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RESEARCH ARTICLE

Synthesis and study of some properties of IPN$_s$ based on (Polyurethane- Epoxy Resin)

Hind M. Saleh*, Ali K. AlLami* ,Widad S.Hanoosh and Salah.S.Hashim****
*University of Missan, College of Science, Chemistry Department
**University of Basrah, College of Science, Chemistry Department

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***Corresponding Author**

Ali K. AlLami

Abstract

A series of interpenetrating polymer network (IPNs) based on polyurethane (PU) and epoxy resin (ER) of bisphenol-A were synthesis. The structural characteristic of these IPNs were doun by FTIR, bulk density, hardness, impact strength and chemical resistance to word alkali and acid medium were studies, the result showed that the modified (PU) have best results than unmodified PU. Also the thermal behavior of these IPNs, were evaluated by TGA & DSC, The results show that the modified PU thermally stable more than unmodified PU

INTRODUCTION

Interpenetrating polymers network (IPNs) are a novel type of polymer alloy consisting of two or more crosslinked polymers. They are more or less intimate mixture of two or more distinct crosslinked polymer. Owing to the mechanical properties of polymer, materials with IPNs are superior to those of ordinary polymer [1-3]. In particular the maximum tensile strength of IPNs is much higher than that of the constituent polymers, therefore many valuable system have been made by taking advantage of the IPNs structure. Our previous works [4-7], have attempted to enhance the mechanical properties by synthesis a series of IPNs. Polyurethanes are thermoplastic elastomers [8,9] with good mechanical properties attested in the first instance by abrasion resistance, toughness and tensile strength. PU present two kinds of domins soft segment (SS) and hard segment (HS) it is well established that the SS domins are constituted by the aliphatic polyester or polyether, while the dissocyanate chains linked with chain extenders are the origins of the HS domins. The SS domins are responsible for the elastomeric performance of polyurethane, whereas the HS domins impart good strength. However, the weak points of PU are high temperature performance and chemical resistance that does not fulfill the domands of applications.

On the other hand ER has long been known as thermosetting polymers that exhibit excellent mechanical and thermal properties along with high resistance to chemical and corrosive media [10, 11]. These outstanding properties are the result of the three-dimensional network pattern of the cured ER. Unfortunately, the high level of the crosslinking confers brittleness to the material. So taking into account all the above facts it is obvious that the adequate joining of PU and ER in a common material would balance the thermo-mechanical properties to a point where the optimum material is reached, this paper will be focused on investigation of PU-ER with increasing content in epoxy.

2. Experimental:

2.1 Materials

ER is a commercial product obtained from bisphenol- A and epichlorohydrine. It was supplied by policolor SA, Bucharest, Romania, under trade name Ropoxide 501 (Scheme 1). The resin has an epoxy equivalent 0.525 equ/100g and a number- average molecular weight (Mn) equal to 380. The resin was cured with triethylene tetraamine (TETA) with mass ratio (1hardener: 3 epoxy resin). PU also is commercial product obtained from caster oil (hydroxyl value160-102mg/KOH) was used without purification and 4,4-diphenyl-methane diisocyanate (MDI) as hardener for PU, ethylene glycol (EG) was used as chain extender. The molar ratio of the component: caster oil: MDI: EG (1:3:3). The reaction was carried out at 80 ^{o}C for 4h in the presence of tinoctaote as catalyst and silicone oil as foam stabilizer

2.2- Characterization Methods

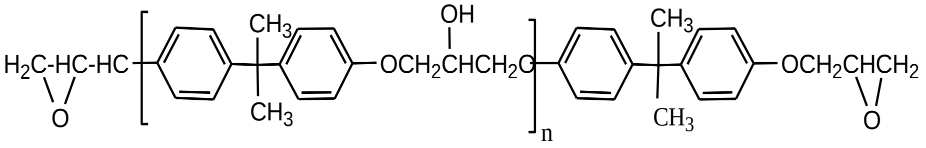
2.2.a- FTIR

FT-IR spectra of the synthesized IPNs in KBr pellets were recorded on a Shimadzu 8400s Fourier transform infrared (FT-IR) spectrometer, where in case of a liquid; a thin film was cast over the NaCl block.

2.2.b- Mechanical tested

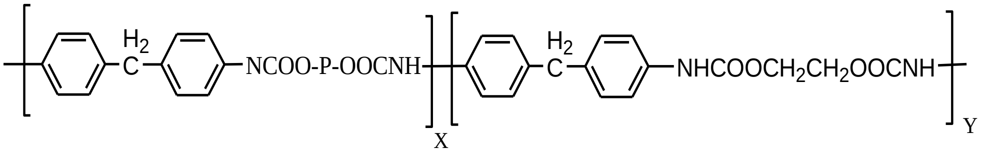
Hardness measurements were made on shore A hardness test apparats using ASTM-2240 methods while impact test measurement using ASTM – D256 method, and Izod impact tester- 6530 Ceast-company with TMI notching cutter model 43-15-1.

[ER]



[TETA] $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

[PU]



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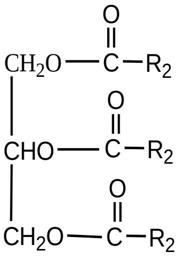

Scheme1. Structures of ER, TETA and PU

2.2.c- Resistance chemical reagents

A cid, alkali and solvent resistance were estimated according to ASTM-D-543-67 method. Sample were hung in the reagent for seven days and tested for change in weight.

2.2.d- Thermogravimetric analysis

The thermal characteristics of the prepared IPNs were evaluated by thermogravimetric analysis (TGA) using a TA-50Q and DSC technique. Measurements were carried out under a nitrogen atmosphere, from 25 to 700 °C, at 50 °C/min, while for DSC from ambient temperature to 300 C^{0} at heating rate 20C^{0} /min.

2.3- Synthesis of (PU- ER) IPNs

IPNs were prepared by mixing the PU and ER in different mass ratio (table 1) in the presence of TETA as cross linking agent of epoxy resin and MDI as hardener for PU. The mixture was stirred at room temperature for 5 min to form a homogeneous mixture, and then the mixture was poured into a glass mold kept in preheated oven maintained at 60 °C. It was kept at this temperature for 24h and at 120 °C for 4h to facilitate the complete network formation. The samples thus formed was cooled slowly and removed from the mold.The IPNs were machine cut into the respective shapes for testing and edges were uniformly to remove imperfections which could lead to errors in the test result.

Table 1. Data on feed composition of individual IPNs

Sample code	Content of PU wt %	Content of Epoxy wt %
PU alone	100	0
PU-10	90	10
PU-20	80	20
PU-30	70	30
PU-40	60	40

Results and Discussion

FT-IR spectrum of PU showed characteristic absorption band at 1712 cm^{-1} and 3356 cm^{-1} corresponding to urethane amid (NH-stretching), also band at 2277 cm^{-1} due to the unreacted NCO group. On the other hand, the FT-IR spectrum of ER showed characteristic band at 3439 cm^{-1} due to hydroxyl groups and absorption band at 913 cm-1 due to epoxy group(12,13), while the spectra of the prepared IPNs showed broad band at 3398 cm-1 characterized to hydroxyl group stretching of urethane linkage with finite contribution from extensive hydrogen bond in the system, further IPNs not show any band at 2277 cm-1 corresponding to NCO group because the reaction of NCO group with hydroxyl group and also epoxy group of the epoxy resin, showed disappear of the band at 906 cm-1 due to the curing reaction of ER with hardener (epoxy group) .Figure (1-3) showed the FTIR spectra

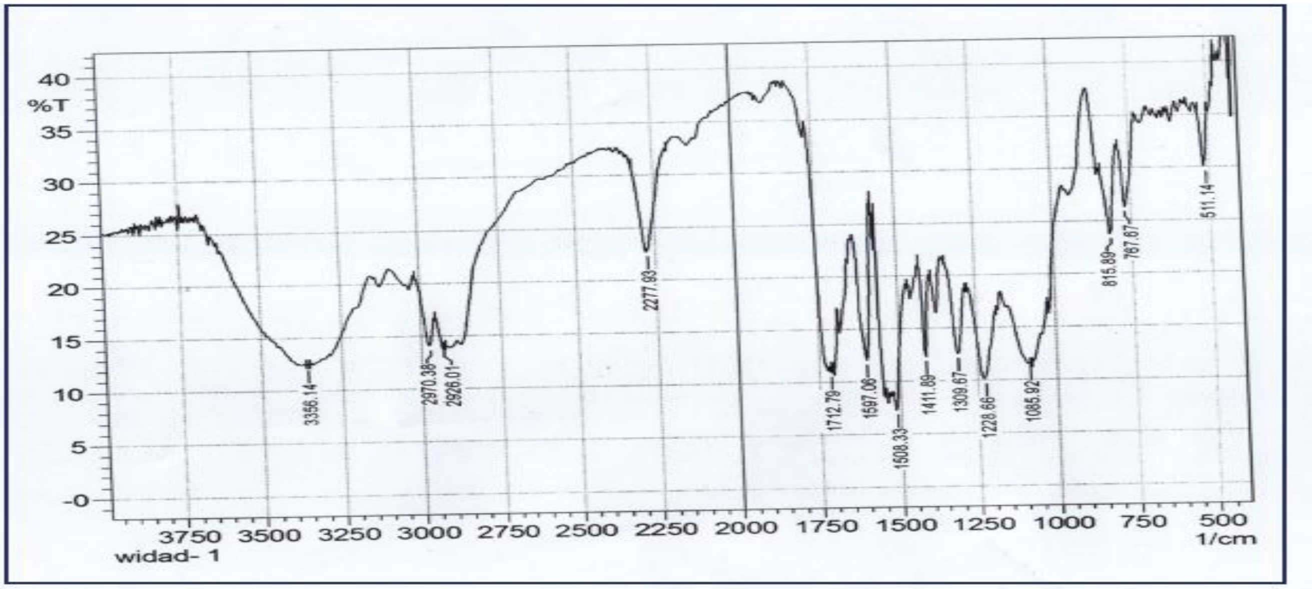

Figure .1- FTIR spectrum of pure poly urethane

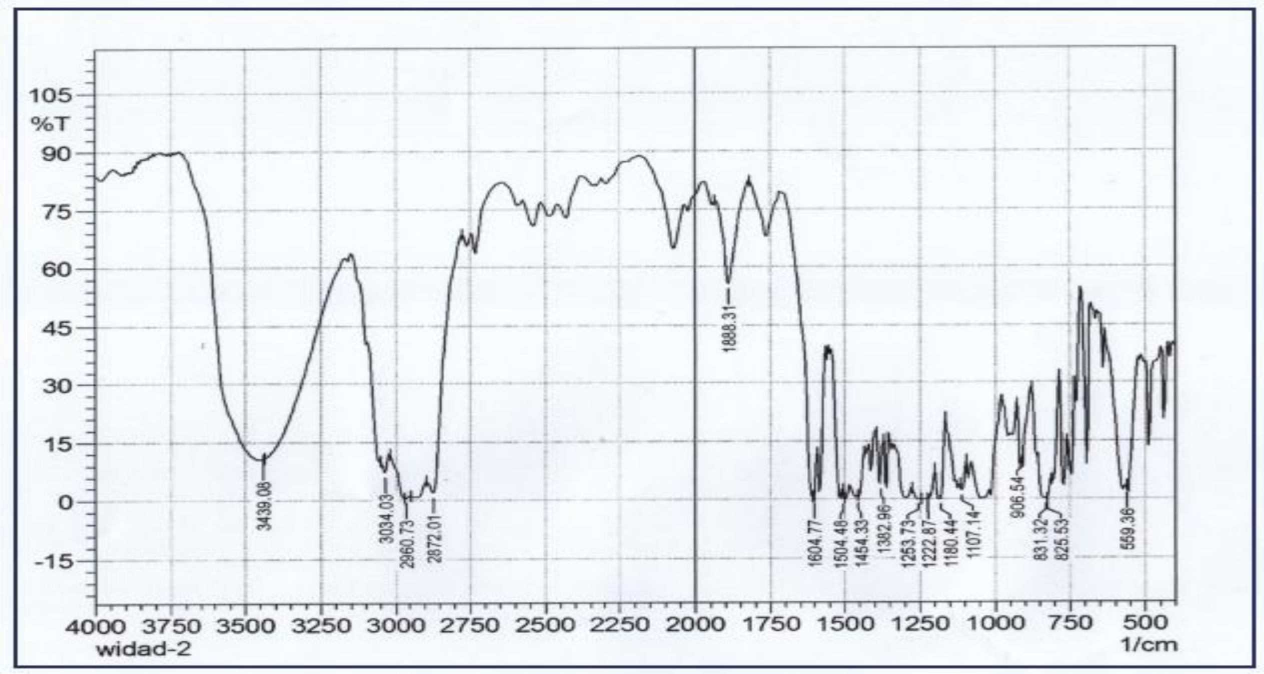

Figure.2- FTIR spectrum of uncured epoxy resin

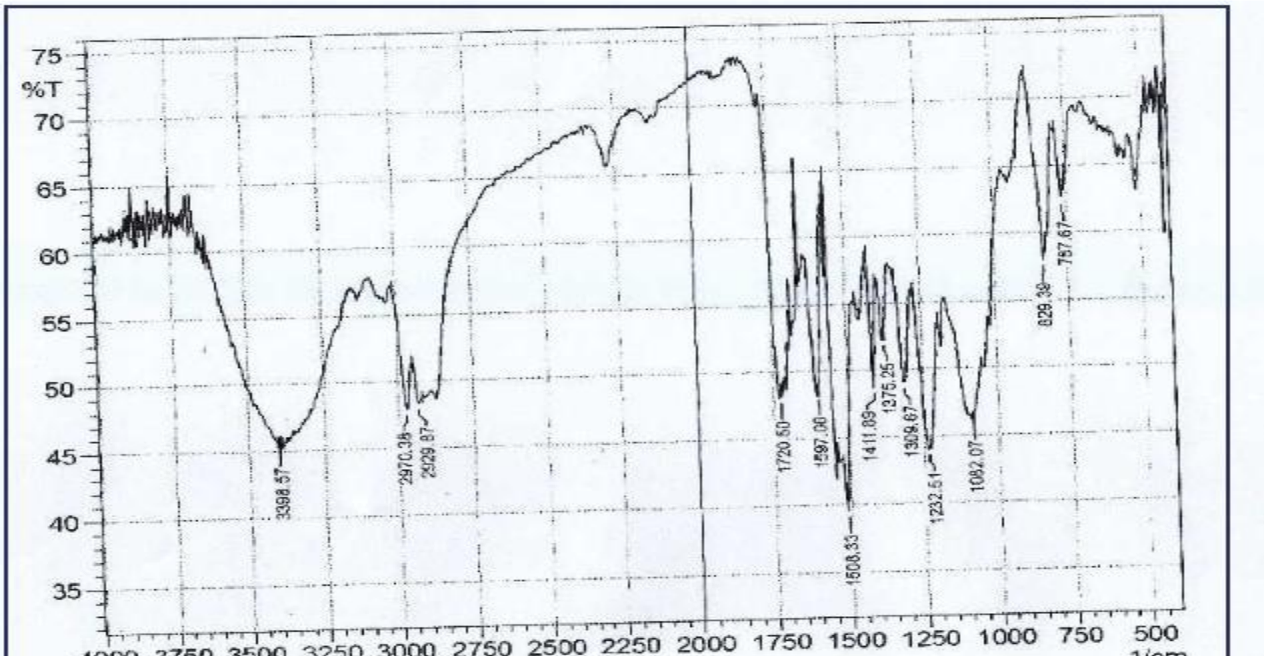

Figure 3- FTIR spectrum of PU/Epoxy resin IPNs

3.2- Chemical resistance

The percentage weight loss of IPNs were determined in H_2SO_4, CH3COOH, HCl, HNO3, NaCl, and NaOH compared to unmodified PU. It is observed that IPNs are stable in acid and alkali, whereas in methylethyl ketone, carbon tetrachloride, and toluene showed varying amount of swelling.

Table 2. Chemical resistance test (% weight loss on treatment with different chemical reagent)

Chemical reagents	PU	IPN-10	IPN-20	IPN-30	IPN-40
25% CH_3COOH	2.0213	1.9316	1.9032	1.8732	1.8166
25% H_2SO_4	4.1231	3.7327	3.5167	3.1572	3.0132
25% HCl	4.3216	4.1723	3.8615	3.7721	3.3162
5% HNO_3	1.7134	1.6213	1.5992	1.5821	1.5432
10% NaOH	0.9325	0.8933	0.8613	0.8505	0.8211
MEK	16.4812	15.2170	15.0132	14.7301	14.2103
CCl4	20.2214	18.7213	18.3210	18.1331	17.8700
Toluene	10.3175	10.1130	9.8732	9.5702	9.1022

Note: IPNs are swelled in solvent MEK, CCl_4, and toluene

3.3- Bulk density measurement

The bulk density of pure PU and modified PU were determined according to (ASTM, D1895B), the results show in table 3 from these results , the value of density increase with increasing content of ER in the prepared IPNs . This increase seems to indicate increased molecular mixing in full IPNs .

Table 3. Effect of epoxy content on the value of density for PU

Sample code	Density gm/ cm^3
PU alone	0.369
PU-10	0.396
PU-20	0.477
PU-30	0.532
PU-40	0.667

3.4- Impact strength and Hardeness test.

The result show that the impact strength was increase with increasing percentage of epoxy resin, This indicate increase the polymer interaction as to PU alone and also the IPNs become more stiffer with increasing epoxy resin. Also in the case of hardness, the value was increase with increasing percentage of epoxy content which due to more efficient interfacial interaction between PU and epoxy resin in the network structure. Table (4) show the result of this study.

Table 4. Shore A hardness and impact strength of the prepared IPNs

Sample code	Hardness Shore A	Impact Strength kj/m^2
PU alone	78	4.621
PU-10	83	4.831
PU-20	85	5.022
PU-30	89	5.361
PU-40	96	5.923

3.5- Thermal analysis

Figures (4-7) shows TGA and DTG curves of the prepared IPNs, from the data result obtained from these figures the decomposition temperature (DT) of these series of IPNs were above 350 C^0 , and the (DT) was increase with increasing percentage of epoxy resin (I.e PU alon had DT at 386 C^0 ,while in the case of 40% epoxy resin in the IPNs the DT was 443 C^0) . Also the char residue was increase and the rate of decomposition was decrease with increasing epoxy resin content, finally the activation energy of decomposition was increase with increasing epoxy resin and this improved result was due to more aromatic fussed structure obtained through introduce epoxy resin in the network structure.

In the case of DSC study figures (8-12) , show the thermogrames of the prepared IPNs and the results shown that these figures had an exothermic peaks in the temperature range (189-204 C^0) , this peaks due to thermal curing of these IPNs , but the temperature of curing was shift from 204C^0 for PU only to 189 C^0 for 40% epoxy resin-PU ,this means that the epoxy resin was improved the reactivity of the IPNs. Also the result indicate the energy of curing will be decrease as the epoxy resin content increase. Tables (5,6) shown the thermal parameter of TGA and DSC of these IPNs .

Table 5 . Thermal stability parameter for the prepared IPNs obtained from TGA curves

Sample name	Decomposition Temperature C^0		Chare residue % at 500 C^0	Rate of decomposition % / min.	Temperature at 50% weight loss C^0	Activation energy Kj/mol
	First decomposition	Second decomposition				
PU	386	425	18	0.211	378	34.21
IPNs-10	416	644	24	0.126	423	38.98
IPNs- 20	424	649	28	0.122	434	42.54
IPNs- 30	443	641	22	0.123	438	43.76
IPNs-40	447	643	29	0.102	439	45.99

Table 6. DSC thermal parameter of the prepared IPNs

Sample code	**Curing temperature**	**Curing energy j/g**
PU alone	204	194
PU-10	198	188
PU-20	207	107
PU-30	199	76
PU-40	189	74

Conclusion:

Interpenetrating polymer network were prepared from polyurethane and epoxy resin showed excellent chemical resistance, hardness, impact strength and thermal resistant than unmodified PU. Hence, it can be concluded that using the IPNs concept, it is possible to design the most desirable material for specific end use requirement.

References:

1. Lee H. K., **Hand Book of Epoxy Resin, New York, MG Graw-Hill** (1967).
2. Troev K. G., G.Tsevl R., R. Tsekora. A., **polymer**., 41(19) , 7017-702, (2000).
3. Jinbo Li**, Polym. Bulletin** 56,377-384, 2006.
4. Spering. L. H, Mishra. V., **Polym. Adv. Technol**., 7,197, (1995).
5. K. Dean, W. D. Cook, M. O. Zipper, P.Burchill, **Polymer**. 42, 1345-1359,(2001).
6. Lin.Ms, Chang. R.J. **, J.Appl.Polym. Sci**: 46,815,(1992).
7. Sarathi. K.T**, Mat.Sci. Eng A**, 445, 567-578,(2007).
8. Clayton,, **Epoxy Resin, Chemistry and Technology, 2nd** edition, Marcel Decker, New York,(1988).
9. Whidad. S. Hanoosh, Emad. Mohamad, **The Malaysia polymer journl**, 4(2), 52-61,(2009).
10. Mahesh**, high perform polymer**, 16, 391-404, (2004).
11. Cherm. S. M., **J. Mater. Sci**., 29, 5435-5440(,1994).
12. Chen. M. K., J. Appl. Polym. Sci, 100, 323-328, (2006).
13. E. I. Zaitsera and A.A. Donskoi, **Polym. Sci. D**, 1(4), 289,(2008).
14. Zhang. S.F, **J.Appl. Polym.Sci**., 75,406-416 (1999).
15. V.G.Chervin,Kauch.Rezina **Polymer** 44 (23) 605-611 (2001)
16. Fellahi. S, Chiki.n, Baker. M., **J.Appl.Polym Sci**., 82, 861-878, (2001).
17. Sakaran. S., **J. Appl. Polym. Sci**., 39,1635-1647,(1990).

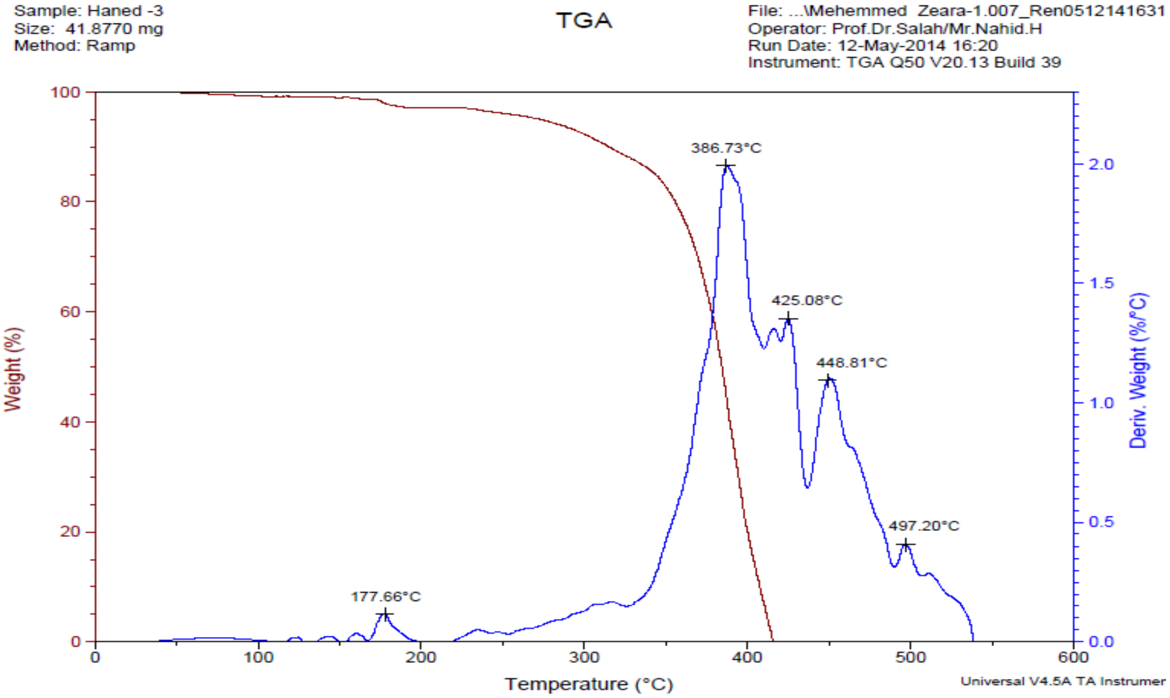

Figure (4) : TGA & DTGA thermogram of the prepared poly urethane

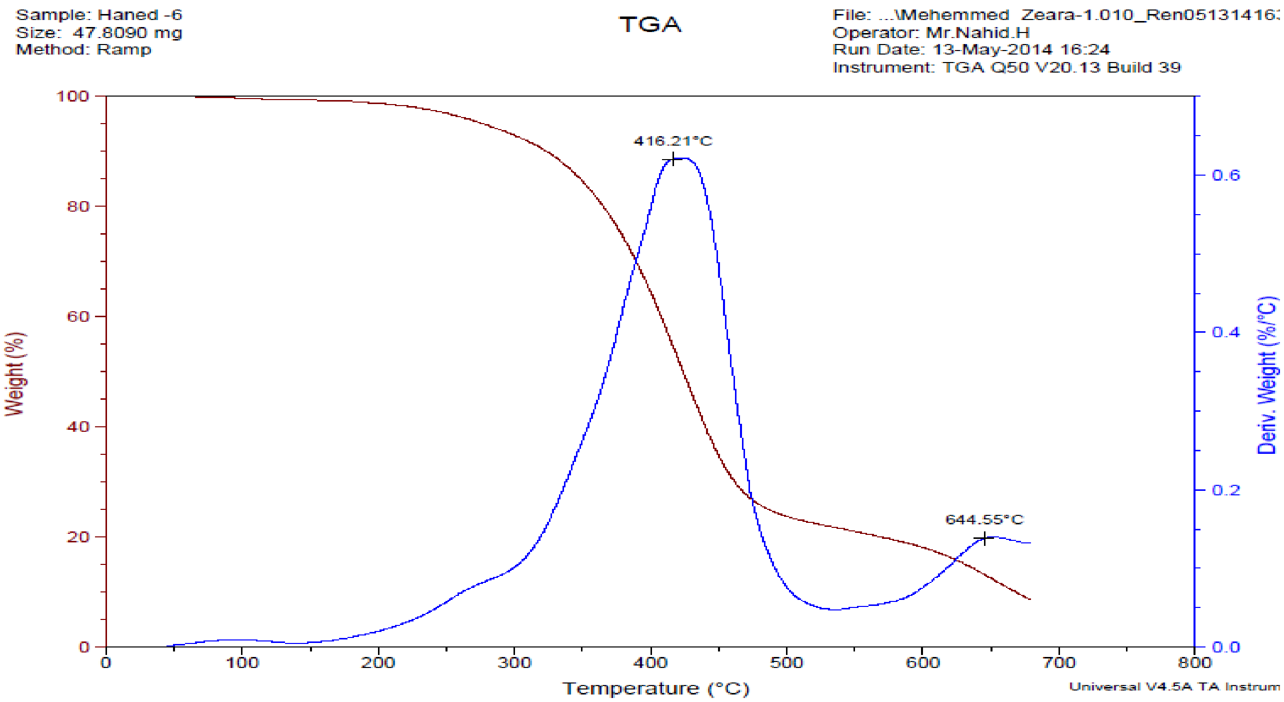

Figure (5) TGA&DTGA thermogram of IPNs-10

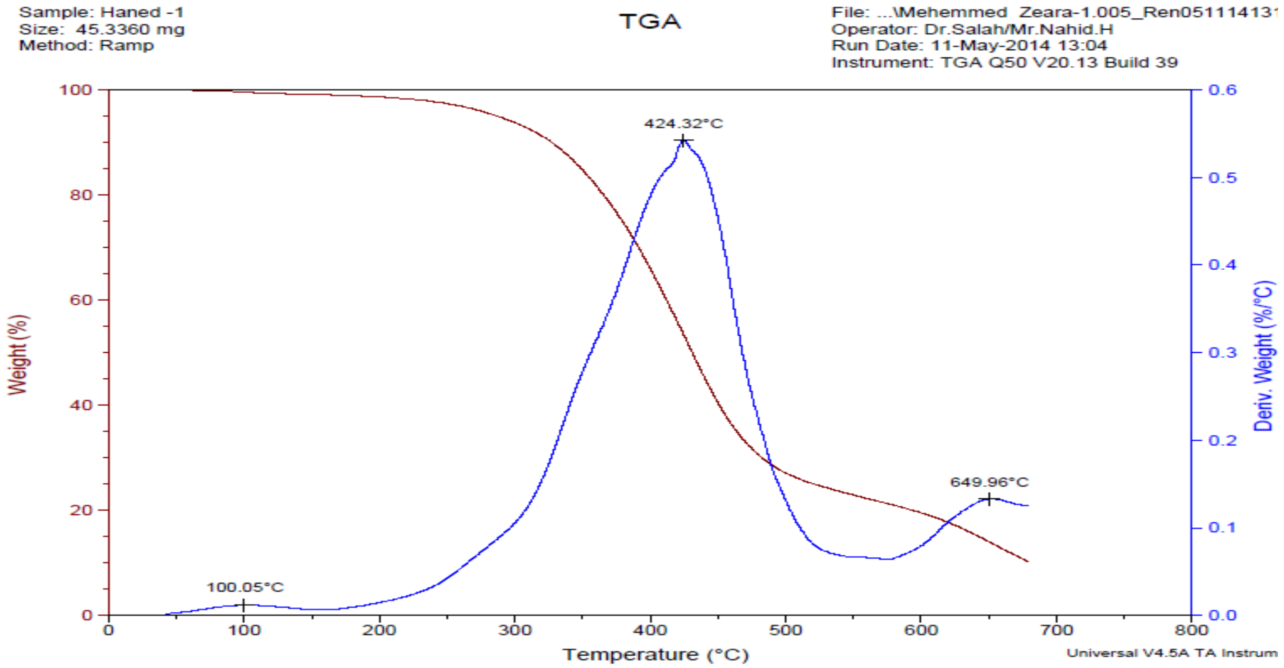

Figure (6) : TGA & DTGA thermogram of IPNs -20

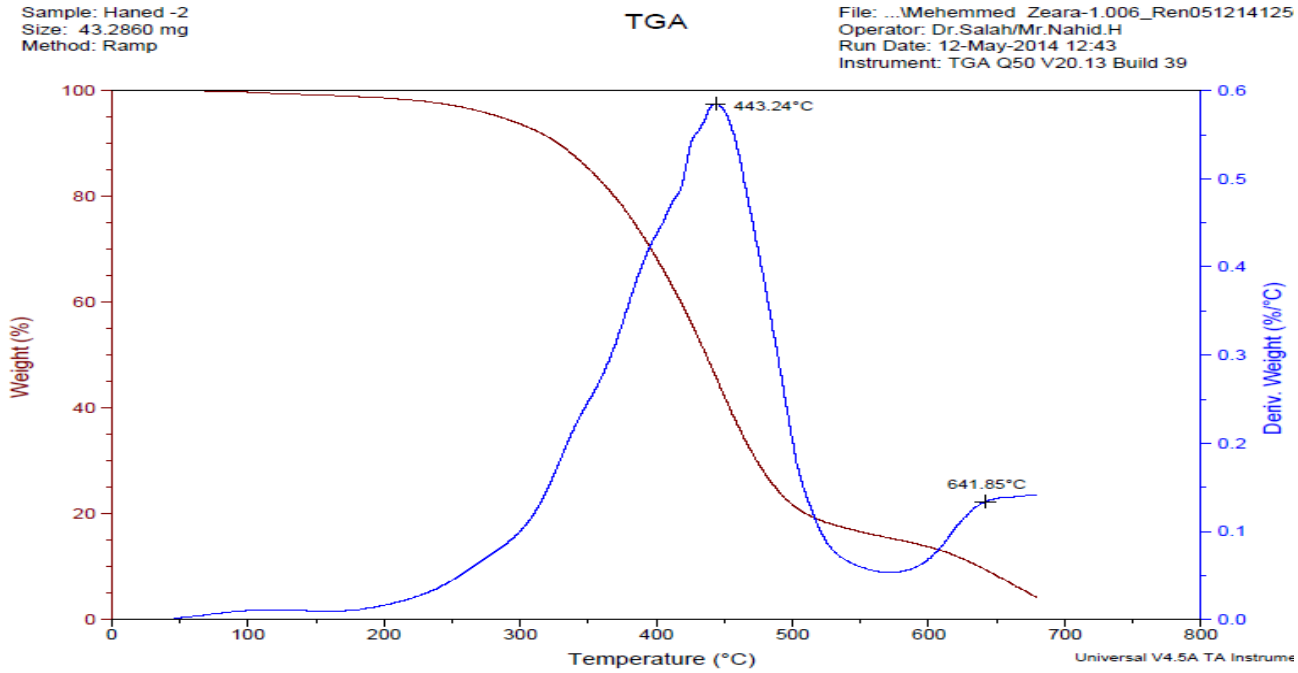

Figure (7) : TGA & DTGA thermogram of IPNs -30

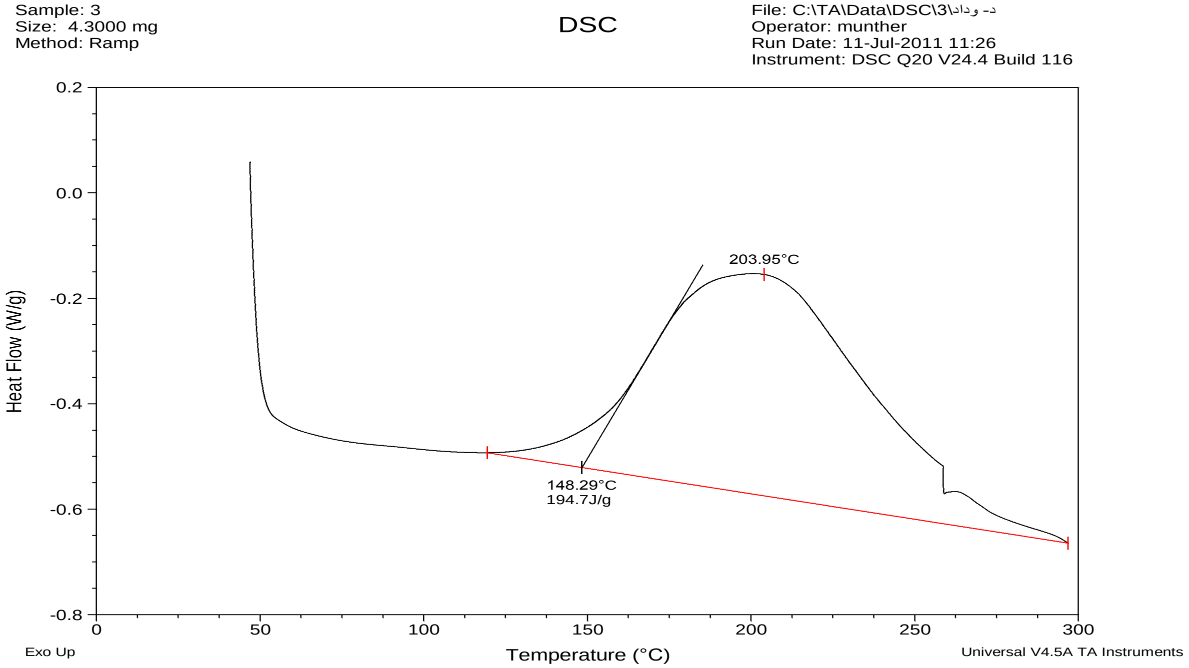

Figure (8) : DSC thermogram of pure poly urethane

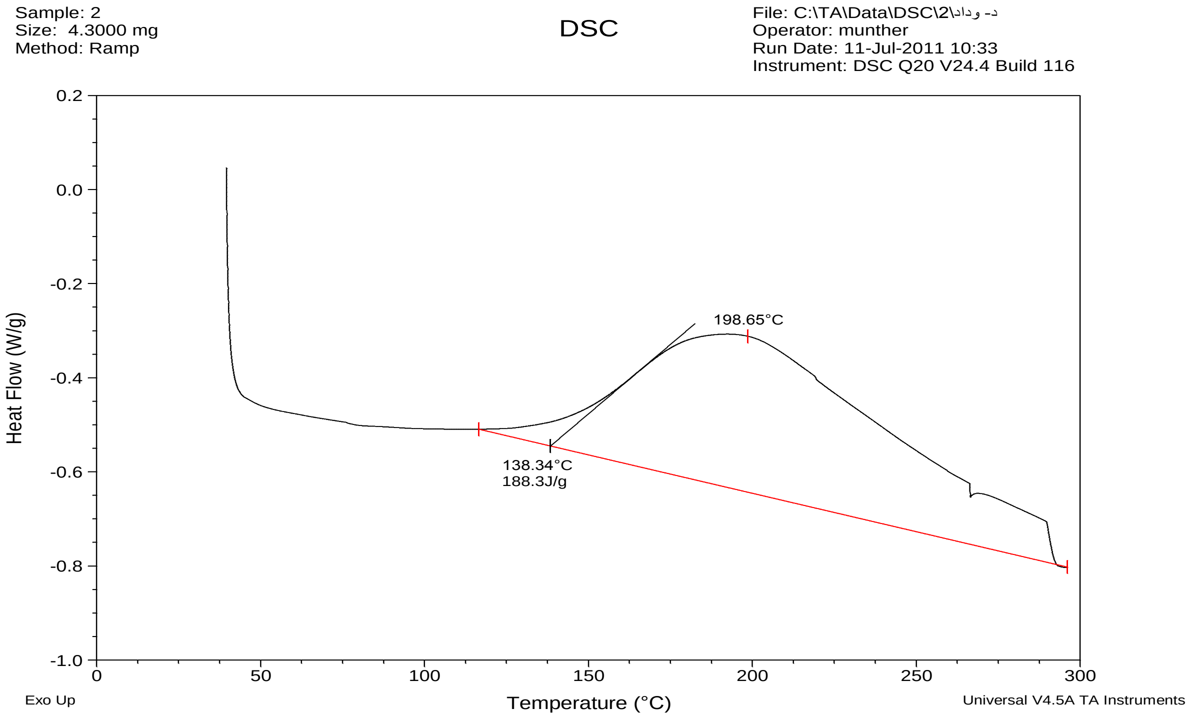

Figure (9) : DSC thermogram of IPNs-10

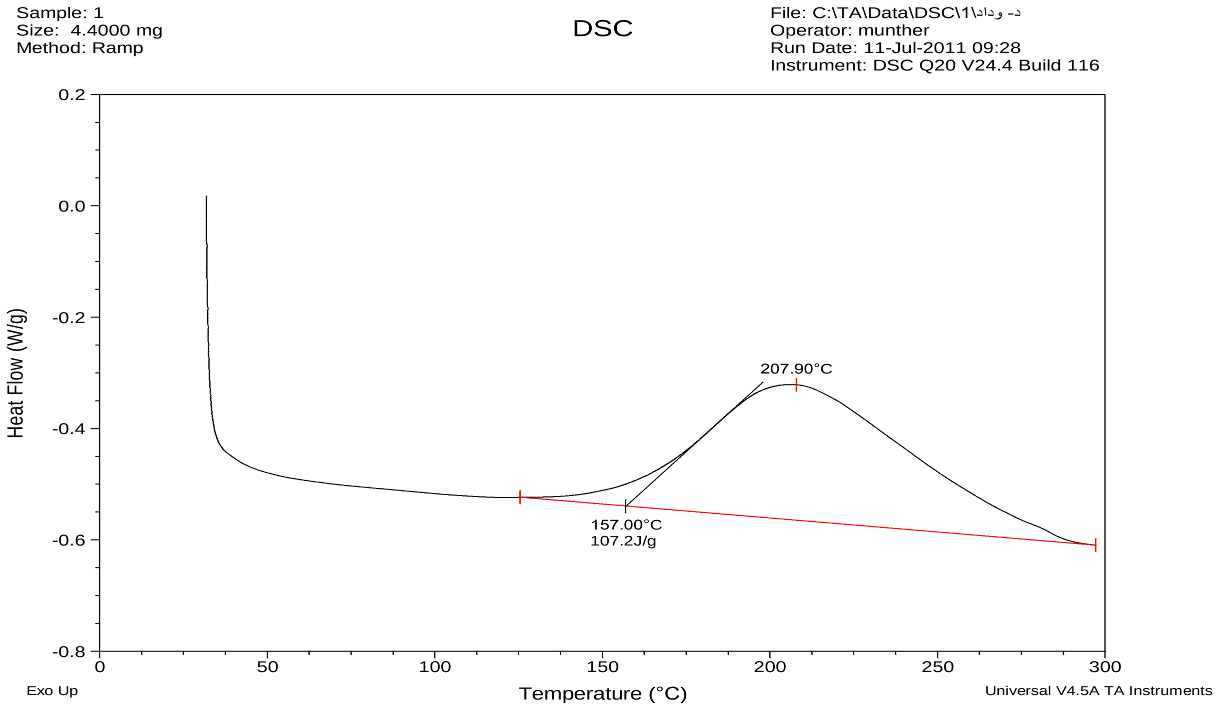

Figure (10) : DSC thermogram of IPNs-20

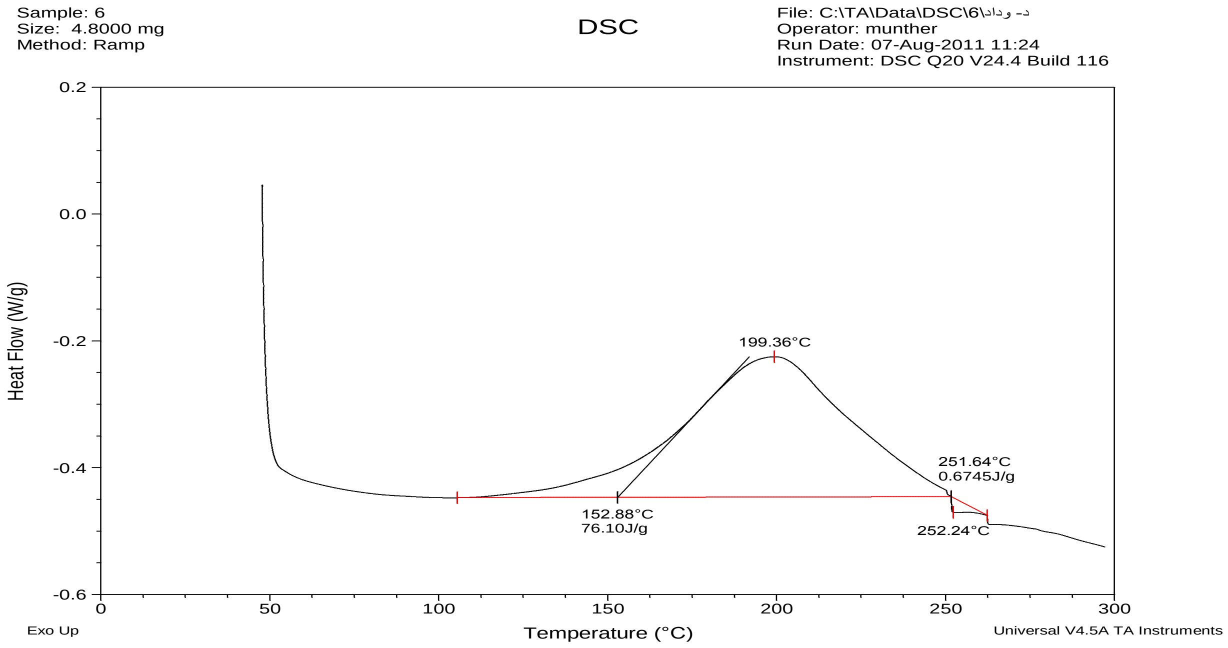

Figure (11) : DSC thermogram of IPNs-30

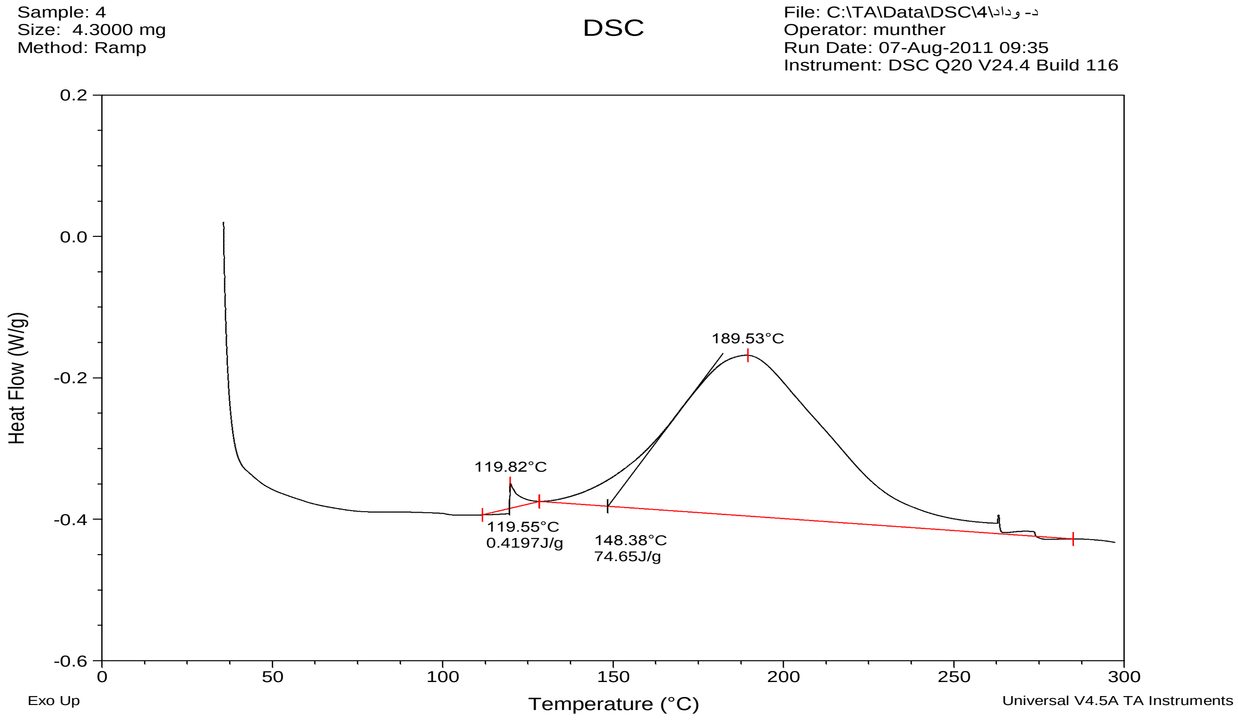

Figure (12) : DSC thermogram of IPNs-40