Polymer Bulletin 61, 225–233 (2008)
DOI 10.1007/s00289-008-0938-2

Polymer Bulletin

Structure-property relationships of hydroxy-terminated polyether based polyurethane network

Chang Kee Kim[a,b], Soo Bin Bae[a], Jae Ryun Ahn[a,c], In Jae Chung[a] (✉)

[a]Department of Chemical and Biomolecular Eng., KAIST, 373-1, Guseong-dong Yuseong-gu, Daejeon 305-701, Korea
[b]Agency for Defense Development, Yuseong Post Office box 35-1,1st Technology Research Center, Rocket Propulsion Directorate, Yuseong-gu, Daejon, Korea
[c]GS-Caltex corporation 1056, Wollae-dong, Yeosu-si, Jeollanam-do 555-260, Korea

E-mail: Chung@kaist.ac.kr; Fax: 82-42-869-3910

Received: 9 December 2007 / Revised version: 29 January 2008 / Accepted: 20 April 2008

Summary

In the present work, the effect of crosslink density on HTPE networks has been studied in swelling, thermal and mechanical properties. The solubility parameters of HTPE PUs were obtained by swelling test. They depended on the molar ratio of N-100 and IPDI and equivalent ratio. It was decreased as the content of N-100 was lowered. The thermal characteristics of the network polymer were examined by DSC results. Thermal behavior of HTPE PU network depended on by dangling chain and chain folding in the series using N-100, with NCO/OH ratio as 1.0, 0.8, 0.6. However, when we performed experiment with IPDI and N-100, with NCO/OH ratio as 1.0, the thermal properties depended on M_c. Moreover, using IPDI with N-100 showed enhanced volume specific energy than using only N-100 in tensile test due to strain induced crystallization.

Introduction

Polyurethane networks impart three-dimensional stability to a solid composite propellant grain and the rubbery nature of the network allows the grain to withstand thermal cycling and pressurization.[1] Hydroxy-terminated polyether (HTPE) propellants have been developed recently as possible replacements for hydroxyl-terminated polybutadiene (HTPB)/ammonium perchlorate (AP) propellants currently used in a number of tactical missile rocket motors.[2] HTPE propellants are revealed that those have similar physical properties with HTPB propellants such as high tensile strength, low glass transition temperature.[3] Moreover, HTPE propellant is claimed that they give a less severe response in slow cook-off tests for insensitive munition (IM) compliance.[4] In the preparation of a propellant, solid particulate oxidizer, plasticizer, burning catalyst, and other minor additives are incorporated into the network via end linking of those functionally active prepolymers which use molecular reactants that have suitable functional groups and desired functionality.

To obtain PU, especially prepolymer which has OH end group, the most widely used reactants for end linking of prepolymer are di- or polyfunctional isocyanates.[5-7] The amount of polyfunctional isocyanates and ratio of NCO/OH in network dominantly affects crosslinking density and M_c of polymer network.[8-10] The crosslink density influences dimensional and thermal stabilities of polymer network.[11]

In this paper we report a study aimed at understanding the behaviors of HTPE propellants, particularly in swelling, thermal and mechanical properties, for the purposes of which we have prepared and characterized a range of isocyanate-cured binder network samples with different crosslink densities.

Experimental

Materials

Hydroxy-terminated polyether (HTPE), TPEG (OH index: 0.67 eq/kg) was supplied by Alliant Techsystem. It is a liquid state copolymer consisted of ethylene oxide and tetrahydrofurane(1:1). Isophorone diisocyanate (IPDI, NCO index: 8.09 eq/kg) and Desmodure N-100 (N-100, NCO index: 5.09 eq/kg) based on hexamethylene diisocyanate (HDI) were obtained from Degusa and Bayer, respectively. Triphenyl bismuth (TPB, 99%) and dinitrosalicilic acid (DNSA, 99%) were purchased from Sharpe and Aldrich. All materials were used without further purification.

Table 1. Formulation parameters and crosslink densities of HTPE PU networks

Designation	NCO/OH	N-100/IPDI (molar ratio)	$X_{th} \times 10^4$ (mol/g)	Density (g/cm^3)
N-10	1.00	10/0	2.440	1.047
N-08	0.80	"	1.999	1.045
N-06	0.60	"	1.536	1.043
NI-73	1.00	7/3	1.831	-
NI-55	"	5/5	1.374	1.045
NI-28	"	2/8	0.595	1.042
NI-19	"	1/9	0.306	1.040

Preparation of HTPE polyurethane networks

The ratio of NCO/OH and N-100/IPDI is important design parameter for obtaining the chemical crosslink in HTPE networks. HTPE network compositions and designation are listed in Table 1. The theoretical crosslink density (X_{th}) was calculated by equation (1),

$$X_{th} = \frac{2}{3M_c} = \sum_{i=1}^{n} \frac{(f_i - 2)m_i}{W_T} \qquad \textbf{(1)}$$

where M_c is average molecular weight between crosslinks, f_i is the functionality of i-th component in the network, m_i is the mole of i_{th} component, and W_T is the network weight. The factor is 2/3 because three chains are shared by two tri-functional branch points.[12] Polyurethane networks were prepared by one shot method. HTPE, N-100, IPDI, TPB(catalyst, 0.131wt %) and DNSA(catalyst activator, 0.066wt %) were mixed with mechanical stirrer at room temperature and degassed in vacuum for 15 min. The mixture was casted into the Teflon molder and cured at 60°C for 8 days.

Determination of equilibrium swelling

Swelling measurements were performed in various solvents, listed in Table 2. About 0.4 g of weighted samples was immersed in solvents until equilibrium was attained. The swollen gels were removed from the solvents, quickly blotted with a dry filter paper and weighed. The equilibrium swelling ratio of networks was determined gravimetrically, assuming the additivity of volume through the following equation (2):

$$Q = 1 + \left(\frac{w_2}{w_1} - 1 \right) \cdot \frac{\rho_2}{\rho_1} \qquad \mathbf{(2)}$$

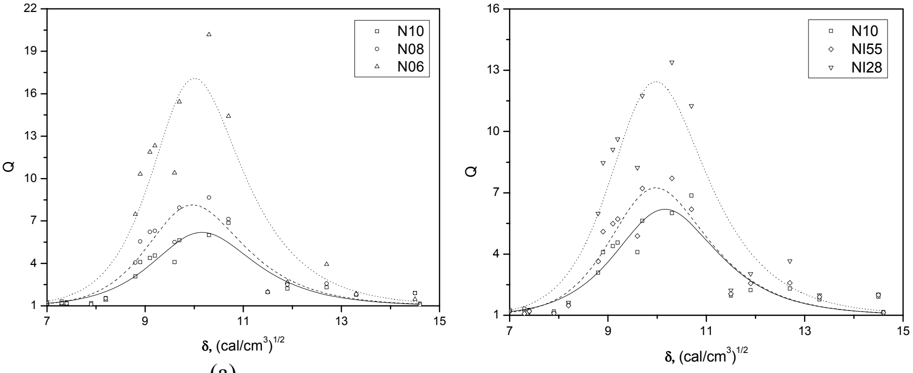
where Q is the swelling ratio of networks by volume, w_1 is weight of the network before swelling, w_2 is the weight of the network at equilibrium swelling, and ρ_1 and ρ_2 are the densities of the solvent and network, respectively.[13]

Table 2. The solubility parameters and densities of the solvents (25°C) used in this study

No	Solvent	ρ (g/cm^3)	δ_1 (cal/cm^3)$^{0.5}$	No	Solvent	ρ (g/cm^3)	δ_1 (cal/cm^3)$^{0.5}$
1	n-pentane	0.626	7.0	11	methylene chloride	1.325	9.7
2	n-hexane	0.659	7.3	12	aniline	1.021	10.3
3	n-heptane	0.684	7.4	13	pyridine	0.978	10.7
4	dodecane	0.750	7.9	14	propyl alcohol	0.804	11.5
5	cyclohexane	0.778	8.2	15	acetonitrile	0.786	11.9
6	diethyl carbonate	0.975	8.8	16	dimethyl sulfoxide	0.790	12.0
7	toluene	0.867	8.9	17	ethanol	1.189	12.7
8	tetrahydrofuran	0.889	9.1	18	propylene-1,2-carbonate	1.101	13.3
9	benzene	0.874	9.2	19	ethylene glycol	1.113	14.6
10	1,1,2-trichloroethane	1.441	9.6				

Differential scanning calorimetry

The thermal properties of samples were examined by using differential scanning calorimeter unit of TA instrument of DSC 940S (V4.1). Differential scanning



(a)

(b)

Figure 1. Graphical representation of the relation between the swelling ratio of (a) HTPE/N-100 and (b) HTPE/N-100/IPDI networks and the solubility parameter of solvents.

calorimetry (DSC) thermograms were recorded in nitrogen atmosphere between −120°C and 50°C. The samples was annealed at 60°C for 5 min and cooled at a rate of 30°C/min using liquid nitrogen to −120°C and then heated at a rate of 5°C/min up to 50°C. The weights of samples used were in the range of 5-10 mg. Glass transition, crystallization and melting peak temperature of selected samples as well as the heat of fusion was recorded on the DSC thermogram.

Tensile tests

Tensile tests (ASTM D638M) of the samples were carried out at 20°C. Stress-strain properties of all samples were tested on Instron computer-controlled tensile tester. The gauge length was fixed to 30.0 mm and the crosshead speed was 50.0 mm/min.

Density measurement

The densities of networks were determined at 25°C through the following equation (3), where d is the density of sample, d_s is the density of silicon oil, w_1 is the weight of sample in air, w_2 is the weight of sample in silicon oil. The data presented are the average of four measurements.

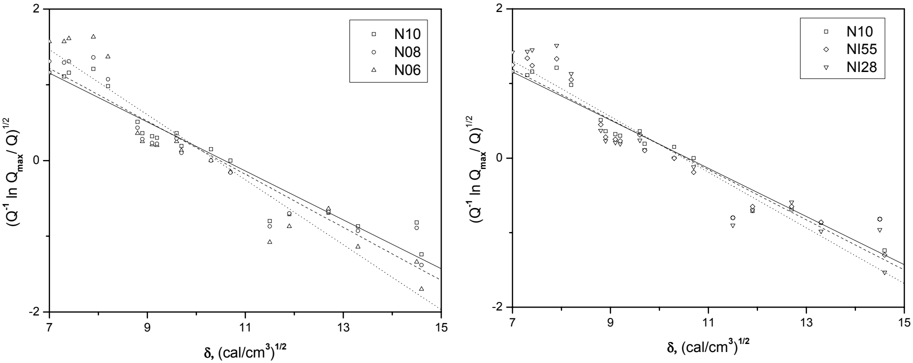
$$d = d_s \times \frac{w_1}{w_1 - w_2} \tag{3}$$

The data was used in equation (2) to calculate swelling ratio and in equation (6) to obtain average molecular weight between crosslink.

Results and discussion

Swelling characteristics

Table 1 describes X_{th} of HTPE network used in the swelling test. When the sample that had lower ratio than NCO/OH 0.5 was cured and then swelled in the good solvent, it perfectly became the sol state. Because the theoretical functionality of



(a) (b)

Figure 2. Linear plot of $[Q^{-1}\ln(Q_{max}/Q)]^{0.5}$ vs. δ of the solvent for (a) HTPE/N-100 and (b) HTPE/N-100 /IPDI networks.

N-100(HDI biuret) adducted with 3mole of HDI and 1mole of H_2O was 3, NCO/OH must be theoretically larger than 0.667 to form the crosslink structure. However, because the cured sample of which NCO/OH is 0.6 forms a gel structure, it can be known that the functionality of N-100 was more than 3. When the cured sample was swelled in the good solvent up to 1/9 of N-100/IPDI in NI series, the gel state was kept well.

According to Gee's theory[14,15], the solubility of a polymer in any solvent strongly depends on the square of the difference between their solubility parameters values, i.e. $(\delta_1-\delta_2)^2$; here δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively. This $(\delta_1-\delta_2)^2$ should be as small as possible for good solubility of a polymer in any solvent. This can be represented for any network through the following equation:

$$[Q^{-1}\ln(Q_{\max}/Q)]^{0.5} = \left|\alpha^{0.5}(\delta_1-\delta_2)\right| \qquad \textbf{(4)}$$

Where Q_{max} is maximum swelling ratio and α is a constant. According to equation (4), a plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus the solubility parameters of a series of solvents will give $\alpha^{1/2}$ and δ_2 values from the slope and intersection of the horizontal axis of the obtained line, respectively. Equation (4) was used for the determination of the solubility parameters of various networks.[16-19] In order to apply this method, the equilibrium swelling values of HTPE networks in various solvents were determined (Figure 1). N10 and the other gels exhibited the largest equilibrium swelling ratio in pyridine (10.7$(cal/cm^3)^{0.5}$) and aniline (10.3$(cal/cm^3)^{0.5}$), respectively. From the plot of the quantities on the left-hand side of equation (4) against δ_1 by using the least squares regression method (Figure 2), the solubility parameters and related constants of HTPE PU gels were listed in Table 3. The solubility parameters and densities of the solvents used in swelling experiments on HTPE PU gels were obtained from Polymer Handbook.[20]

Table 3. The solubility parameters and constants of the HTPE PU networks, calculated by eq. (4)

Designation	$\alpha^{1/2}$	$\alpha^{1/2}\cdot\delta_2$	δ_2 $(cal/cm^3)^{1/2}$	R
N10	0.32300	3.41532	10.57	0.96318
N08	0.35017	3.66966	10.48	0.95395
N06	0.42931	4.46924	10.41	0.95185
NI55	0.33624	3.54313	10.54	0.95265
NI28	0.37285	3.91167	10.49	0.94699

Figure 3 described the solubility parameter of network shown in Table 3 by the content of N-100. When the content of N-100 was 0%, the solubility parameter of HTPE or HTPE/IPDI linear polymer was calculated by using an extrapolation. It was 10.13 and 10.47 $(cal/cm^3)^{0.5}$, respectively. It can be known that the urethane linkage was formed by reaction between IPDI and HTPE and so the polarity and the solubility parameter had larger values than those for HTPE.

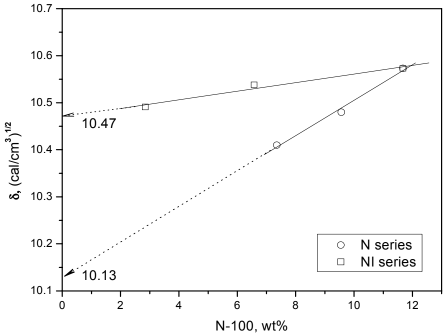


Figure 3. The relationship between the amount of N-100 and solubility parameters of HTPE polyurethane networks.

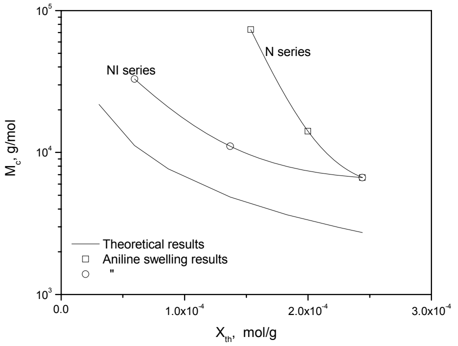


Figure 4. The relationship between X_{th} and M_c resulted from swelling test.

Figure 4 shows the average molecular weight between crosslink (M_c) of the sample obtained from swell test with aniline by using the Flory-Rehner Equation (6).[21] The polymer-solvent interaction parameters were calculated from Equation (5) by using the solubility parameters of the network described in Table 3 and the solubility parameters of solvent used in the swell test. 0.34 was used for the entropy term χ_s.[22]

$$\chi_{12} = \chi_s + \frac{V_1(\delta_1 - \delta_2)^2}{RT} \qquad \textbf{(5)}$$

All of the N and NI series had all higher values of M_c than the theoretical value. It is because the urethane reaction yield is not 100%. Both of those series also show the tendency that as X_{th} is lowered, M_c value became greater. In N series, N10 reacted with equivalent ratio has the lower value of M_c than N08 and N06 because the dangling chain is more formed as NCO/OH is lowered. In NI series, though the dangling chain effect does not exist because those materials are all reacted with equivalent ratio of NCO/OH of 1.0, M_c is lengthened as the content of IPDI increases. This is attributed to the fact that IPDI has only two functional groups but N-100 has more than three, and IPDI aids to extend the inter-cross-linking distance (D_{ic}) of HTPE, whereas N-100 makes D_{ic} to be shorter. In particular, the M_c values of NI corresponds to theoretical value in that tendency represented in Figure 4 is very similar.

$$M_c = \frac{-\rho V_1 (v_2^{1/3} v_0^{2/3} - 2v_2 / f)}{\ln(1 - v_2) + v_2 + \chi_{12} v_2^2} \qquad \textbf{(6)}$$

ρ = density (g/cm³)
V_1 = molar volume of the swelling solvent (cm³/mol)
f = functionality of cross-linker
χ_{12} = Flory-Huggins polymer-solvent interaction parameter
v_2 = volume fraction of network polymer in the swollen gel
v_o = volume fraction of network polymer in the unswollen network

Thermal properties

Figure 5 displays the data on the crosslink density change with the temperature for N and NI series.

In N series, as the crosslink density was raised, the glass transition temperature (T_g) was escalated. It is attributed to the reduction of chain mobility. The crystallization temperature, T_c, was also elevated as M_c was lowered because the energy required for the chain folding increased owing to the increase of crosslink density. However, strangely to say, melting temperature(T_m)(Figure5) and heat of fusion (ΔH_f) (Figure 6) were fallen as M_c decreases. It may be interpreted that the dangling chain is easy to form crystallites. As M_c increases, the larger crystallites may be formed and it requires more energy for melting.

In NI series, as the crosslink density increased, T_g was not almost changed. Although mobility was activated by increase of M_c, as the amount of IPDI increased, the urethane linkage was more formed and the polar interaction of polymer chains become stronger and it is confirmed from Figure 3. This phenomenon might brought offset effect in T_g.

Comparing with N series, NI series has relatively higher T_c. NI series is more difficult to form crystallites because dangling chain does not exist and chain folding less occurs. Moreover, NI series has more urethane linkage which has high polarity. Because this interaction, the movement is hindered and forming crystal become more difficult. The NI series shows the opposite tendency comparing with N series in T_c. With increase of crosslinking density, the growth of crystallites is depressed[23] and the energy is less required to form smaller crystal. Hence, smaller crystal can be able to form at lower T. N10, involved both in N and NI series, has lowest T_c because the size of crystallite is smallest. In NI series, T_m and ΔH_f of network chain are diminished as M_c is decreased. Accordingly, the chain mobility increases, and there would be more crystallites formed by folding of free chains. T_m and ΔH_f is relatively low, compared with N series because low formation of dangling chain.

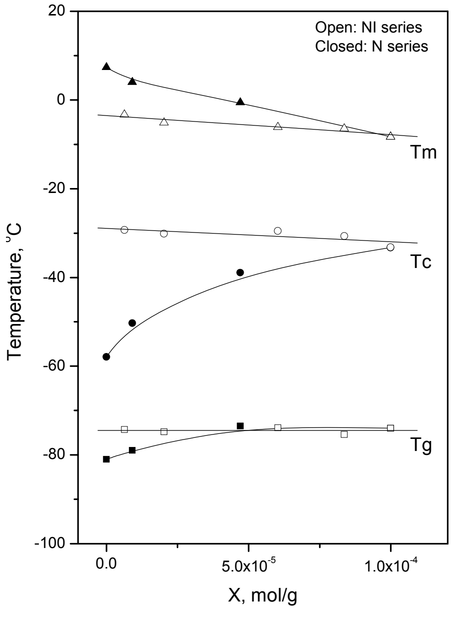


Figure 5. DSC test results as a function of crosslink density resulted from swelling tests.

Tensile properties

Figure 7 described the stress-strain curve of network by NCO/OH and the molar ratio of N-100 and IPDI. Each series show the tendency that as the crosslinking density increases, strain commonly decreases in inversely with modulus. It is attributed that this accompanies decrease in average inter-cross-linking distance (D_{ic}). The cross-linked chains are ruptured successively by extension and it occurs well at shorter D_{ic} (lower M_c) because the localization of the stress occurs more easily.

In N series, the stress-strain curve is decided by NCO/OH ratio because it affects the amount of dangling chain. In N06 which has lowest cross-link-density, the dangling chain sleeps well as strain increase, and the energy is absorbed. Accordingly, N06 has lower E and higher elongation at break, relatively. However, N10 has very high crosslinking density and little dangling chain, the chains is not so well moved by elongation and so it has higher modulus and low elongation break. N08 shows intermediate property between N06 and N10.

NI series, as the amount of IPDI increases, M_c increases and modulus decreases at first, but modulus is abruptly elevated as strain is increased. This phenomenon is very dominant in NI 19 and N28 than N55. It can be interpreted that the longer M_c is well arranged and forms enhanced molecular orientation by inducing strain. Comparing with N series, NI series has enhanced storing ability of volume specific energy because the orientation of Mc needs to absorb energy. Hence, it should be noted that crosslinking by combination of N100 and IPDI may enhance the property of HTPE propellant.

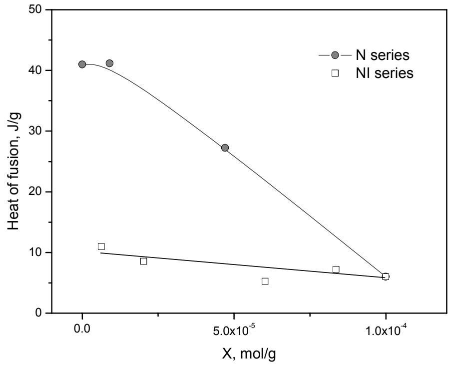


Figure 6. Heat of fusion as a function of crosslink density resulted from swelling tests.

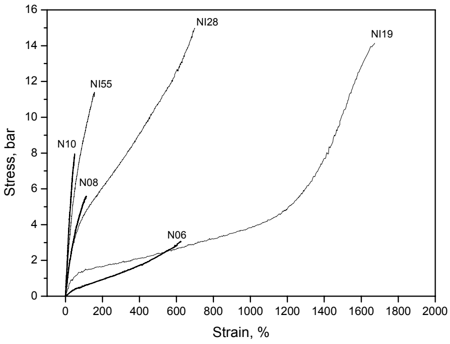


Figure 7. Stress-strain curves of HTPE polyurethane networks.

Conclusions

Through swelling test, the solubility parameters of HTPE PU network polymers were obtained. Those were depended on the molar ratio of N-100 and IPDI, and equivalent ratio. Solubility parameters were decreased as the content of N-100 was lowered. Moreover, the solubility parameter of HTPE and HTPE/IPDI PU calculated by extrapolation. Through examining solubility parameters, M_c of the samples was obtained. NI series showed similar trend of M_c vs. crosslinking density with theoretical value.

Thermal behavior of N series may be depended on by dangling chain and chain folding in the N series. However, in NI series, the thermal properties may be depended on M_c. NI series showed conspicuously larger volume specific energy than N series in tensile test due to strain-induced crystallization.

References

1. Davenas, A. Solid Rocket Propulsion Technology; Pergamon: Elmsford, Korea, 1993.
2. Giants, T. W. Case Bonded linear Systems for Solid Rocket Motors 1991, Ad-A242 297, The Aerospace Co., El Segundo, CA.
3. Caro, R. I. Bellerby JM, Kronfli E International Annual Conference of ICT 2006, 37, 138.
4. NIMIC NEWSLETTER, "Solid Rocket Propellant for Improved IM Response-Part 2 IM Propellant Examples," 1st Quarter 2003, pp. 2.
5. Burel, F.; Feldman A, Bunel C. Polymer 2005, 46, 15.
6. Kothandaraman, H.; Venkatarao, K.; Tha-noo, B.C. Polymer Journal 1989, 21, 829.
7. Buckley, C.P.; Prisacariu C, Caraculacu A. Polymer 2007, 48, 1388.
8. Otts, D.B.; Urban, M.W. Polymer 2005, 46, 8699.
9. Eroglu, Mehmet S. J Appl Polym Sci 1998, 70, 1129.
10. Ero&Gvreve:lu, Mehmet S. J Appl Polym Sci 1998, 70, 1129.
11. Choi, S.S. J Appl Polym Sci 2000, 75, 1378.
12. Oberth, A.E. AIAA Journal 1978, 16, 919.
13. Rabek J.F. Experimetal Methods in Polymer Chemistry, John Wiley & Son, 1980, pp. 55.
14. Gee G. Trans Faraday Sco 1942, 38, 418.
15. Gee G. Trans Inst Rubber Ind 1943, 18, 266.
16. Yagi, Y.; Inomata, H.; Saito, S. Macromolecules 1992, 25, 2997.
17. Hamurucu, E.E.; Baysal, B.M. J Polym Sci: Polym Phys Part B 1994, 32, 591.
18. Eroglu, M.S.; Baysal B.M.; Guven, O. Polymer 1997, 38, 1945.
19. Sen, M.; Guven, O. J. Polym Sci Part B: Polym Phys 1998, 36, 213.
20. Bandrup J and Immergut EH, Polymer Handbook, 3rd ed, Wiley, New York, 1989.
21. Flory, P.J.; Rhener, J.Jr. J Chem Physics 1943, 11, 521.
22. Barton AFM, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, 1985, pp. 245.
23. Gohil RM, Phillips PJ. Polymer 1986, 27, 1696.