Synthesis and Evaluation of some new DDT resins and their IPNs

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Abstract:

Acrylate resin derived from tetramethylol DDT resin have been synthesized and characterized by IR, NMR and CHN. Several IPNs were prepared from the unsaturated resins and commercial unsaturated polyester (palatal).Also the amine resins was used as hardener for epoxy resins and resole.The new IPNs were curable at room temperature according their curing characteristics were investigated by DSC technique, several parameters were found; i.e. curing temp., rate of curing, curing energy and activation energy.The thermal stability and thermo-oxidative stability of new resins and their IPNs were studied by TGA technique in the presence of inert atmosphere. Several thermal stability parameters were calculated from TG thermograms. The obtained results confirmed the outstanding thermal stability of new IPN's.

الخلاصة:

حضرت راتنجات الاكريلات المشتقة من راتنجات (tetramethylol DDT) و شخصت بواسطة طيف الأشعة تحت الحمراء (IR) و طيف الرنين النووي المغناطيسي (H^1-NMR) و تحليل العناصر (CHN). حضرت العديد من البوليمرات شبكية التداخل (IPN's) من راتنجات غير مشبعة و راتنجات البولي استر التجارية الغير مشبعة (palatal). و كذلك استخدمت راتنجات الامين كمواد تقسية لراتنجات الايبوكسي و الريسول. تم تقسية البوليمرات شبكية التداخل الجديدة (IPNs) بدرجة حرارة الغرفة. و تم تعيين خصائص التقسية بواسطة تقنية المسح التفاضلي المسعري (DSC)، وجدت العديد من المتغيرات مثل درجة حرارة التقسية، معدل التقسية، طاقة التقسية و طاقة التنشيط. درست الخواص الحرارية للراتنجات الجديدة و بوليمراتها الشبكية التداخل (IPN's) بواسطة تقنية التحليل الحراري الوزني (TGA) في جو خامل. تم حساب العديد من المتغيرات الحرارية من المنحنى الحراري الوزني. اظهرت النتائج الاستقرارية الحرارية الواضحة للبوليمرات شبكية التداخل الجديدة (IPN's).

Introduction:

Blending polymers is a useful technique to obtain properties not readily achieved in homo polymers, thus the interpenetrating polymer network's (IPN's) were investigated as a special case of polymer blends and may be defined [1-3] as two network being synthesis and/or crosslinked in the presence of the other and they possess several interesting characteristics in comparison to normal polymer blends. Thus, formation of IPN's is the only way intimately combining crosslinked polymers resulting mixtures exhibiting only limited phase separation since normal blending of polymers results in a multiphase morphology due to the will known thermodynamic incompatibility of polymers. The properties of polymer-polymer mixtures well depend on phase morphology and phase interaction as well as composition. The IPN's can be distinguished from simple polymer blends and copolymers (graft, & blocks) in two ways [1].

a-   The IPN's swells, but does not dissolve in solvents.

b-   The creep and flow properties are suppressed.

The IPN's have been investigated and used in several areas due to their outstanding properties and they known by some others as polymer alloys [1,4] which forms an interesting area of compositing materials which have being widely used in industry for various application i.e. compositing blending materials [5,6], thermal and electrical insulators [7,8] polymeric foams [8,9], matrices of reinforced materials [8-10] and fiber [9,10].

Experimental:
Chemicals:
i- Acrylic acid, sodium hydroxide, and formaldehyde were supplied from Fluka Co.
ii- 1,1,1- trichloro- 2,2 – bis(4-hydroxy phenyl) ethane was supplied from BDH Co.
iii- Ethyl methyl peroxide, cobalt accelerator and polyester were supplied by H&W Co.

Apparatus:
i- IR spectra was recorded on a Pye-Unicam model SP3-300 Infrared Spectrometer.
ii- The ^{1}H NMR spectra was obtained with jeol, JNM-FT-NMR model 90 spectrometer using CD_2Cl_2 as solvents and TMS as internal standard.
iii- The CHN analysis was performed on EA-1108 CarloErba elemental analyzer.
iv- Du Pont thermo analysis models 1090 and 990 with DSC and TGA unit were used in this study after being calibrated with calcium oxalate standard and indium 99.999% for TGA and DSC respectively.

Methylolic resin of DDT was prepared according to ref. (11).
Synthesis of Acrylic ester of DDT
Methylolic resin of DDT (0.1 mole) was added dropwise during (1 h) to the mixture of acrylic acid (1 mole) and (0.5 mL) of conc. Sulfuric acid. The mixture was heated with continuous mixing to (50 °C) for (5 h). The reaction mixture was cold and neutralized with saturated solution of sodium bicarbonate, the ester layer was extracted by methylene chloride and purification by washing with distilled water several times.

Preparation of IPN's
Several types of IPN's consisting different weight percentage from unsaturated new resins and palatal were prepared by efficient mixing of predetermined quantities from the two component constituents as shown in table (1).

Table (1): Typical formula of the IPN's

Acrylic resin %	Acrylic resin wt. (g)	Unsaturated polyester (g)	Peroxide (g)	Co-octate (g)
5	0.05	0.95	0.05	0.05
10	0.1	0.90	0.05	0.05
15	0.15	0.85	0.05	0.05
20	0.2	0.80	0.05	0.05
30	0.3	0.70	0.05	0.05

Mixing was continued after the addition of catalyst and activator for further 5 min at room temperature overnight then post cured at 100°C for (3 h).

Results and discussion:
The characterization of the new acrylate DDT was determined by elemental analysis CHN, Infrared (IR) and nuclear magnetic resonance (NMR).
The CHN result shown in table (2). A reasonable agreement between the actual calculated data was found.

Table (2): The quantitative elemental analysis CHN

%	C	H	N
Calculated	55.10	4.13	0.00
Found	55.73	4.52	0.00

The IR spectrum fig (1) showed that the absorption band at (1700 cm^{-1})related to the acrylate carbonyl groups. The (CCl_3) group was identified by the sharp band at (816 cm^{-1}) related to C-Cl.

The ^{1}H-NMR spectrum for the new acrylate resin are shown in fig (2), the analysis data optioned were in good agreement with element analysis and infrared IR confirming the expected structure.
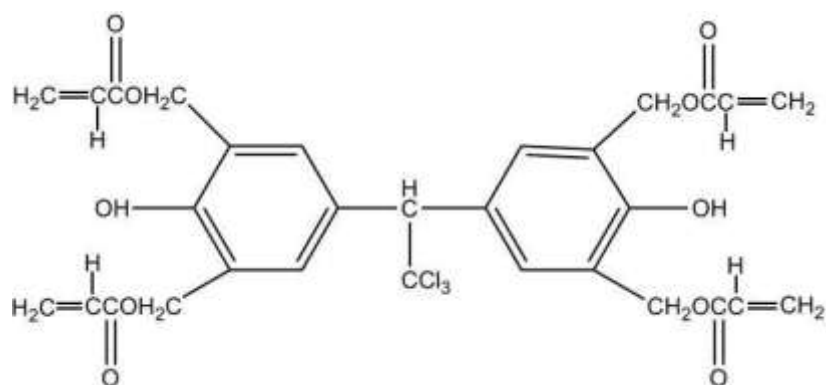
The curing reaction of acrylate DDT and their IPN's were investigated using DSC technique. Samples were prepared according to section (2-5), (5 mg) from the sample was examined in the DSC apparatus under nitrogen mentioned as 30 mm/man at constant heating rate (20°C/man). The DSC thermogram obtained in the curing stage showed that the curing consists an exothermic reaction which take place at high temperatures for the acrylate DDT as shown in fig (3), several curing parameter were evaluated from the DSC thermograms and listed in table (3).

Table (3): DSC curing parameters

Wt%	Ci °C	C_{op} °C	C_f °C	E_{cur} j/g	ΔE kj/mol	Temperature range
0	34	83	140	86.4	113.4	34-60
5	34	87	140	82.1	87.5	34-60
10	60	90	130	50.4	83.0	60-70
20	60	90	140	43.2	66.5	60-70
30	78	96	116	29.2	44.3	78-83
100	60	106	124	41.4	71.1	60-80

Where C_{op} : optimum curing temperature ; ΔE: activation energy ; Ci: initial curing temperature ; E_{cur} : curing energy; C_f : final curing temperature.
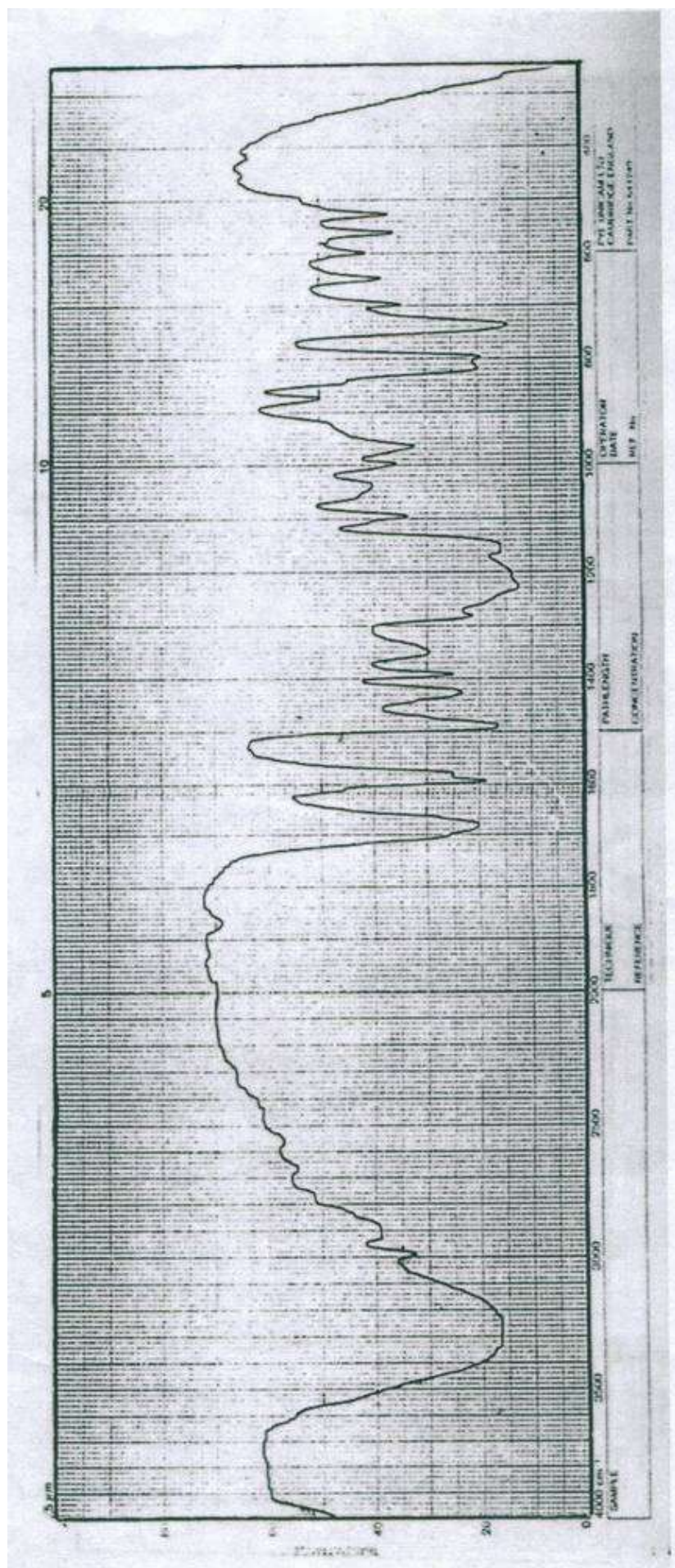
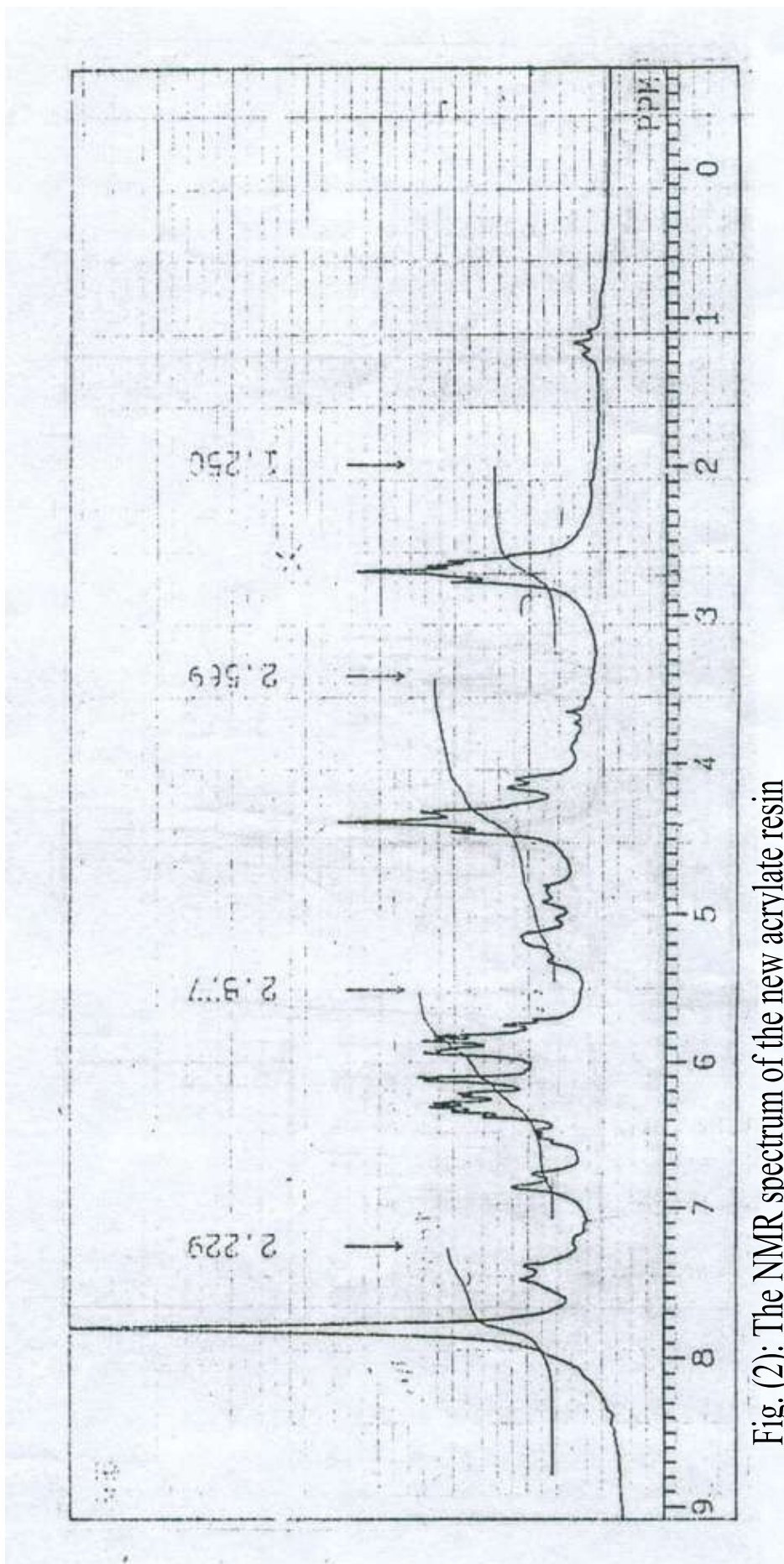Fig. (1): The IR spectrum of the new acrylate DDT resin

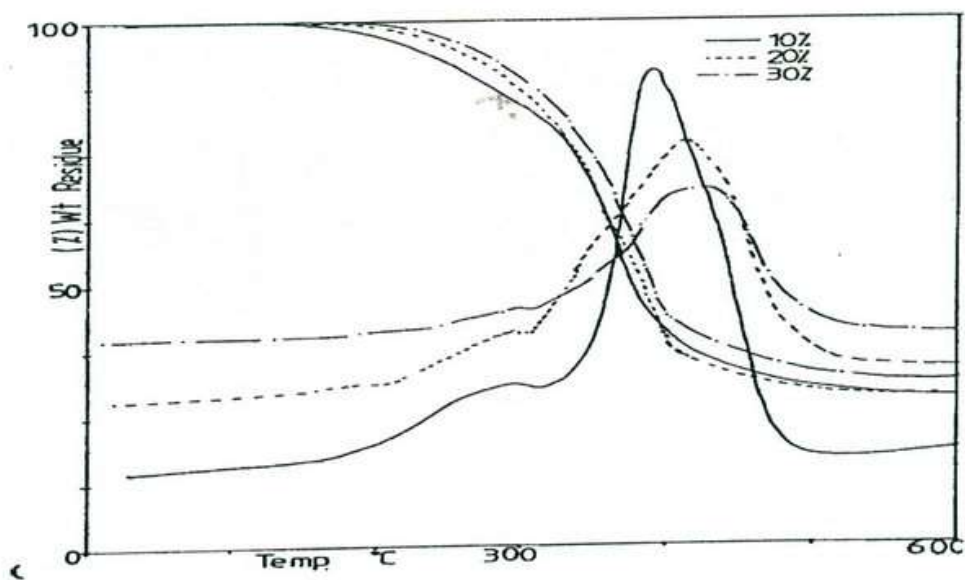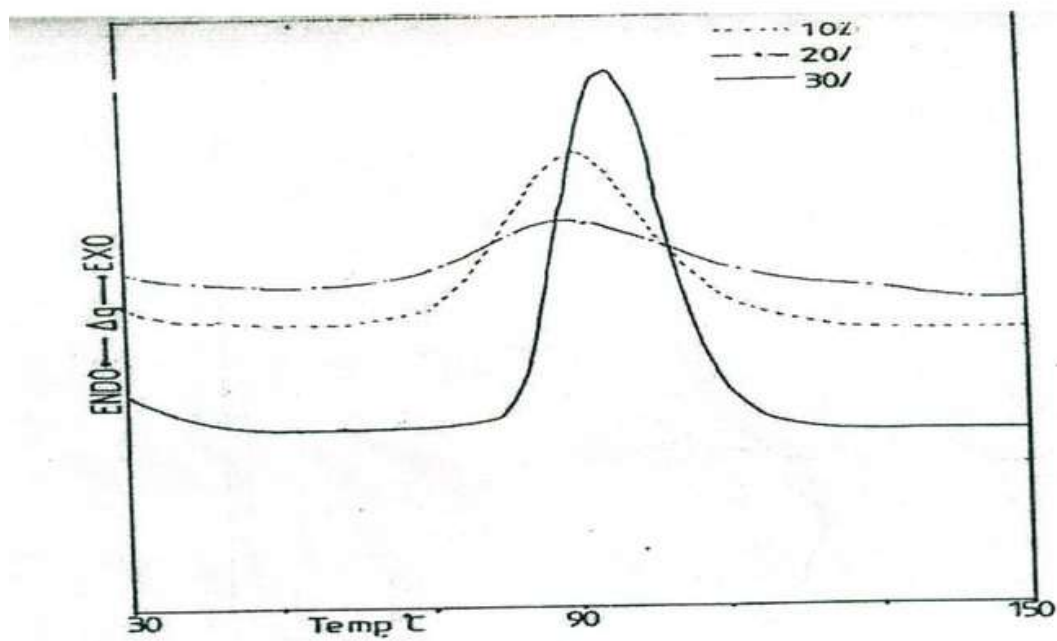Fig. (2): The NMR spectrum of the new acrylate resin

Fig. (3): The DSC thermogram for the new acrylate resin

The thermal stability investigation of the unsaturated polyester IPN's consisting of different wt% from acrylate DDT are shown in fig (3) and thermal stability parameters listed in table (4) showed that the IPN's containing acrylate DDT decomposed at two stages.

Table (4): Thermals stability parameters determined from TGA.

Wt%	Ti	T_{op}		T_f	R %/min	ΔE kj/mole
		a	b			
0	170	-	370	430	7.2	16.6
5	170	-	390	490	6.9	35.8
10	150	290	390	500	6.0	42.5
20	200	290	410	520	6.0	27.6
30	200	295	420	530	5.7	19.4
100	120	-	300	550	7.2	29.0

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