

Thermal Characterizations of Semi-Interpenetrating Polymer Networks Composed of Poly(ethylene oxide) and Poly(*N*-isopropylacrylamide)

Seon Jeong Kim,¹ Chang Kee Lee,¹ Young Moo Lee,² Kyu Back Lee,³ Yong Doo Park,³ Sun I. Kim¹

¹Department of Biomedical Engineering, Hanyang University, Sungdong P.O. Box 55, Seoul 113-605, Korea

²School of Chemical Engineering, Hanyang University, Seoul, Korea

³Department of Biomedical Engineering, Korea University, Seoul, Korea

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ABSTRACT: Poly(*N*-isopropylacrylamide) (PNIPAAm)/poly(ethylene oxide) (PEO) semi-interpenetrating polymer networks (semi-IPNs) synthesized by radical polymerization of *N*-isopropylacrylamide (NIPAAm) in the presence of PEO. The thermal characterizations of the semi-IPNs were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA). The melting temperature (T_m) of semi-IPNs appeared at around 60°C using DSC. DEA was employed to ascertain the glass transition temperature (T_g) and determine

the activation energy (E_a) of semi-IPNs. From the results of DEA, semi-IPNs exhibited one T_g , indicating the presence of phase separation in the semi-IPN, and T_g s of semi-IPNs were observed with increasing PNIPAAm content. The thermal decomposition of semi-IPNa was investigated using TGA and appeared at around 370°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3922–3927, 2003

Key words: poly(*N*-isopropylacrylamide); poly(ethylene oxide); thermal properties; activation energy

INTRODUCTION

The interpenetrating polymer network (IPN) is an assembly of interpenetrating networks of two crosslinked polymers (having or without having mutual chemical interaction), at least one of which is synthesized and crosslinked in presence of the other.¹ If only one component of the assembly is crosslinked leaving the other in linear form, the system is termed as a semi-IPN.^{2,3} Many semi-IPNs are generally formed from water-soluble polymers by crosslinking them either using radiation or chemicals, or by polymerizing hydrophilic monomers in the presence of a crosslinker. Crosslinked polymers seem to be one of the candidates to improve wet strength. Semi-IPNs have been studied with a particular emphasis being put on their reversible volume changes in response to external stimuli, such as pH, solvent composition, temperature, ionic concentration, and electric field.^{4,5}

Poly(ethylene oxide) (PEO), one of the materials used for semi-IPNs, is one of the most extensively studied water soluble polymers in the last decades, and in general, has been used as a component of

innumerable polymer networks with the purpose of analyzing properties such as miscibility, crystallization processes, and interaction parameters. PEO is applied as a component of biomedical devices such as wound coverings, drug delivery systems, haemodialysis membrane, other electrochemical devices, etc.^{6–10} Poly(*N*-isopropylacrylamide) (PNIPAAm) is famous for exhibiting a lower critical solution temperature (LCST), around 32°C, in aqueous solution; that is, it dissolves in water below the LCST and precipitates from the solution above the LCST. PNIPAAm, with a crosslinked structure, is characterized by a temperature responsive nature in which it swells in water below the LCST and shrinks in water above the LCST.¹¹

Many researchers have reported on IPN types. Okano¹² and Lee et al.¹³ reported innovative pH and temperature responsive copolymers composed of PEO and PNIPAAm. Kweon et al.¹⁴ reported on thermal, thermomechanical, and electrochemical characterization of PEO-based IPN. Imai et al.¹⁵ reported on activation energy for crystallization of PEO-based blend. Yoshida and Kaneko et al.^{16,17} prepared thermosensitive PNIPAAm hydrogels having PNIPAAm chains grafted on the backbone of the PNIPAAm network.

In the present article, semi-IPNs composed of PEO and PNIPAAm were prepared by the simultaneous IPN method. The thermal properties of the semi-IPNs were investigated using differential scanning calorim-

Correspondence to: S. I. Kim (sunkim@hanyang.ac.kr).

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TABLE I
Feed Compositions and Designations of Semi-IPNs

Sample designation ^a	PEO (wt %)	NIPAAm (wt %)
EN5050	50	50
EN3565	35	65
EN2080	20	80

etry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA). In addition, DEA was used also to determine activation energy of semi-IPN.

EXPERIMENTAL

Materials

PEO with molecular weight of 1×10^5 , *N*-isopropylacrylamide (NIPAAm), *N,N'*-methylenebisacrylamide (MBAAm) and ammonium persulfate (APS) were purchased from Aldrich Chemical Co. (Milwaukee, WI). PEO and NIPAAm were recrystallized from benzene/*n*-hexane before being used. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was purchased from Yakuri Chemical Co. (Japan). MBAAm, APS, and TMEDA were used for semi-IPN preparation without further purification, and all other chemical reagents used were extra pure grade.

Preparation of semi-IPNs

The polymerization of the PEO/PNIPAAm semi-IPNs was carried out in deionized water solution at room temperature for 16 h using APS and TMEDA as a pair of redox initiators with the crosslinking agent MBAAm. The contents of the redox initiators (APS and TEMED) were 1 wt % of the monomer, and the contents of crosslinking agent were 3 mol % of the monomer. PEO is added to NIPAAm and the mixture undergoes polymerization, resulting in PNIPAAm, which is a semi-IPN in film form. Three semi-IPNs were prepared from 50 : 50, 35 : 65, and 20 : 80 weight ratios of PEO/NIPAAm, denoted as EN5050, EN3565, and EN2080, respectively. The designation of each sample is listed in Table I. The dry films were removed from the Petri dishes (glass) and were immersed in deionized water at room temperature for at least 48 h and the water was changed approximately every 6 h to wash out PEO and the unreacted materials.

Characterization methods of semi-IPN

DSC was performed with a DSC 2010 instrument (TA Instruments) contained in a refrigerator cooling system (RCS) in a nitrogen atmosphere. The thermal properties of the semi-IPNs were determined using two heating scans. The first, which was conducted to

eliminate residual water and solvent, was carried out at a rate of 20°C/min from room temperature up to 120°C and kept at the latter temperature for 10 min. The second was carried out at a heating rate of 10°C/min from -65 to 350°C. To remove moisture absorbed during weighing, the sample was weighed and returned to the vacuum desiccators for a minimum of 4 h before the DSC experiment. Thermal decomposition was carried out with a thermogravimetric analyzer (TA Instruments SDT 2960 Simultaneous DSC-TGA), by heating the samples from room temperature to 800°C at a heating rate of 10°C/min under a nitrogen flow. Dielectric measurements were conducted to observe the glass transition temperatures (T_g s) and relaxational behavior of semi-IPNs. Measurements of $\tan \delta$ were carried out using DEA (TA Instruments DEA 2970) with a parallel plate ceramic sensor. The experiment was done from -100 to 200°C at a rate of 3°C/min with dry nitrogen adjusted to a flow rate of 50 mL/min. The upper ram was lowered to exert 250 Newton of force on the sample. Applied frequency ranges were 1, 10, 50, 100, 300, 500, 700, and 1000 Hz. The electrode was calibrated before each measurement.

RESULTS AND DISCUSSION

Figure 1 shows the DSC melting thermograms of PEO and semi-IPNs. PEO and semi-IPNs reveal a sharp melting endothermic peak at around 60°C. Very broad and weak melting peaks of PNIPAAm segments within semi-IPNs are observed at around 300°C because of a decrease in the PNIPAAm segment mobility by the crosslinking of PNIPAAm. Therefore, the endothermic peak of PEO decreased rapidly as the content of PNIPAAm increased. The depression of the melting peak indicates that the ordered association of the PEO molecules was decreased by the presence of PNIPAAm.

In the semi-IPNs, it becomes difficult to detect the peaks of T_g clearly in the DSC curve. Figure 2 shows $\tan \delta$ vs temperature obtained from the EN3565 film in the dielectric analysis. In general, the T_g of crosslinked polymer is difficult to detect using the ordinary DSC technique, whereas the dielectric study of such complex systems can reveal details of the phase structure

TABLE II
Glass Transition Temperature (T_g), Activation Energy (E_a), and Melting Enthalpy of Semi-IPNs

	Semi-IPN		
	EN5050	EN3565	EN2080
T_g (°C)	-35.1	-22.2	-14.8
E_a (kJ/mol)	2.29	3.84	5.39
Melting enthalpy (J/g)	128.7	102.8	70.8

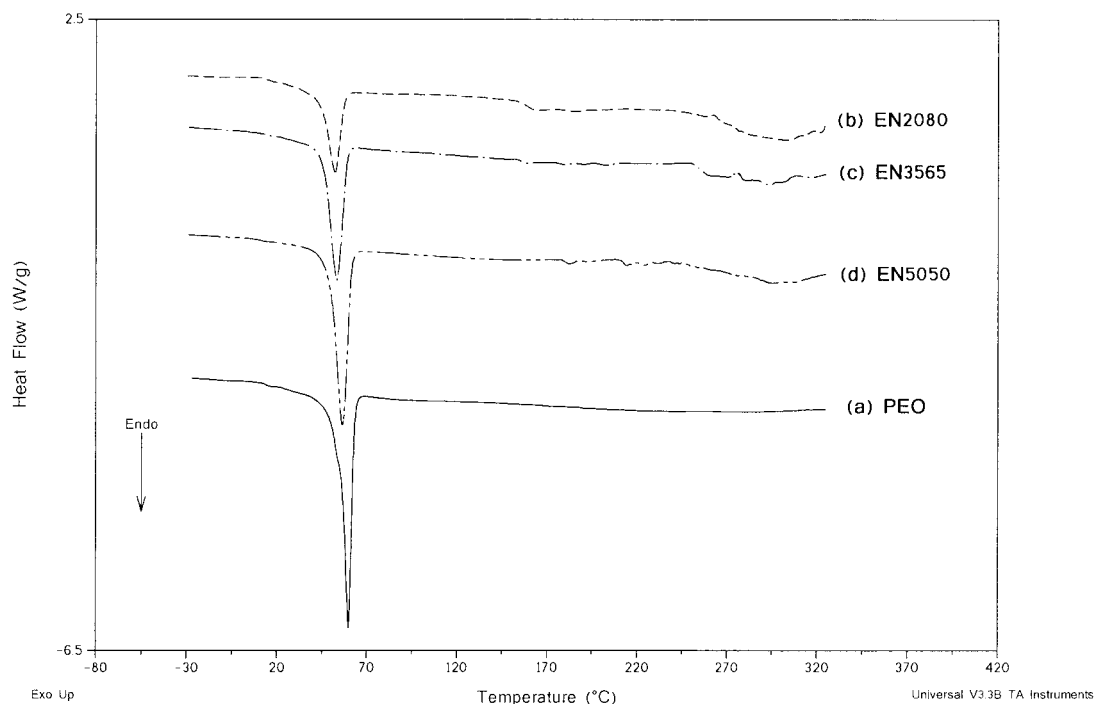


Figure 1 DSC melting endotherms of semi-IPNs at a heating rate of 10°C/min from -65 to 350°C.

and provide information about modes of motion in the semi-IPN. Therefore, DEA was employed to determine the T_g of each component in the semi-IPNs. Figure 2 exhibits the $\log(\tan \delta)$ of the semi-IPNs depending on temperature at 1, 10, 50, 100, 300, 500,

700, and 1000 Hz. Two relaxation peaks appeared at around -40 and 60°C in the semi-IPNs. The peak temperature for $\tan \delta$ can be seen to correspond well with that observed using DSC. In a manner identical to that illustrated in DSC analysis of Figure 1, the T_g

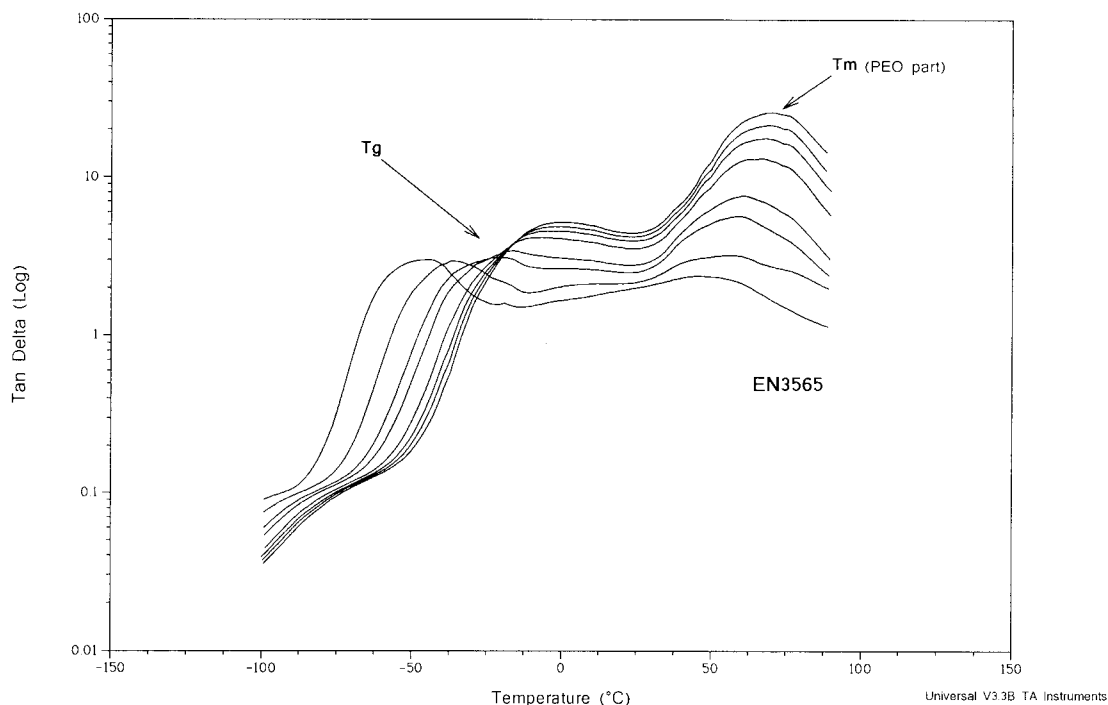


Figure 2 Dielectric analysis of the semi-IPNs ($\log \tan \delta$ data vs semi-IPN temperature).

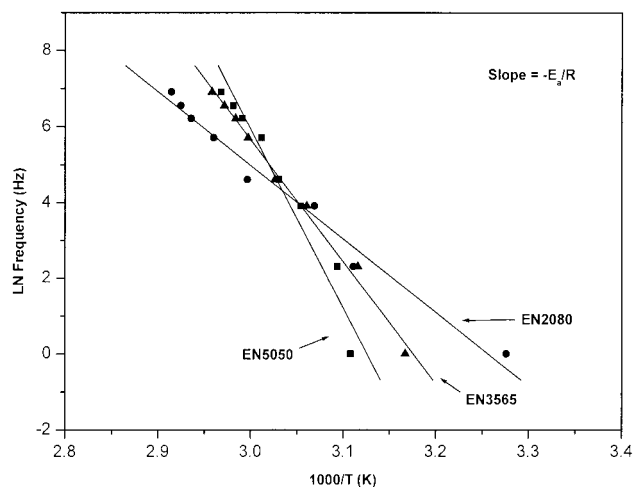


Figure 3 Arrhenius plot of ln frequency vs $1000/T$ for semi-IPNs (EN5050 (■), EN3565 (▲), and EN2080 (●)).

for PEO can be determined from dielectric property measurements. In Figure 2, the maximum temperature in each of the $\tan \delta$ curves between -50 and -5°C was assigned to the T_g of PEO in semi-IPNs. Another maximum temperature in each $\tan \delta$ curve between 50 and 75°C was thought to be the melting temperature (T_m) of PEO in semi-IPN, as was seen from DSC analysis. In fact, the T_g of PEO itself was -65°C from DSC analysis. DEA showed that the T_g in semi-IPNs was higher than that of PEO and nearly increased to about -30°C . The T_g of the PEO becomes higher as the DEA mea-

surement frequency is increased. This is a general consequence attributed to a decrease in the steric effects hindering the micro-Brownian motion of the main chain. The T_g s of each semi-IPN were -35.1°C (EN5050), -22°C (EN3565), and -14.8°C (EN2080). The T_g of PEO in semi-IPNs increased because of an increase of PNIPAAm segments in the semi-IPNs.

In addition, the frequency dependent nature of these transitions lends itself to further analyses. One of these further analysis, DEA, measures the activation energies of molecular relaxations.¹⁸ Because the shift of $\tan \delta$ peaks with frequency is key to the measurement, a series of analysis frequencies were used. The energy of activation can be obtained by performing a linear least squares analysis (Arrhenius plot) on the plot of $\ln(\text{frequency})$ vs $1/T_{\max}$, where T_{\max} is the temperature that corresponds to the $\tan \delta$ peak maximum at various test frequencies. The slope of the resultant plot when multiplied by the gas constant R ($8.314 \text{ J/mol} \cdot \text{K}$) revealed the energy of activation (E_a). Because of the T_m of PEO in semi-IPNs, Arrhenius plots constructed for transition around at 50°C of each semi-IPN (EN2080, EN3565, and EN5050) by plotting $\ln(\text{frequency})$ vs $1000/T_{\max}$ are shown in Figure 3. Activation energies determined from the slope are 2.29 kJ/mol (EN2080), 3.84 kJ/mol (EN3565), and 5.39 kJ/mol (EN5050). The activation energy of semi-IPN decreased as the content of PNIPAAm increased. This may be due to the PNIPAAm in semi-IPN not being fully crosslinked, or possibly be due to the weak in-

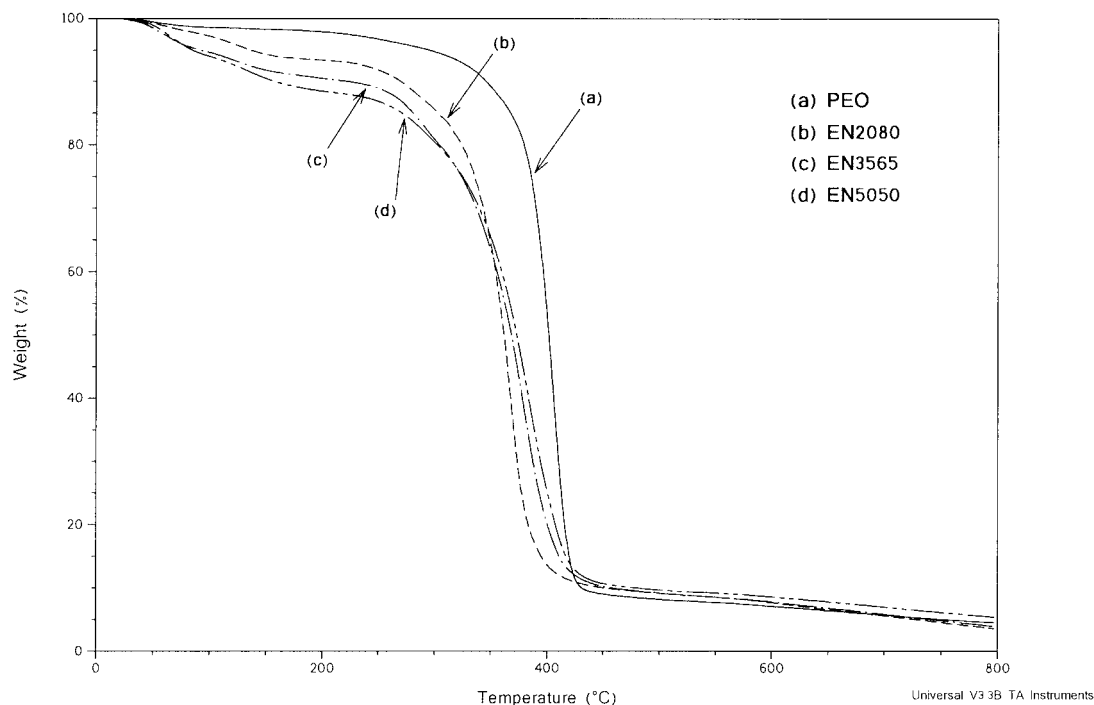


Figure 4 TGA thermograms of semi-IPNs at a heating rate of $10^\circ\text{C}/\text{min}$ from 25 to 800°C .

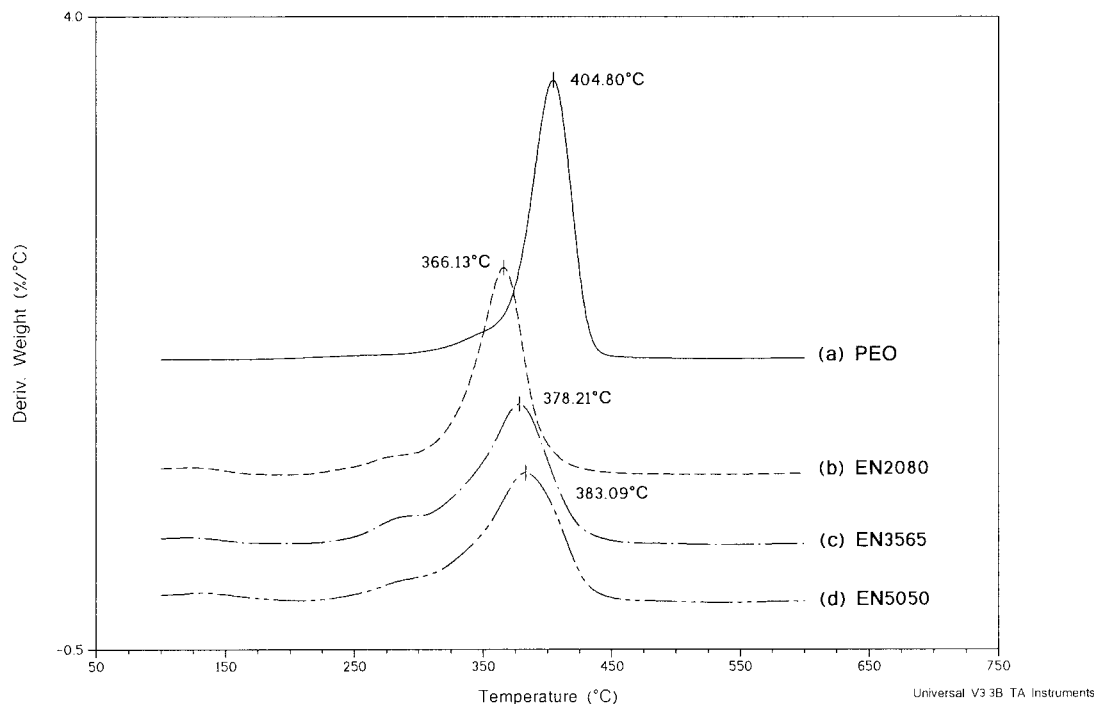


Figure 5 Derivative of the thermogravimetric thermograms of semi-IPNs [$d(W/W_0)/dT$].

teraction of the PNIPAAm molecule and a weaker dissociation energy of PNIPAAm than of PEO. These are summarized in Table II.

The thermal stability and thermal decomposition of PEO and semi-IPNs were investigated using TGA. Figure 4 shows the thermogravimetric curves of semi-IPN and PEO. For PEO, it was observed that no significant degradation occurred before 250°C (weight loss of 2%). The total degradation of PEO was observed in a single stage and was completed by 450°C. For semi-IPN, degradation took place in two stages. The first stage began at 125°C with a weight loss of

7–12% and the second stage, up to 360°C, was completed by 450°C. The first stage could be attributed to the loss of bound water; bound water does not evaporate although semi-IPNs were sufficiently dry before measurement because of the water molecules that are bound to polymer molecules through hydrogen bonds.

Figure 5 shows the derivative of the thermogravimetric thermograms of semi-IPNs. PEO was more thermally stable than semi-IPNs because the peak of PEO appeared at a higher temperature than that of semi-IPNs. As the content of PNIPAAm increased, the semi-IPN peak decreased rapidly because PNIPAAm thermal stability is lower than that of PEO.

Figure 6 shows the isothermal temperature profile and weight loss at 450°C, representative of the semi-IPNs studied. For EN3565, up to 90% weight was lost occurred while it was being heated up to the desired isothermal temperature. There was no weight loss of EN3565 for 2 h at 450°C.

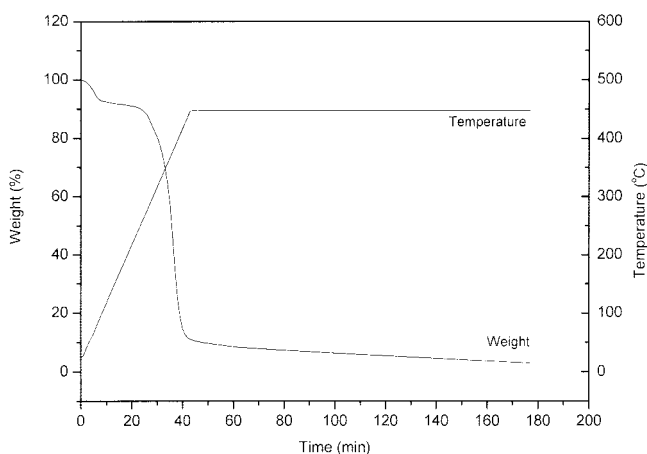


Figure 6 TGA iso-thermograms of semi-IPN (EN3565) at a heating rate of 10°C/min from 25 to 450°C for 120 min, showing the thermal stability.

CONCLUSIONS

The thermal properties of the semi-IPNs were investigated using DSC, DEA, and TGA. From the results of DSC, PEO revealed a relatively large exothermic peak at near 60°C. On the other hand, very weak and very broad melting exothermic peaks of PNIPAAm segments in the semi-IPNs were difficult to detect the peaks. From the results of DEA, two relaxation peaks appeared at around -30 and 60°C in the semi-IPNs,

and the T_g s of PEO in semi-IPNs increased to -35.1°C (EN5050), -22.2°C (EN3565), and -14.8°C (EN2080) as content of PNIPAAm increased. On the other hand, the activation energy of semi-IPNs decreased to 5.39 kJ/mol (EN5050), 3.84 kJ/mol (EN3565), and 2.29 kJ/mol (EN2080) as content of PNIPAAm increased in semi-IPNs. From the results of TGA, the thermal decomposition temperature of semi-IPN decreased rapidly as the content of PNIPAAm increased.

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