, a superposition of the rheological data measured will be obtained on the log G'(ω)-log G"(ω) plots. Using the information in Fig. 1, log G' versus log G" plots are presented in Fig. 3. It is clearly observed from Fig. 3 that there is a good superposition having a master curve of slope 2, which implies an apparent limiting behavior of $G'(\omega) \sim G''(\omega)^2$, for all blend compositions. Therefore, it may be said that all the blends are in similar miscible states after melt blending due to some degree of transreaction. It is consistent with the previous report(Lee, *et al.*, 1997).

The primary factor to be investigated now is the extent of the transreaction induced during melt blending and the corresponding influence on rheological properties. It should be noted that the transreactions of the blends could progress even during the rheological measurement. It usually takes 20 min to obtain the first data and then 20 min more is needed to finish the measurement. Therefore, the effects of the transreaction time must be considered during this period of time but a major part of the reaction takes place within the first 20 min as reported elsewhere(Lee, *et al.*, 1997). It is also based on the fact that the rheological data measured do not show any more change after 20 min.

Fig. 4 shows the DSC thermograms of PET, PEN, and their blends of various compositions reacted during melt extrusion and rheological measurements. The pure PET shows a Tg at 80.3°C and a Tm at 254.5°C, preceded by a cold crystallization temperature peak at 132°C. The pure PEN shows a Tg at 123.7°C and a Tm at 270.0°C, preceded by a cold crystallization temperature peak at 189.5°C. The melting points decrease and the crystallization temperature increases for PEN10 and PEN90. The melting peaks completely disappeared for PEN30, PEN50, and PEN70 because of significant transreactions. The DSC thermograms of PEN/PET blends formed during the extrusion and rheological measurements show a single T_g for all blend compositions. It means that all the blends are in a miscible state after melt blending and rheological measurements due to transreactions. This is coincident with the results of the rheological experiment.

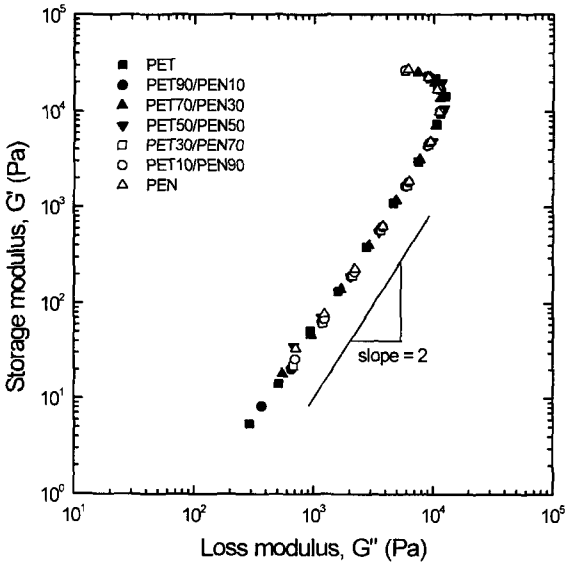

Fig. 3. Log G'-log G" plots of PEN, PET and their blends by using the data in Fig. 1.

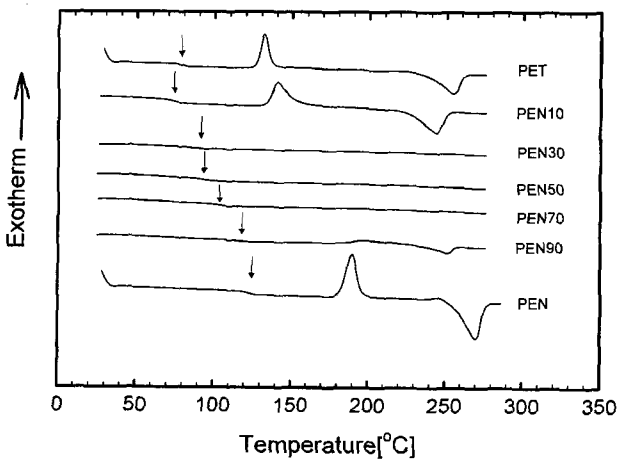

Fig. 4. DSC thermograms of PET, PEN and their blends of several compositions reacted during the melt extrusion and rheological measurements.

Fig. 5 shows the ^{1}H n.m.r. spectra of the blends in the range from 4.8 to 5.1 ppm which is corresponding to the region of the ethylene moiety. The peaks for PEN, PEN/PET copolymer, and PET units are assigned at 4.98, 4.93, and 4.88, respectively. The relative peak areas of the three signals indicate the concentrations of (ethylene 2,6-naphthalate)-(ethylene 2,6-naphthalate) (EN-EN), (ethylene 2,6-naphthalate)-(ethylene terephthalate) (EN-ET), and (ethylene terephthalate)-(ethylene terephthalate) (ET-ET) dyad sequences in the reacted blends. The extent of reaction is defined as

$$C = \left(\frac{\frac{\text{new peak}}{2}}{\frac{\text{new peak}}{2} + \text{bigger peak}} \right)$$

This gives the reacted ratio of the major component in each blend composition.

Table1 illustrates the variations of the reaction between PEN and PET depending on the blend compositions. The extent of the transreaction is higher in PET 50, the composition of which is near the molar ratio of 1 to 1, than any other blend composition because the possibility of transreaction is higher when the number of the PET ester group and the PEN ester group is similar to each other. To investigate the polymer sequence, which

influences the properties of the polymer, some parameters can be defined(Park, *et al.*, 1996).

$P_{NT} = \frac{F_{NT}}{F_N}$: Probability that the EN unit reacts with the ET unit in the PEN chain.

Table 1. The extent of transreaction and composition of ethylene moieties.

Code	Before transraion(%)	After transreaction(%)				
	PEN	PET	F_{NN}	F_{TT}	F_{TEN}	Extent of reaction
PEN10	8.1	91.9	3.5	87.3	9.2	5
PEN30	25.4	74.6	15	64.2	20.8	14
PEN50	45.2	55.8	28.6	40.2	31.2	23
PEN70	64.9	35.1	53.9	24.1	22	17
PEN90	87.7	12.3	80.7	5.3	14	8

F_{NN}; Mole fraction EN-EN dyad.
F_{TT}; Mole fraction ET-ET dyad.
F_{REN}; Mole fraction EN-ET dyad.

$$C = \left(\frac{\frac{\text{new peak}}{2}}{\frac{\text{new peak}}{2} + \text{bigger peak}} \right)$$; Extent of reaction

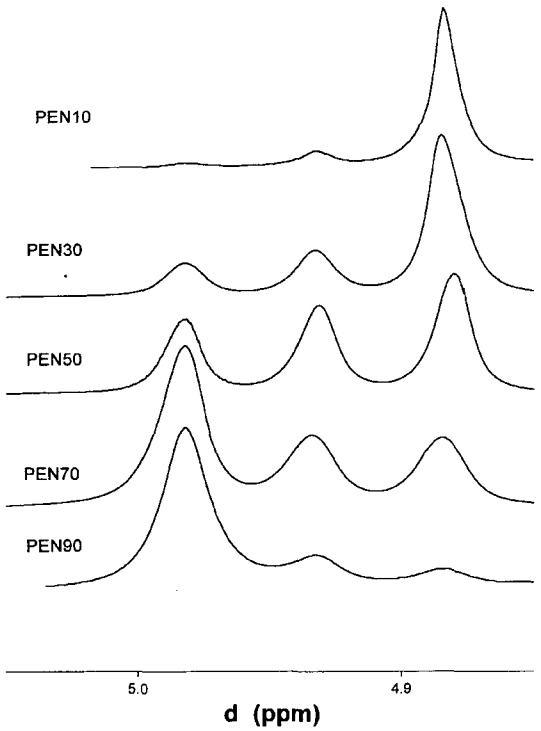

Fig. 5. H n.m.r. spectra for PEN10, PEN30, PEN50, PEN70 and PEN90 reacted during the melt extrusion and the rheological measurements.

$P_{NT} = \frac{F_{TN}}{F_T}$: Probability that the ET unit reacts with the EN unit in the PET chain.

Where, $F_{TEN} = F_{NT} + F_{TN}$: The overall amount of EN-ET units,

$F_N = \frac{F_{TEN}}{2} + F_{NN}$: The total amount of EN units,

$F_T = \frac{F_{TEN}}{2} + F_{TT}$: The total amount of ET units.

$B = P_{NT} + P_{TN}$: Degree of randomness.

$L_{NT} = \frac{1}{P_{NT}}$, $L_{TN} = \frac{1}{P_{TN}}$: Block length of PEN, PET.

The results using these parameters are summarized in Table2. P_{NT}=0.57 for PEN10 means that one of the two EN units, on an average, in the PEN-chain reacts with an ET unit in the PET chain. In other words, the most PEN transreact with ET units in PET chains. The result was that all the PEN molecules became EN/ET copolymers. The randomness factor, B, for PEN10 and PEN90 indicates the degree of randomness in the produced copolymers through the transreactions, but it should be remembered that there are still a lot of homopolymers left in the sample. The degree of randomness is surely proportional to the extent of the transreaction for other compositions too.Therefore, in order to understand the rheological properties of the

Table 2. Probability, block length and degree of randomness of the copolymer by transreaction.

	F_N	F_T	P_{NT}	P_{TN}	B	L_{NT}	L_{TN}
PEN10	8.1	91.9	0.57	0.05	0.62	1.75	20
PEN30	25.4	74.6	0.41	0.14	0.55	2.44	7.14
PEN50	45.2	55.8	0.35	0.28	0.63	2.86	3.57
PEN70	64.9	35.1	0.17	0.31	0.48	5.88	3.23
PEN90	87.7	12.3	0.08	0.57	0.65	12.5	1.75

$P_{NT} = \frac{F_{NT}}{F_N}$: Probability that the EN unit reacts with the ET unit in PEN chain.

$P_{TN} = \frac{F_{TN}}{F_T}$: Probability that the ET unit reacts with the EN unit in PET chain.

Where, $F_{TEN} = F_{NT} + F_{TN}$: The overall amount of EN-ET units,

$F_N = \frac{F_{TEN}}{2} + F_{NN}$: The total amount of EN units,

$F_T = \frac{F_{TEN}}{2} + F_{TT}$: The total amount of ET units,

$B = P_{NT} + P_{TN}$: Degree of randomness.

$L_{NT} = \frac{1}{P_{NT}}$, $L_{TN} = \frac{1}{P_{TN}}$: Block length of PEN, PET.

blends, it is better to characterize the polymer sequence structure using the block length instead. For example, the sequence of the block copolymer, as result of the transreaction of the PEN10 blend system, is as follows: The 1.75 EN units are continuously connected and then 20 ET units are continuously connected. Therefore, PEN10 and PEN30 maintain a relatively strong PET character after the transreactions while PEN70 and PEN90 have a strong PEN character. Meanwhile, the sequence of the copolymer, as result of the transreaction of the PEN50 blend system, is as follows: The 2.86 EN units are continuously connected and the 3.57 ET units are also continuously connected. This copolymer is a random copolymer rather than a block copolymer.

It was found that PEN50 exhibited the EN-ET random copolymer characteristics while PEN30 and PEN70 had the block copolymer chracteristics after the extrusion and rheological measurements in the ^{1}H n.m.r. analysis. Therefore, the PEN50 has the lowest complex viscosity. Because this random copolymer has a different property with block copolymer, which has a strong main block character. Consequently, the level of transreactions in the molten state has a great effect on the copolymer sequence and the copolymer sequence has a great influence on the complex viscosity.

In summary, the effects of the transreactions on the thermal and rheological properties of the PEN/PET blends have been studied. The reactions proceed during the melt processing and rheological measurements, and their extent are dependent on the blend compositions. Rheological measurements show that the PEN50 shows a remarkable decrease in the complex viscosity. The magnitude of the decrease may be associated with the progress of the transreactions between the EN and ET units of the two polymers and the produced copolymer sequence. ^{1}H n.m.r. spectra of the reacted blends support a such conclusion. However, it is observed that there is no difference in the miscibility for all the blend compositions, even with different levels of the transreactions, in the rheological window. The DSC thermograms of the reacted blends are concurrent with this result.

Therefore, when one would like to develop a reactive blend, the extent of reaction during blending should be carefully controlled in order to accommodate the extra reaction during processing.

Acknowledgment

This work is somewhat related to the project on polymer blends supported by the Center for Advanced Functional Polymers, and authors are thankful for its partial support.

References

Stewart, M.E., A.J. Cox and D.M. Naylor, 1993, Reactive processing of poly(ethylene 2,6-naphthalene dicarboxylate)/ poly (ethylene terephthalate)blends *Polymer* **34**, 4060.

Yoon, K.H., S.C. Lee and O.O. Park, 1994, Thermal properties of poly(ethylene 2,6-naphthalate) and poly(ethylene terephthalate) blends, *Polym. J.* **26**, 816.

Lee, S.C., K.H. Yoon, I.H. Park, H.C. Kim and T.W. Son, 1997, Phase behavior and transesterification in poly(ethylene 2,6-naphthalate) and poly(ethylene terephthalate) blends, *Polymer* **38**, 4831.

Chuang, H.K. and C.D. Han, 1984, "Rheological behavior of polymer blends," *J. Appl. Polym. Sci.* **29**, 2205.

Park, S.S., J.H. Jeong, T.J. Kim, D.J. Kim and S.S. Im, 1996, "Sequence Distribution and Thermal Properties of Poly(butylene succinate-co-butylene terephthalate) Copolyester," *J. Korea Chemical Soc.* **40**, 87.

Ihm, D.W., S.Y. Park, C.G. Chang, Y.S. Kim and H.K. Lee, 1996, "Miscibility of Poly(ethylene terephthalate)/Poly(ethylene 2,6-naphthalate) Blends by Transesterification," *J. Polym. Sci.: Part A: Polym. Chem.* **34**, 2841.