Synthesis and characterization of Eesterthiourea chloral acrylate resin and their Interpenetrating polymer networks (IPNs).

Hadi.Z. Al-Sawaad
University of Basrah, college of science, chemistry department.

Abstract:

Esterthioureachloralacrylate resin was synthesized by condensation reaction between chloral and thiourea which then react with acrylic acid to form the mentioned resin. Several new IPNs based on new resin of epoxy were polymerized i.e.,. (1:1, 1:2, 1:3) portions of epoxy hardeners respectively, have been prepared . curing of the new IPNs was studied by DSC as a function of temperature, several curing parameters were determined i.e.,. rate of curing , curing energy and activation energy, according the optimum curing conditions were found. The obtained results showed that the curing energy of new resin decrease in presence of different portion of epoxy: hardeners and initial temperature of curing decrease as epoxy: hardeners portion increase.

الخلاصة:

في هذه الدراسة تم تحضير راتنج thioureadichloral من خلال مفاعلة مولين من الكلورالللامائي (chloraldihydrate) مع واحد مول من الثايويوريا (thiourea) للحصول على راتنج الثايويوريا ثنائي الكلورال(Thioureadichloral resin) ثم تم مفاعلة الراتنج الناتج مع مولين من حامض الاكريليك(Acrylic acid) للحصول على الراتنج الاستري غير المشبع ثنائي اكريلات كلورال ثايويوريا(Esterthioureadichloralacrylarte) وقد شخصت النماذج المحضرة بتقنية مطياف الاشعة تحت الحمراء. ثم تم تحضير سبائك بوليمرية (راتنجات بوليمرية شبكية التداخل) من الراتنج الاستري مع نسب مختلفة من الايبوكسي : امين(المصلب للايبوكسي) بنسب(1:1, 1:2, 1:3) امين :ايبوكسي على التوالي وقد درست تقسية هذه البوليمرات شبكية التداخل مقارنة مع تقسية الاستر الاكريلي باستخدام تقنية DSC كدالة لدرجة الحرارة وقد اظهرت النتائج بان طاقة تنشيط التقسية للراتنج المحضر تزداد بوجود الايبوكسي: امين وتزداد قيمتها كلما ازدادت نسبة الايبوكسي: امين, كما ان درجة بداية التقسية تزداد كلما ازدادت نسبة الايبوكسي : امين.

Keywords: thiourea, chloral, acrylate, curing , DSC study, Resin.

1.Introduction:

Blending of polymers is a useful technique to obtain properties not readily achieved in homopolymers. Thus, the interpenetrating polymer networks(IPNS) were investigated as special case of polymer blends and may be defined as two networks being synthesized and/or crosslinked in the presence of other and they posses several interesting characteristics compared with the normal polymer blends.

Generally, Interpenetrating polymer networks (IPNs) can be classified according to method synthesized into[1]:

1. Sequential IPNs.
2. Simultaneous IPNs.
3. Semi IPNs.
4. Joint IPNs.

Acrylic resins can be defined as unsaturated esters derived from acrylic acid and its derivative. These resins that have acrosslinking property due to unsaturated (C=C) in their structure. Differential scanning calorimetry (DSC) is the most widely used of the thermal techniques available to the analyst and provides a fast and easy to use method of obtaining a wealth of information about a material, whatever the end use was investigated. It has found use in many wide ranging applications including polymers and plastics, foods and pharmaceuticals, glasses and ceramics, proteins and life science materials; in fact virtually any material, allowing the analyst to quickly measure the basic properties of the material [2].

Epoxy resins are widely used in industrial applications owing to their many attractive properties, such as excellent chemical and solvent resistance, good thermal and electrical properties. At present epoxy resins are extensively used in technical applications such as coatings, composites and as structural adhesives[3]. Use of epoxy resins in high performance structural material is getting more and more popular. The thermal stability of the epoxy resins was significantly leveled up both in the initial decomposition temperature (IDT) and the integral procedural decomposition temperature (IPDT)[4]. Thus, the interpenetrating systems (IPN) based on epoxy resins modified with imide compounds were prepared which exhibited good thermal and mechanical properties Additionally, since imide groups could provide char formation in the condensed phase to improve polymers flame retardant properties, epoxy resins modified with imide compounds through chemical reactions or physical blending have been reported to show good flame retardant properties [5-9].

Interpenetrating polymer networks (IPNs) are physical mixtures of different homopolymers or copolymers, in which different component networks penetrate fully one another, i.e., are being cross-linked [10-13]. They are produced in order to improve certain final use of processing properties so that the property spectrum of bulk plastics can approach that of engineering plastics in an economical viable way. Such IPNs may be derived from thermoplastics, thermosets or elastomeric materials. Much of the work on IPNs based on different systems have been reported [14-16] . Mainly they are prepared in the form of film [17], alloy [18], foam [19], glass fiber reinforced composites [20] have developed simply, effectively and less expensive IPNs based on castor oil and other systems. Many IPNs are also prepared from epoxy resin/thermoplastics resin [21-22]. Polymer networks have been used and investigated for a long time.1 Desired properties can be achieved more easily in interpenetrating polymer networks (IPNs) in which two (or more) components are held together mainly by topological constraints. Depending on the method of synthesis, the overall composition, the thermodynamical miscibility of the components, the cross-link density and crystallinity, one can obtain IPNs with dispersed-phase domains ranging from a few millimeters to a few tens of nanometers. Miscibility and specific intermolecular interactions in such systems are much more complicated than in linear polymer blends. Kinetic factors, the curing program, and the topological structures of the system are closely coupled with the thermodynamics of mixing[23-29].

In this study three types of IPNs were prepared from three portions of epoxy:hardener with esterthiourea acrylate, DSC study was achieved to explained the thermal stability of the produce IPNs.

The aim of present study was to study the DSC data which that obtained from curing the above mentioned resin and its IPNs which an important for future study the behavior of this resin as fire retardans and other uses

2.Experimental:

2.1. Chemicals:

Chloral, Acrylic acid, phosphoric acid, thiourea, sodium bicarbonate methylenchloride, sulphuric acid and ethanol. were supplied by Fluka company , commercial amine as hardener., commercial ethyl methyl ketone peroxide as initiator and cobalt octanoate as activator

2.2. Apparatus

1. IR spectra were recorded on a pye-unicam model SP3-300 infrared spectrometer.
2. Dupont thermoanalysers model 990 with DSC unit were used to study of curing after being calibrated with indium(99.99%).

The DSC and IR spectra were measured in University of Basrah, College of Science, chemistry department.

2.3.Procedures: the mentioned resins were prepared according to the procedures in Ref [30].

2.3.1. Synthesis of N,N-bis(2,2,2-trichloro-1-hydroxyethyl)thiourea:

(7.60)g((1)mole) of thiourea,(16.55)g ((2)) moles of chloral hydrate and (150)ml distilled water were charged tonreaction vessel, the mixture was mixed as 80ºC , after 3hours the reaction mixture was cooled, filtered and purified by washing with distilled water several times to remove the unreacted materials then recrystallised from DMSO and water three times.

2.3.2. Synthesis of acrylic ester of thiourea chloral resin:

The reaction vessel was charged with(7.20)g ((1) mole) of acrylic acid and (0.5) ml Conc. Sulphuric acid which immersed in an oil bath, the reaction mixture was heated with continuous mixing at 50ºC. at same time (2.59)g ((0.1) mole) of thiourea chloral resin as (10%) solution in acrylic acid was added drop wise to the reaction vessel during (1) hour. The temperature was maintained for (5) hours. Then the reaction mixtures was cooled and neutralized with saturated solution of sodium bicarbonate. The ester layer was extracted by methylenchloride and purified by washing with distilled water several times. The organic layer was evaporated with rotary evaporator then dried under reduced pressure (0.1) mmHg.

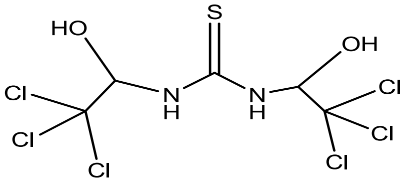
3. Results and discussions:

3.1. Infrared spectroscopy: All samples were characterized as thin film which sodium chloride disc used for characterization.

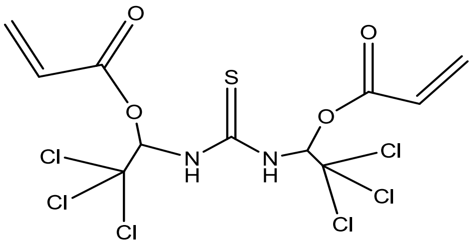
Comp.	C-H stretch	C=S	O-H stretch	N-H stretch	C-N	C=O	C-O	C=C	C-H bend	O-H bend	N-H bend	C-Cl
TUC	2900*	1380	3140	3280	1410 vw*	-	1100	-	1240	1540	1630	820
TEA	2860*	1450vw*	-	2940	1410	1630 Asy m*	1060	1620w*	1190	-	1700	820

Table 1 showed the all bands cm^{-1} in that characterized by IR spectroscopy.
Where:
TUC: thioureadichloral.
TEA: thioureaesterdiacrylate.

The structures of the above compounds can explained in Schem1.

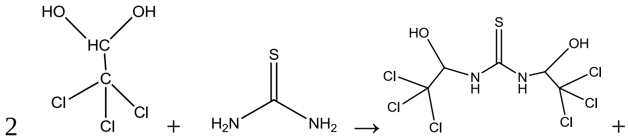


(A) : thioureadichloral (TUC).

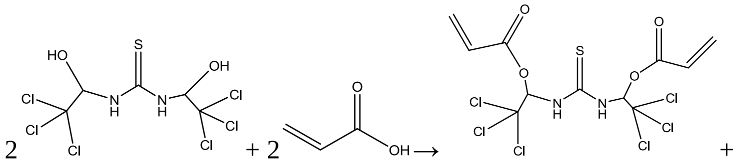


(B): 1, 1’-thiocarbonylbis (azanediyl) bis (2, 2, 2-trichloroethane-1, 1-diyl) diacrylate (TEA)
Scheme 1 the structure of the compounds derives from thiourea.

The reactions that produced the thioureadichloral (TUC) and thioureaesterdiacrylate (TEA) can be explained below in equations 1 and 2 respectively.



+ $2H_2O$ ……1



+ $2H_2O$ ……………..2

From Table 1 presence of (C=C) in compound TEA at 1620cm^{-1} indicating to synthesis the acrylate resin. Hence, the presence of (N-H) stretching and bending in TUC and TEA respectively indicates to substitution of the only two active protons by two chloral hydrate groups in TUC. On the other hand presence of (C=O) band in 1630 and 1640 cm^{-1} for asymmetric and symmetric stretching vibration for carbonyl group respectively a good indication for synthesis the both esters. Other bands like(O-H) can give an indication to formation at 3240 cm^{-1} in case of TUC while ,it disappears in case of TEA that indication to the etherification process happened for TUC to for TEA. On the other hand the doublet bands of free amino groups of thiourea disappear as TUC formed to stay only singlet band in TUC and TEA as stretching band at 3280 and 2940 cm^{-1} and for bending at 1630 and 1725 cm^{-1} respectively

Figures 1-2 explained the IR spectra of the mentioned synthesized resins.

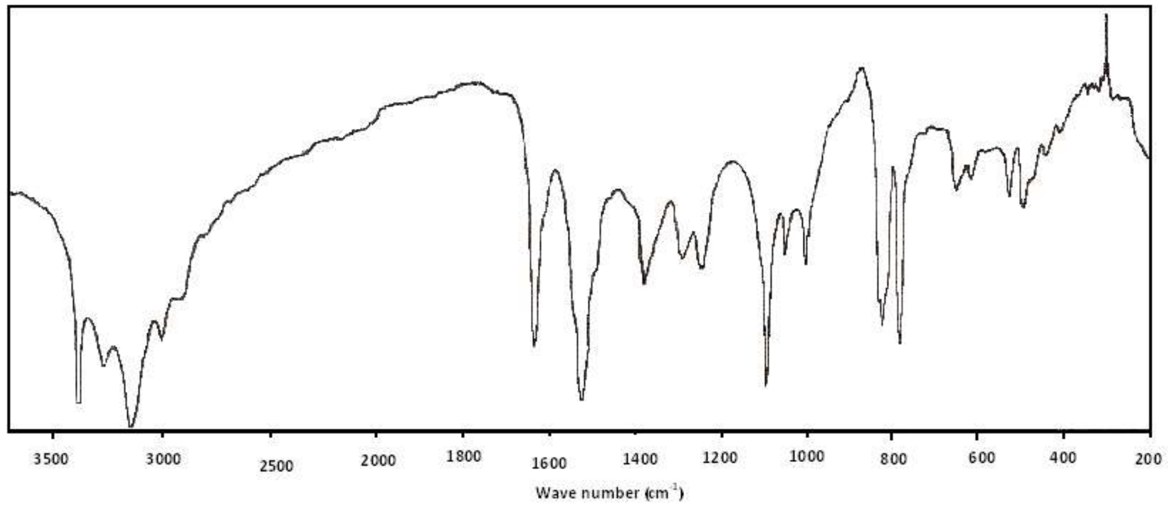


Figure 1: IR spectrum for thioureadichloral.

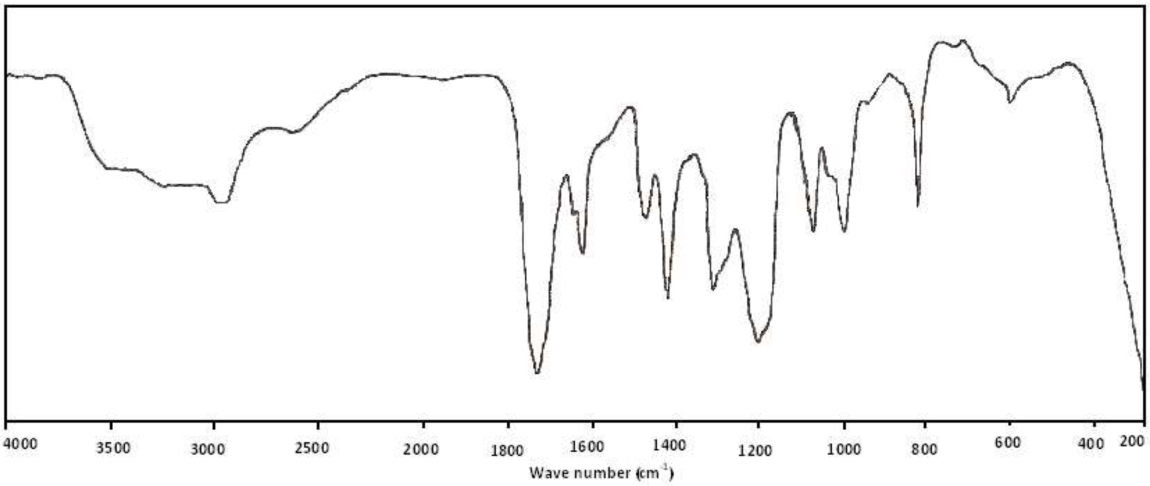


Figure 2: IR spectrum for diesterthiochloral.

3.2. DSC study:

DSC scanning can be defined as technique in which several parameters like curing, degradation, melting, crystalanity, etc can be measured , also physicochemical properties like activation energy, rate of reaction, heat of reaction and kinetic of reactions can be obtained. Thus, DSC is a technique that exothermic or endothermic energy is measured as a function of temperature at constant time or as a function of time at constant temperature.

From the DSC thermograms of all the systems, the initial temperature of curing (Ti), the optimum temperature of curing (Top) and final temp (Tf) were noted and the calculation of kinetic parameters is also given in Table 2.

Polyesters and epoxy are both families of thermosetting resins. The fundamental difference is the type of reactive chemical group that is involved in the crosslinking reaction. For polyesters, the reactive group is a double bond between two carbon atoms. For epoxy, the reactive group is a small 3-membered ring of two carbon atoms and an oxygen atom called the epoxy ring. We can appreciate the differences in crosslinking reactions and conditions without delving into the chemistries involved. Polyesters are crosslinked by adding a small amount of peroxide initiator (catalyst) to a solvent system of the resin. Then, either with heat or at room temperature, and perhaps with the addition of additional chemicals, the resin cures. Epoxy does not use peroxides and are often not solvated. Curing an epoxy is accomplished by adding a curative (hardener), but the conditions for curing can vary widely depending on the natures of resin and the curative, as well as the requirements of the manufacturing operation and the properties of the final product. When compared with the polyester crosslinking process and the properties of polyester products, the epoxy system and product properties are far more versatile [31].

In this study three types of sequential IPNs were prepared between curing acrylate resin with different portions of epoxy: hardeners i.e.,.(1:1, 1:2, 1:3) respectively by using the ethyl methyl ketone peroxide as initiator and cobalt octanoate as activator (trace) for polymerization the double bond of the unsaturated ester (acrylate resin). Hence, IPNs has integrated properties for the two networks that formed it.

Table 2 show the parameters that obtained from DSC scanning decreasing activation energy for ester in IPNs in large values, decreasing in IPNs with the portion (2:1) epoxy :hardener larger than other two IPNs may be belong to increasing compatibility between epoxy: hardener network in this portion of epoxy : hardener with ester network whereas, curing rate also slow down value as increasing epoxy percentage in epoxy: hardener network can be observed due to physical interaction between two networks that retard the curing rate[2].

No.	Resin	T_i (ºC)	T_{op} (ºC)	T_f (ºC)	ΔE (Kj/mole)	R (ºC/min)	T_i (ºC)	T_{op} (ºC)	T_f (ºC)	ΔE (Kj/mole)
1	ETCA	63	66	72	10.10	6.6	….	….	….	….
2	ETCE1	60	71	85	36.7	2.54	120	140	155	67.17
3	ETCE2	58	68	83	32.00	2.19	112	145	170	43.1
4	ETCE3	59	69	85	50.30	1.33	112	130	147	84.60

Table 2 DSC parameters values that calculated from DSC thermo grams.

ETCA:esterthioureachloral acrylate.
ETCE1:esterthioureachloral epoxy:hardner(1:1).
ETCE2:esterthioureachloral epoxy:hardner(2:1).
ETCE3:esterthioureachloral epoxy:hardner(3:1).

The DSC thermograms can be explained in figures 3-5 as shown below.

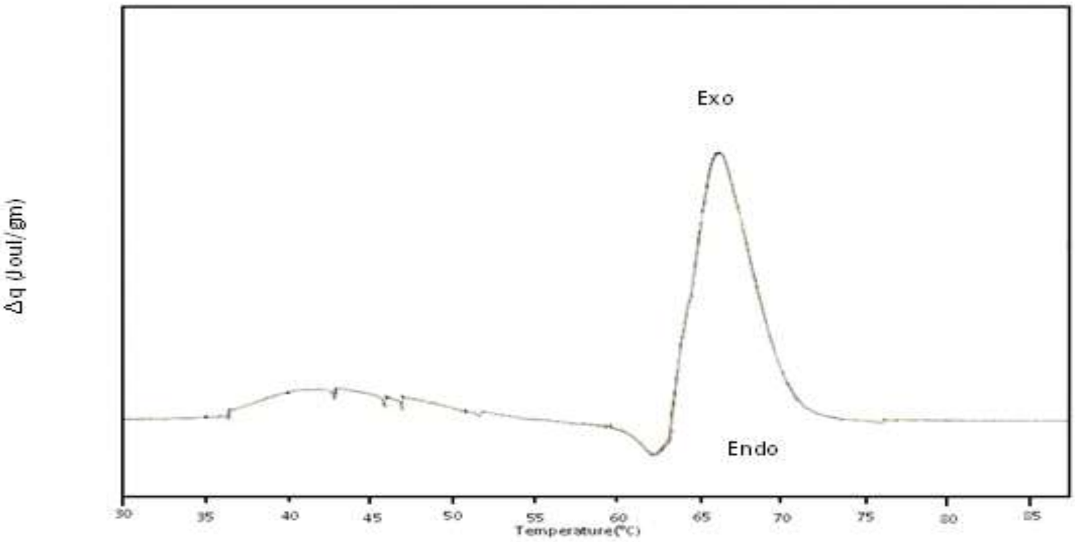


Figure 3: DSC thermogram for esterthioureachloral acrylate.

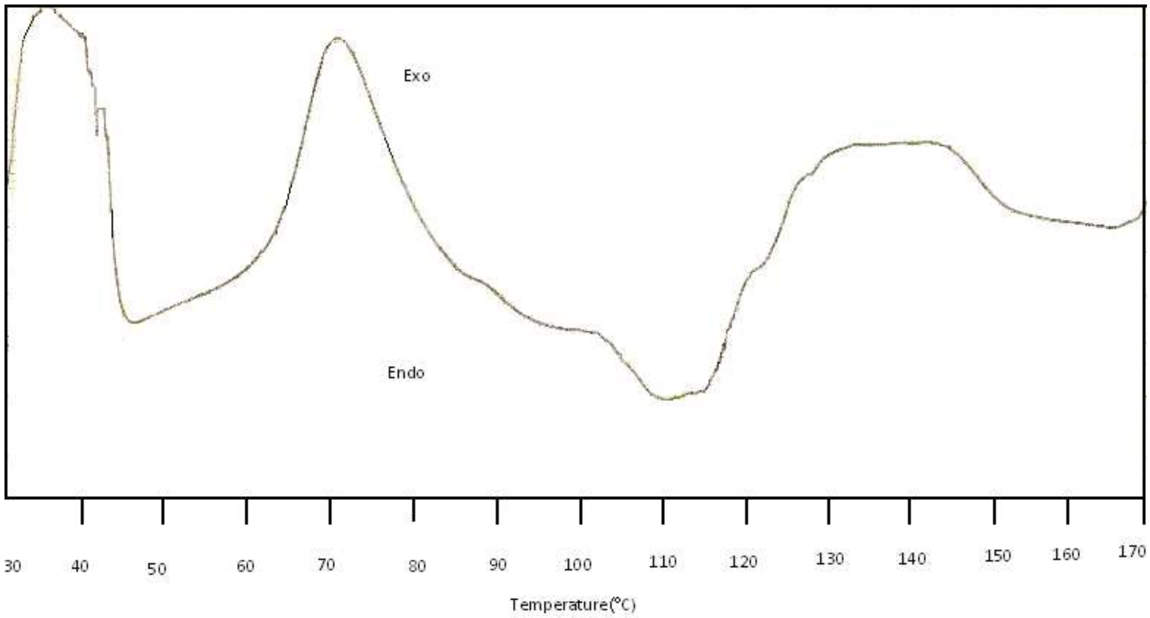


Figure 4: DSC thermogram for esterthioureachloral epoxy:hardner(1:1).

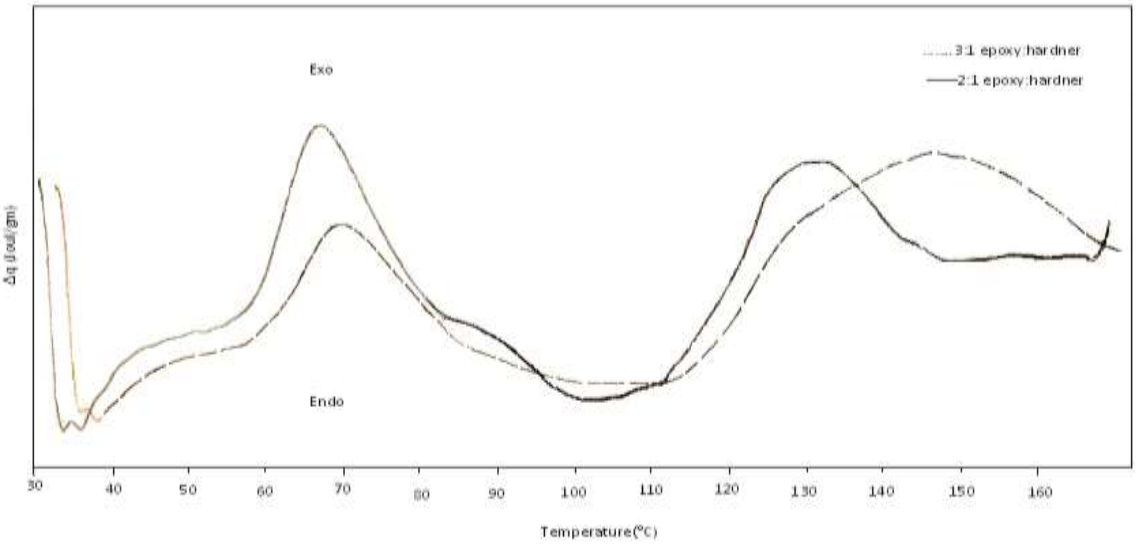


Figure 5: DSC thermogram for esterthioureachloral epoxy:hardner(1`:2) and esterthioureachloral epoxy:hardner(1`:3) respectively.

According to the data that adopted from Table 2, the curing of all above components explained an exo band that means the curing processes behave as an exothermic processes, especially the ETCA that has curing process with low activation energy (10.10) kJ/mole with curing rate 6.60 °C/min. this can be attributed to the easily curing the (C=C) as in figure 4 where the DSC thermogram reveal the sharp exo peak with 63, 66, and 72°C for T_i, T_{op}, and T_f respectively. Thus, preparing of three types of IPNs that result from the physical mixing between each one of the three networks of epoxy: hardener portions i.e. (1:1), (2:1), and (3:1) respectively with homopolymer of actylate resin raise the activation energy of curing, T_{op}, and T_f , but decrease in T_i, due to decreasing in curing rate in acrylate curing because of the presence of the epoxy: hardener network for each type of IPNs that retard the curing process[1]. On the other hand comparison between the above three types of IPNs reveal that the IPNs that prepared form the epoxy: hardener with portion (2:1) with acrylate has low activation energy and T_{op}, and T_f for acrylate and degradation of epoxy: hardener networks respectively as in Table2 that means at this portion of epoxy: hardener the IPNs has more compatibility than other two types. As in figures (4-5) the types of the above three IPNs is sequential semi IPNs, semi because the physical mixing between homopolymer (linear) acrylate resin with the epoxy: hardener network, and sequential because two sequential peaks that appeared as in figures (4-5).

5. Conclusion:

The conclusions can be summarized as:

1. IPNs leads to decreasing activation energy of curing the acrylate resin due to compatibility between two networks the retard the curing reaction of acrylate, and slow down the curing rate as well as providing the relative thermal stability for the degradation of epoxy : hardnner network.
2. The above results it is obvious in the portion (2:1) of epoxy: hardener network compared with other two network due to physical interaction between two networks whereas epoxy hardner network has the ability to hydrogen bonding opening (oxiran ring) with the ester acrylate network.
3. DSC thermograms reveal that the type of IPNs is sequential because of presence two peaks the firs belong to acrylate resin and the second belong to the epoxy: hardener network in each case of the three portions.

Acknowledgment:

I am would like to thanks prof.Dr.Salah Shakir in chemistry department, college of science, university of Basrah to his efforts for running the DSC thermograms and for his advisements.

References:

1. Al-Luaibi,S.Sh, Ph.D thesis, chem.dept, college of Sci, Univ. of Basrah, Iraq,(1995).
2. Al-Sawaad,.Z, M.Sc thesis, chem.dept, college of Sci, Univ. of Basrah,Iraq,(2001).
3. Hay,J.N,Woodfine.B, Davies,M. Highperporm polym.8,35,(1996).
4. Park, S. J.; Kim, H. C.; Lee, H. I.; Suh, D. H. *Macromolecules, 43*, 693. (2001)
5. Kumar, A. A.; Alagar, M.; Rao, RMVGK. *Polymer, 43*,693, (2002).
6. Musto, P.; Martuscelli, E.; Ragosta, G.; Scarinzi, G. *J. Appl. Polm.Sci.*,*69*,1029, (1998).
7. Kumar, A. A.; Alagar, M.; Rao, RMVGK. *J. Appl. Polym. Sci., 81*, 2330, (2001).
8. Kumar, A. A.; Alagar, M.; Rao, RMVGK. *J. Appl. Polym. Sci., 81*, 38,(2001).
9. Han, J. L.; Chen, Y. C.; Li, K. Y.; Hsieh, K. H. *J. Appl. Polym.Sci. ,70*, 529. (1998).
10. Frisch H.L . and Klempner D., *Adv. Macramol.* Chem :, 2, 149,(1970).
11. Lipatov Yu .S.and Sergeeva, *Interpenetrating PolymericNetworks,* Nankova Dumka, Kiev, (1979).
12. Klempner D ., Angew. *Chem.,* 17, 97,(1978).
13. 4. Sperling L .H ., *Interpenetrating Polymer Networks andRelated Materials,* Plenum Press, New York,(1981).
14. Ika P.V ., Frisch H .L. and Frisch K .C ., J. *Polym. Sei. Polym .Chem.,* 23, 1163,(1985).
15. Kim S.C., Klempner D., Frisch K .C., Radigan W. and FrischH.L., *Macromolecules,* 9, 258,(1976).
16. Siegfried . D .L ., Thomas D .A. and Sperling L.H ., *J. Appl.Polym. Sci., 26,* 141,1981.
17. Frisch K.C ., Frisch H .L., and Klempner D., *US. Pat.* 4, 302,553, (1981).
18. Klempner D . and Frisch K.C ., *Polymer Alloys,* Plenum Press,New York,(1977).
19. Gurvey V .V., *Advance* in *!PNs,* Ed . by Klempner D., andFrisch K .C ., Technomic, Lancaster, U .S.A ., Vol . 2, 239,(1990).

20. SutharB.P. and Patel M., J. *Appl. Polym* . Set, 33, 67,(1987).
21. Cassidy E.F ., Frisch K. C. and Frisch H . L ., J. *Polym. Ser.*, 22,2267, (1984).
22. Allard D., Fontanille M. and Prud'homme R. E., *J. Polym.Sci.*, 22, 3827, (1984).
23. Ioannis M. Kalogeras,*,† Andreas Stathopoulos,† Aglaia Vassilikou-Dova, and Witold Brostow, *J. Phys. Chem. B*, *111*, 2774-2782, (2007).
24. Akutsu U., Inoki M., Daicho N., Kasashima Y., Srirasish,N., Marushima I.: Curing behavior and properties of epoxy resins cured with the diamine having the quinoxaline or triazine structure. Journal of Applied Polymer Science, 69, 1737–1741 (1998).
25. Vabrik Y., Czajlik I., Túry G., Rusznák I., Ille A., Víg A.: A study of epoxy resin-acrylated polyurethane semi-interpenetrating polymer networks. Journal of Applied Polymer Science, 68, 111–119 (1998).
26. Lin M. S., Liu C. C., Lee C. T.: Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy. Journal of Applied Polymer Science, 72, 585–592 (1999).
27. Li Y., Shen S., Liu Y., Gao J.: Kinetics of 4,4′-diaminodiphenylmethane curing of bisphenol-S epoxy resin.Journal of Applied Polymer Science, 73, 1799–1803 (1999).
28. Deng B-L., Hu Y-S., Chen L-A., Chiu W-Y., Wu TR.: The curing reaction and physical properties of DGEBA/DETA epoxy resin blended with propyl ester phosphazene. Journal of Applied Polymer Science, 74, 229–237 (1999).
29. Kaji M., Nakahara K., Endo T.: Synthesis of a bifunctional epoxy monomer containing biphenyl moiety and properties of its cured polymer with phenol novolac. Journal of Applied Polymer Science, 74,690–698 (1999).
30. Jabbar,F.J, M.Sc thesis, chem.dept, college of Sci, Univ. of Basrah,Iraq,(1992).
31. Koro de la Caba,1 Pedro Guerrero, aki Mondragon & Jose • M. Kenny, Polymer International 45 ,333-338, (1998)