

Hard and Tough Epoxy Resins Modified with Thermosetting Materials

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Abstract

Epoxy resins were modified by some thermosetting materials using unsaturated polyesters which were cured with styrene, MMA, and MA. When unsaturated Polyester (as thermosetting material) was used, and cured with styrene showed better results than acrylic monomers. Thermal stability rised on modification of epoxy resins with unsaturated polyester. The new formulation had converted the epoxy resin from hard brittle material to hard and tough material.

Thermal analysis were studied using (DSC) and physico-mechanical characteristics were measured.

Introduction

Epoxy resins are very important thermosetting polymers because of their wide use as structural adhesives and matrix resins for fiber composites, but cured resins are brittle and have poor resistance to cracking propagation(1).

The toughness of epoxy resins has been increased by blending them with reactive liquid rubbers such as carboxyl terminated butadiene acrylonitrile rubbers(CTBN), or epoxy containing acrylic elastomers(2,3).

Engineering thermoplastics are interesting materials as modifiers for epoxy resin. From the view point of the maintenance of their mechanical and thermal properties.

As alternatives for reactivating rubber to improve the toughness of epoxy resin, many kinds of ductile thermoplastics have been used, and they included poly (ether sulphones)(4,5), poly

(etherimides)(6,7), poly (ether betone)(8,9), poly (phenylene oxide), and aromatic polyesters(11-13).

This work reports the use of thermosetting plastics, namely unsaturated polyester, using styrene, MMA and MA as crosslinking agents.

Experimental Part

- 1) Materials were obtained from their sources in almost highest purity. The epoxy resin was a commercial bisphenol-A, Araldite GY 216 (Ciba-Geigy) unsaturated polyester of phthalic anhydride, and 1,2-Propylene glycol, was kindly offered by That-Al sawari chemical industries-Baghdad.
- 2) The nitrogen gas which was used throughout these experiments to provide an inert atmosphere, was purified from oxygen, carbon dioxide and then dried by passing its stream through a purification column and dedicated drying system.
- 3) Preparation of unsaturated polyester: Propylene glycol (2.2 mole) was heated (80 °C) and stirred under nitrogen: Maliec unhydride (2.0 moles) was added and the mixture was heated to (150°C) for 1hr. Then the temperature was raised to (190°C) over 4 hrs., and it then mentained at this temperatare for 1hr. under vaccume. The temperature was lowered to (170°C). The vacuum was removed and the reaction mixture was permitted to (100°C) after the acid number was determined. About (0.02g) hydroquinon was added as inhibitor.(14).
- 4) Acid number determination
A sample of polyester (1.0g) was weighted to the nearest milligram in (100ml) conical flask, and pure acetone (75ml) was added to dissolve the sample. The mixture was titrated with standard alcoholic KOH solution (0.1N), using phenolphthalene as an indicator. The acid number was calculated as the number of milligrams of KOH per gram of polymer.
- 5) Cross linking of polyester with styrene or methyl methacrylate:
A mixture of polyester at (100°C) and fixed amount of styrene was stirred then the mixture was kept at (25°C), and it was relatively stable at room temperature then stored under nitrogen in a dark bottle. Copolymerization of the solution was affected by adding calculated

system. The mixture was heated to (60°C) and the time in which the mixture formed a hard tough solid was determined.

6) Determination of acetone unextractable material:

A Soxhlet method adopted in ASTM Standard. Accurate weight (0.2g) samples were extracted with acetone for 8 hrs. The samples were dried after extraction in vacuum oven at (50°C) until a constant weight was obtained. The acetone unextractable value (x) was calculated using the following equation:

$$X\% = A/B \times 100$$

Where A = Weight of the dry sample after extraction

B = weight of sample before extraction.

7) Physico-Mechanical properties measurements:-

standard methods were used to obtain most satisfactory results.

8) Thermal analysis of the samples were carried out using Perkin-Elmer-DSC-7 series Thermal analysis system.

Results and Discussion

Epoxy resins are very important thermosetting polymers because of their wide use as structural adhesion matrix resins for fiber composites, but cured resins are brittle and have poor resistance to crack propagation.

The toughness of epoxy resins has been increased by blending them with reactive liquid rubbers(19,18).

Various kinds of ductile thermoplastics have been used as alternatives to reactive rubber for improving the toughness of epoxy resins(17).

In this work, we used unsaturated polyester as modifiers with using styrene, MMA and MA as crosslinks.

Tables (1-5) show the representative results for the modification of the epoxy resins with the polymers mentioned above. When no free radical initiator was used (Table-1), the yield of crosslinked epoxy resin was decreased from 86% to 71%, however on increasing hardening time solidification occurred under the prevailing experimental conditions, increasing the yield again to 83%. (The yield is determined as the percentage of acetone unextracted material).

It can be shown that introducing benzoyl peroxide as initiator for unsaturated polyester crosslinking. The time necessary for hardening was clearly reduced and the yield was essentially the same. This means that crosslinking is absent from benzoyl peroxide. This is

due to thermal crosslinking of polyester, while in the second case, it is due to free radical initiator polymerization.

Results of epoxy resin and unsaturated polyester crosslinking with styrene are reported in Table-3. The yield is increased when unsaturated polyester is introducing beside styrene in the same weight content.

However, on changing the weight ratio of styrene to polyester, excess styrene brought about decrease in yield. This might be due to the high viscosity of such complicated system so that diffusion of monomer to the reactive free radical site will be difficult and residual monomer will remain in the reaction mixture, exerting the same sort of plasticization effect which makes the hardening time longer.

Table (4) shows the results of crosslinking of unsaturated polyester in the presence of styrene as monomer and PMMA as polymerized powder. MMA/PMMA mixture was polymerized to give 100% yield in 24 hrs. polymerization of MMA/Polyester in the presence of PMMA powder, decreased the hardening time and also the yield was decreased to a value around 90%. Results of polymerization in the presence of styrene instead of MMA are reported in table (5). Changing content of PMMA or polymer will tend to decrease the reaction yield, and the result matches the general trend observed in case of preparation of simultaneous interpenetrating network already reported(18).

Differential Scanning Colorimetry (DSC):

Fig -1- A and B represent crosslinking of unsaturated polyester with methyl methacrylat monomer in A and styrene monomer in B. The transition temp. is decreased for the samples cured by PMMA, while it is raised for the samples cured by unsaturated polyester. Also , all is decreased for those samples and this might be due to plasticizing effects of the residual monomer used.

Physico-Mechanical properties:

The measurement of physico-mechanical properties of PMMA alone and brittleness of polymethyl methacrylat is reduced as it is obvious from the values reported for impact strength. The general trend is that as polyester content is increased the impact strength is creased.

The hardness generally decreases profoundly from that of pure PMMA and attain lowest value at (0.75) wt% of unsaturated polyester

content. The same general trend is followed and the results are clear on comparing hardness of pure PMMA with deferent formulation containing styrene unsaturated polyester.

Concerning the difference in values of compression reveal that little deference in values yielded by this test could not indicate special features.

There are some plastics whose tensile strength and compressive load characteristics differ. As an example is polystyrene, which is tougher under compressive load but very brittle in tension(19). Regarding the modification of epoxy resins samples (2,3) in table (8) indicate practically doubling the value of impact strength of pure epoxy resin or introducing either unsaturated polyester alone or polyester together with styrene monomer, it also indicates that the presence of styrene reduced the hardness of the sample in spite of the decreased compression strength.

The hardness of samples modified remained practically the same, this means that the new modification has converted the epoxy resin from hard and brittle material to hard and tough one. That's to say, that the introducing of unsaturated polyesters and MMA/ PMMA converted the epoxy resin from brittle material to atough one only.

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Table (1) Reaction Between Epoxy Resin and Polyester at 90°C

No.	Formula (gm.)	Hardening Time (hrs.)	Yield %
A ₁	Epoxy resin = 0.5 Hardener = 0.05	3.15	86
A ₂	Epoxy resin = 0.5 Hardener = 0.05 Polyester = 0.1	2.30	75
A ₄	Epoxy resin = 0.5 Hardener = 0.05 Polyester = 0.2	2.40	71
A ₅	Epoxy resin = 0.5 Hardener = 0.05 Polyester = 0.3	3.15	83

Table (2) Reaction Between Epoxy Resin and Polyester in Presence of Initiator at 90°C

No.	Formula (gm.)	Initiator Bz ₂ O ₂	Hardening Time (hrs.)	Yield %
A ₆	Epoxy resin = 0.5 Hardener = 0.05 Polyester = 0.1	0.025	-	83
A ₇	Epoxy resin = 0.5 Hardener = 0.05 Polyester = 0.2	0.025	1.45	72
A ₈	Epoxy resin = 0.5 Hardener = 0.05 Polyester = 0.3	0.025	3.0	70

Table (3) Reaction Between Epoxy Resin and Styrene and Polyester in Presence of Initiator at 90°C

No.	Formula (gm.)	Initiator B ₂ O ₂	Hardening Time (hrs.)	Yield %
B ₁	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.05 Polyester = 0.05	0.025	5.30	86
B ₂	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.1 Polyester = 0.1	0.025	3.15	72
B ₃	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.15 Polyester = 0.15	0.025	4.30	83
B ₄	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.025 Polyester = 0.05	0.025	4.30	68
B ₅	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.20 Polyester = 0.10	0.025	4.30	70

Table (4) Reaction of MMA, PMMA and Polyester in Presence of Initiator at 60°C

No.	Formula (gm.)	Initiator B ₂ O ₂	Hardening Time (hrs.)	Yield %
1	MMA = 5.34 PMMA = 0.2	0.025	24	100
1a	MMA = 5.34 PMMA = 0.2	AIBN 0.025	24	93
2	MMA = 5.34 PMMA = 0.15 Polyester = 0.1	0.025	12.10	90
3	MMA = 5.34 PMMA = 0.15 Polyester = 0.25	0.025	15.30	90
4	MMA = 5.34 PMMA = 0.2 Polyester = 0.1	0.025	12.50	91
5	MMA = 5.34 PMMA = 0.15 Polyester 0.75	0.025	12.50	89
6	MMA = 5.34 PMMA = 0.25 Polyester = 0.15	0.025	18.30	88

Table (5) Reaction Between Styrene, PMMA and Polyester in Presence of Initiator at 60°

No.	Formula (gm.)	Initiator Bz_2O_2	Hardening Time (hrs.)	Yield %
1	Styrene = 5.34 PMMA = 0.2	0.025	14	91
2	Styrene = 5.34 PMMA = 0.2 Polyester = 0.1	0.025	19	83
3	Styrene = 5.34 PMMA = 0.20 Polyester = 0.50	0.025	15.0	88
4	Styrene = 5.34 PMMA = 0.25 Polyester = 0.2	0.025	15.30	82
5	Styrene = 5.34 PMMA = 0.15 Polyester = 0.75	0.025	17.20	90
6	Styrene = 5.34 PMMA = 0.20 Polyester = 1.0	0.025	12.10	89
7	Styrene = 5.34 PMMA = 0.15 Polyester = 1.0	0.025	17.0	87
8	Styrene = 5.34 PMMA = 0.15 Polyester = 1.0	0.025	17.15	89
9	Styrene = 5.34 PMMA = 0.2 Polyester = 1.25	0.025	15.30	86

Table (6) Physico- Mechanical Properties of Samples Unsaturation Polyester Cured in the Presence of MMA at 60°C

No	Formula	Initiator Bz_2O_2	Impact strength	Compression Strength Kg/cm ²	Hardness	Yield %	Hardening Time (hrs.)
1	MMA=5.0 PMMA=0.2	0.025	3.0	687.2136	3094.94	100	24
2	MMA=5.0 PMMA=0.2	0.025	1.045	-	-		12
3	MMA=5.0 PMMA=0.2 Polyester=0.25	0.025	3.6	780.924	2119.221	92	15.0
4	MMA=5.0 PMMA=0.2 Polyester=0.1	0.025	-	791.336	1940.117	90	12.50
5	MMA=5.0 PMMA=0.2 Polyester=0.5	0.025	3.8	708.0383	909.006	90	12.10
6	MMA=5.0 PMMA=0.15 Polyester=0.75	0.025	3.9	770.512	1299.878	89	12.50
7	MMA=5.0 PMMA=0.2 Polyester=1.5	0.025	3.5	728.862	2811.033	88	18.45

Table (7) Physico- Mechanical Properties of Unsaturation Polyester Cured in the Presence of Styrene at 60°C

No	Formula	Initiator B ₂ O ₂	Impact strength	Compression Strength Kg/cm ²	Hardness	Yield %	Hardening Time (hrs.)
1	Styrene = 5.0 MMA= 0.2 Polyester=0.25	0.025	3.1	760.099	1515.077	86	19
2	Styrene = 5.0 MMA= 0.15 Polyester=0.25	0.025	2.0	676.801	236.556	82	15.30
3	Styrene = 5.0 MMA= 0.2 Polyester=1.0	0.025	-	749.685	1780.656	89	12.20
4	Styrene = 5.0 MMA= 0.15 Polyester=0.1	0.025	0.5	718.450	282.317	88	17.15
5	MMA=5.0 PMMA=0.2 Polyester=0.5	0.025	-	801.174	1641.842	92	16.15

Table (8) Physico- Mechanical Properties of Epoxy Resins Modified with Acrylic and Styrene Unsaturation Polyester Resins at 90°C

No	Formula	Initiator B ₂ O ₂	Impact strength	Compression Strength Kg/cm ²	Hardness	Yield %	Hardening Time (hrs.)
1	Epoxy resin =0.5 Hardener=0.05	0.025	3.1	666.389	338.386	86	4.15
2	Epoxy resin =0.5 Hardener=0.05 Polyester=0.25	0.025	2.0	208.246	445.105	83	3.15
3	Epoxy resin =0.5 Hardener=0.05 Styrene = 0.15 Polyester=0.15	0.025	-	93.710	443.652	83	3.15

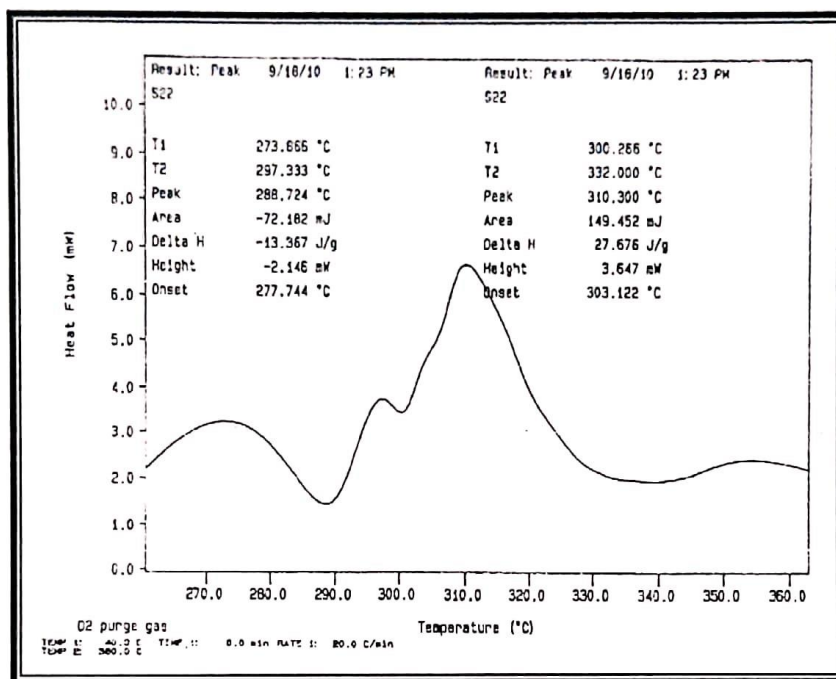


Fig. (1-A): DSC curve MMA/ polyester resin

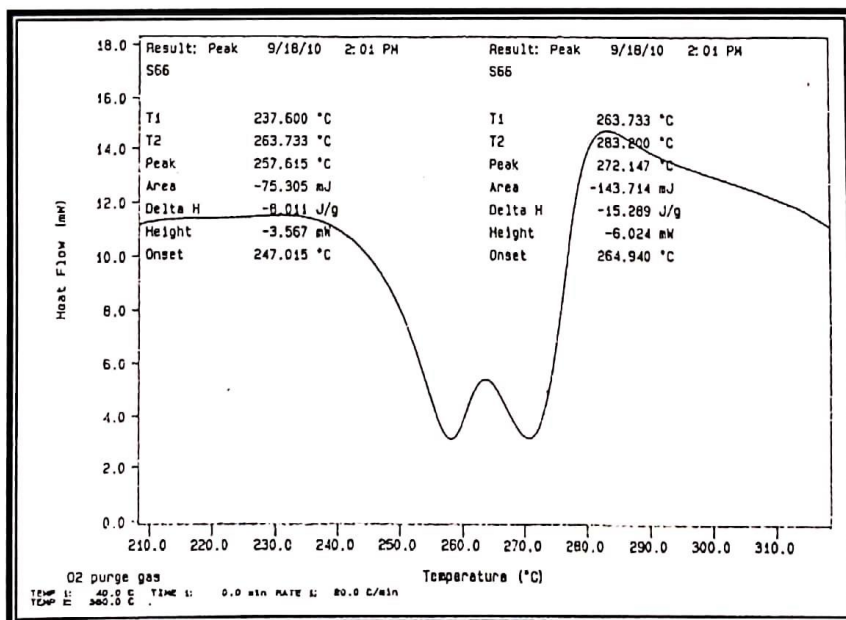


Fig. (1-B): DSC curve for styrene / PMMA/ polyester

راتنج ايبوكسي صلب ومتماسك محوراً بمواد متصلدة حرارياً

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الخلاصة

تم تحويل راتنجات الايبوكسي باستخدام مواد متصلدة حرارياً مثل البولي استرات غير المشبعة وتقسيتها باستخدام مونيترات الستايرين والمثيل ميثاكريلات والميثاكريلات. وكان تأثير مونيتر الستايرين افضل من تأثير المونيترات الاكريلية. وظهرت النتائج زيادة الثبات الحراري جراء استخدام البولي استرات غير المشبعة وتحول الراتنج من كونه مادة صلبة هشة الى مادة صلبة متماسكة. تمت دراسة الخواص الحرارية باستخدام تقنية (DSC) وقيست ايضاً الصفات الفيزيوميكانيكية.