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Toughining of Epoxy-Resins Using Thermoplastic Materials as Modifiers

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Abstracts

Epoxy resins were modified using thermoplastics, such as polystyrene and poly (methylmethacrylate) (PMMA) or their monomers polymerized in situe.

The modifications showed good results specially when (PMMA) was used. Thermal analysis of the modified polymers were studied using (DSC) and other physico-mechanical properties measurement.

Introduction

Most bulk engineering materials are composites of two or more phases dispersed on a microscopic scales to obtain optimum properties.

The strength and toughness of metallic alloys and engineering plastics are achieved by combining high strength phases with tough ductile phases.(1)

Epoxy resins are important thermosetting polymers and they have wide use as structural adhesives and matrix resins for fiber reinforced composite but the curred resins are brittle and have poor resistance to crack propagation.

Previously, there are some researches in which reducing the internal stress by modification of epoxy networks with such a functional liquid rubbers such as caroboxyl terminated butadiene-acrylonitrile compolymer (2). In these cases, the modified epoxy resins had heterogeneous structure that the elastomer dispresed as domains in the continuous phase of epoxy resins(2).

Various kinds of thermoplastics have been used for improving the toughness of epoxy resins, thermoplastics are interestic materials as modifiers for epoxy resins from the view point of the maintainance of mechanical and thermal properties for the matrix resins (3-5).

This paper reports the modification of cured bisphenol-A epoxy resins with poly (methylmethacrylate) and polystyrene obtained by polymerization in situe.

Experimental part

Materials: The following materials were obtained from the sources indicated in their highest purities:-

- Styrene.
- Methylmethacrylate, BDH.
- Poly (methylmethacrylate), BDH.
- Benzoyl peroxide, BDH.
- Azobis – (2-isobutyro nitrile), BDH.
- Cobalt naphthenate 6% cobalt, Fluka.
- Lead naphthenate 24% lead, Fluka.
- The epoxy resins was a commercial bisphenol-A, araldite G4 216 (siba-Geigy) with a weight per- equivalent (WPE) = 187 g/eq. The hardener HY 216, (G.F) (glass Fibers). E. (Woren Roving) (W.R) d. (2-6).

Experimental Techniques

Purification and drying of nitrogen gas: The nitrogen gas that has been used throughout these experiments, to provide an inert atmosphere, was purified from oxygen (O_2) and carbon dioxide and then dried, by passing the gas stream from the cylinder through the purification columns and deticated drying system.

Modification of epoxy resins with MMA, Styrene and other additives: General, method; certain amounts of epoxy resins were placed in beaker and calculated amounts of monomers were then added, followed by initiator, accelator and hardener. The mixture was then stirred until the paste obtained a paste. The paste was passed in a round test tube ($\phi = 1.5$cm) placed in a water bath adjusted to required temperature. The time of hardening was recorded (the details are summarized in the results section).

Determination of gelation time (manual methods): The gelation time of resins was carried out according to British phastic standers committee. Reaction mixture (2.05 gm) was mixed with calculated amount of each of hardener and or initiator or catalyst in a suitable test tube. The mixture was stirred with a rod by moving it incomplete revolution of diameter of the tube over 15 min. until gelation occurs, at prescised temperature (90°C).

Viscosity measurement: The viscosity was measured using ubbelohde suspended level viscometer modified by Ravikov. Flow times were determined at 30 ± 0.1 °C and so the relative viscosity. The viscosity number (reduced specific viscosity) was calculated.

The viscosity of five different concentrations (0.08, 0.06, 0.04, 0.03, 0.2%) were determined and $\eta sp/c$ was then plotted against 'C', a straight line was obtained in accordance with Huggins equation (7).

$\eta sp/c = [\eta] + K\,[\eta]^2 c$

Where $[\eta]$ is the limiting viscosity number.

C, is the concentration in mg/ 100 ml.

K, is the Huggins constant.

Determination of Aceton Unextractable Material

The method used for the determination of aceton unextractable is soxhelet method adopted ASTM standard method. The apparatus is made entirely of glass and designed so that the condensed extracting solvent in contact with the sample is at temperature not much below its boiling point. Accurately, weight (0.2 gm) samples were placed in a filter paper basket and then introduced in the siphon cup of the soxhelet and extracted with aceton for 8 hrs. The samples were dried after the extraction with vacuum over at (50 °C) until a constant weight was attained. The acetone unextratable value (x) was calculated according to the following eqution:

$X\% = A/B * 100$

Where A = weight of dry sample after extraction

B = weight of sample before extraction

Thermal Analysis

Thermal analysis was studied and it was measured using Perkin-Elmer-DSC- 7 series thermal analysis system.

Results and Discussion

Epoxy resins were mixed with styrene monomer in presence of dibenzoyl peroxide as initiator, the results were reported in table (1); when the amount of styrene monomer was increased with a fixed amount of initiator in samples B1 and B2, the yiled was increased while the hardening time was decreased. In samples (C1 & C2), the amount of styrene was fixed and the amount of the initiator was increased led to the increase of the yield while the hardening time still the same, sample (C3) showed almost the same yield and higher hardening time. In table (2), the results of a group of experiments are recorded, mixtures of epoxy resins with MMA or both MMA and styrene at 90 °C in deferent ratio. When a mixture of MMA and PMMA was initiated with benzoyl peroxide, the yield was 100% over 24 hrs. The replacement of styrene (in the same amount) by MMA the yield decreased to 91% and the hardening time became 14 hrs. Samples 3 and 4 decleared the effect of using styrene instead of MMA, leading to higher yield with the same hardening time, while sample 5 in which, both styrene and MMA were used, the yield was almost the same, but the hardening time was decreased to 3hrs.

The molecular weight of PMMA was determined by measuring the intrinsic viscosity in acetone using Mark-Houwink equation,

$X\% = A/B * 100$

Where A = weight of dry sample after extraction
B = weight of sample before extraction.

$[\eta] = K\,[M]^{\alpha}$ where $K = 6.4 \times 10^{-5}$

$\alpha = 0.71$ at 30 °C

The value of $Mwt = 1.63 \times 10^{5}$, this value matched with typical values known for standard poly(methyl methacrylate) (6).

Effect of Co-catalyst

The use of a combination of a peroxide and suitable promoter (Co-catalyst), e.g cobalt naphthenate, lead naphthenate and others may led to maximizing molding operation.

A drier is an additive to coatings which accelerates or controls the hardening of applied films by catalyzing the oxidative polymerization of oleoresins vehicle component(8)

Tables (3-7) show the effect of mixed peroxide, metal naphthemates with styrene and MMA. in addition to cobalt naphthenate in a very small concentration, the drying time almost the same. However, on increasing the concentration of cobalt naphthenate from 0.03 gm to 0.06 gm the yield was increased. Using lead naphthenate instead of cobalt naphthenate at the same amount of lead naphthanote. table (4).

Table (5) gives the results of trials made to use lead and cobalt naphthenates at one time. However, theresults obtained indicated the occurrence of anatogsim and the hardening time increased, while the yield was still the same. In table (6), peroxide concentratio increased from 0.03 to 0.04 using a mixture of cobalt and lead naphthenates as driers, the hardening time increased to 9 hrs. While the yield still the same. Cobalt in oleo resinous paint is considered as top-drying metal because it operates at the film surface and induces the initial tack free film state film hardening cobalt possibly acts as oxygen. carrier thereby aiding in the stabilization of the biradical from the oxygen molecule. This might be accomplished by the association of O_2 molecule with the unfilled orbitals of the transition metals thereby enhancing its activity during the attack at an activated methylene group and it may be illustrated as follows:

$$M + .O^{\cdot} + O^{\cdot} \rightarrow M - O - O^{\cdot} \xrightarrow{\text{-CH2-CH=CH-}} \text{M-O-OH} + \text{-}^{\cdot}\text{CH-CH = CH-}$$

It was reported by Martin (9) that the hydroperoxide ROOH may dissociate into free radical which may lead to certain oxidation reactions which frequently involve chain scission and yield valatile decomposition products such as forming an acetic acid, aldehyds and related compounds.

The last product will combine with epoxy hardener forming salts which no longer can cure epoxy resins consequently, and the hardening time will increase, and that explained makes it obvious why cobalt naphthenate and lead naphthenate accelerate hardening of polyester and polymerization of vinyl monomers when they are alone but cannot do so in the presence of epoxy-hardener system. The same results are obtained on using AMIBN as initiator. This again proves the above conclusion when MMA is used in presence of both lead and cobalt naphthenates in lower concentrations.

Deferential Scanning Calorimetery (DSC): DSC-Thermograms of some mixtures are showed in figs. (1-4) using perkin-Elmer-7-series thermal analysis system. Fig (1) represents poly(methylmethacrylate) prepared alone using benzoyl peroxide as initiator. Fig.(2) shows thermogram of epoxy resin cured with hardener alone, while figs. (3,4) show the thermogram of the mixture of epoxy resin and styrene alone or with MMA. On using styrene instead of MMA, the starting and end flow temperatures are still lower. The value of ΔH is also lower. This difference might be due to plasticizing effects of the residual monomers used(10).

Conclusion

All the modified resins processes gave good yields, and when benzoyl peroxide was used as initiator mode the solidified time shorter.

Acrylic monomers gave better results than that of styrene monomer, and the polymerization conditions used in modification process produced highly viscous polymer by using methylmethaacrylate monomer.

The reduced accelerators (lead and cobalt naphthanate) had not any effect on the yield of the products.

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Table (1) Curing of epoxy resin in the presence of styrene and initiator at 90°C

No.	Formula (gm.)	Initiator Bz_2O_2	Hardening Time (hrs.)	Yield %
B_1	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.1	0.025	5.3	76
B_2	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.2	0.025	4.45	83
C_1	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.3	0.030	3.45	60
C_2	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.30	0.035	3.45	75
C_3	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.30	0.040	4.10	73

Table (2) Curing epoxy resin in the presence of methyl metacrylate (MMA) or both (MMA) and styrene at 90°C

No.	Formula (gm.)	Initiator Bz_2O_2	Hardening Time (hrs.)	Yield %
1	MMA= 5.34 PMMA= 0.2	0.025	24	100
2	Styrene= 5.43 PMMA=0.2	0.025	14	91
3	Epoxy resin = 0.5 Hardener = 0.05 MMA= 0.2	0.030	4.30	77
4	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.2 MMA= 0.1	0.03	3	77
5	Epoxy resin = 0.5 Hardener = 0.05 Styrene= 0.15		4.5	80

Table (3) Curing between epoxyi resin styrene Polyester and MMA in presence of Initiator at 90°C

No.	Formula (gm.)	Initiator $B_{Z2}O_2$	Accelerator	Hardening Time (hrs.)	Yield %
D_1	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3	0.040	Copaltnaphthenate 0.03	4.25	71
D_3	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 Polyester = 0.10	0.030	Copaltnaphthenate 0.03	4.15	77
D_2	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3	0.040	Copaltnaphthenate 0.06	4.25	89
D_6	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 Polyester = 0.10	0.030	Copaltnaphthenate 0.06	5.0	78
D_4	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 Polyester = 0.10	0.040	Copaltnaphthenate 0.06	4.15	71

Table (4) Curing between epoxy resin, styrene and MMA in presence of initiator and accelerator at 90°C

No.	Formula (gm.)	Initiator $B_{Z2}O_2$	Accelerator	Hardening Time (hrs.)	Yield %
D7	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3	0.040	Leadnaphthenate 0.03	6.0	58
D8	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 Polyester = 0.10	0.030	Leadnaphthenate 0.03	3.0	61
D9	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3	0.030	Leadnaphthenate 0.03	3.0	63

Table (5) Reaction between epoxy resin, styrene and MMA in presence of initiator and accelerator at 90°C

No.	Formula (gm.)	Initiator $B_{Z2}O_2$	Accelerator	Hardening Time (hrs.)	Yield %
D14	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.2 MMA= 0.1	0.03	Leadnaphthenate 0.15 Copaltnaphthenate 0.15	6.45	73
D15	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 MMA= 0.2	0.03	Leadnaphthenate 0.15 Copaltnaphthenate 0.15	6.45	73
D16	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 MMA= 0.15	0.03	Leadnaphthenate 0.15 Copaltnaphthenate 0.15	6.45	77

Table (6) Reaction between epoxy resin, styrene and MMA in presence of initiator and accelerator at 90°C

No.	Formula (gm.)	Initiator $B_{z2}O_2$	Accelerator	Hardening Time (hrs.)	Yield %
D19	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.15 MMA= 0.15	0.040	Leadnaphthenate 0.15 Copaltnaphthenate 0.15	9.0	74
D18	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.1 MMA= 0.2	0.040	Leadnaphthenate 0.15 Copaltnaphthenate 0.15	9.0	75
D16	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3 MMA= 0.15	0.030	Leadnaphthenate 0.15 Copaltnaphthenate 0.15	8.0	68

Table (7) Reaction between epoxy resin, styrene and MMA in presence of initiator and accelerator at 90°C

No.	Formula (gm.)	Initiator $B_{z2}O_2$	Accelerator	Hardening Time (hrs.)	Yield %
D10	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.3	0.040	Leadnaphthenate 0.06 Copaltnaphthenate 0.06	3.50	58
D11	Epoxy resin = 0.5 Hardener = 0.05 Styrene = 0.1 MMA= 0.2	0.030	Leadnaphthenate 0.06 Copaltnaphthenate 0.06	3.50	73

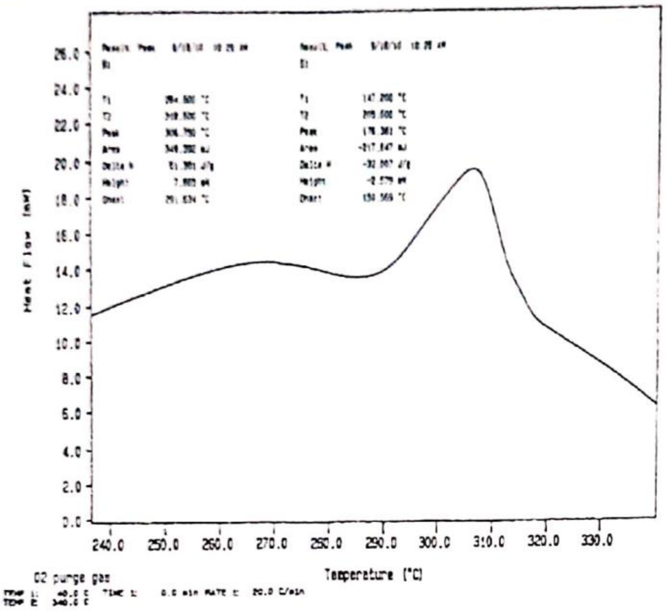

Fig. (1) DSC curve for MMA/ PMMA

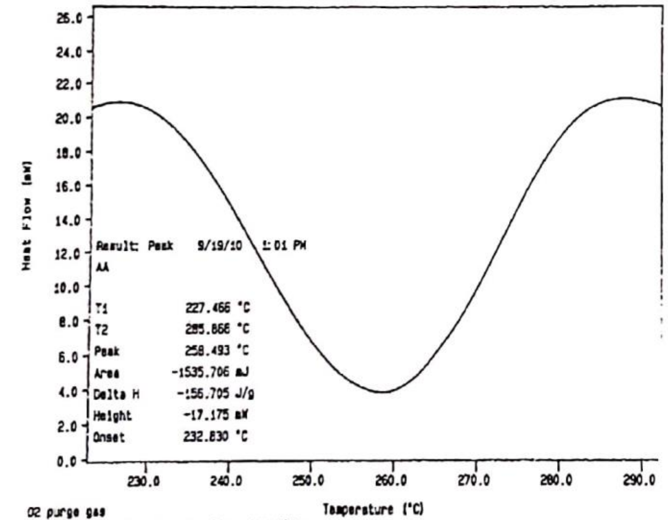

Fig. (2) DSC curve for epoxy resin

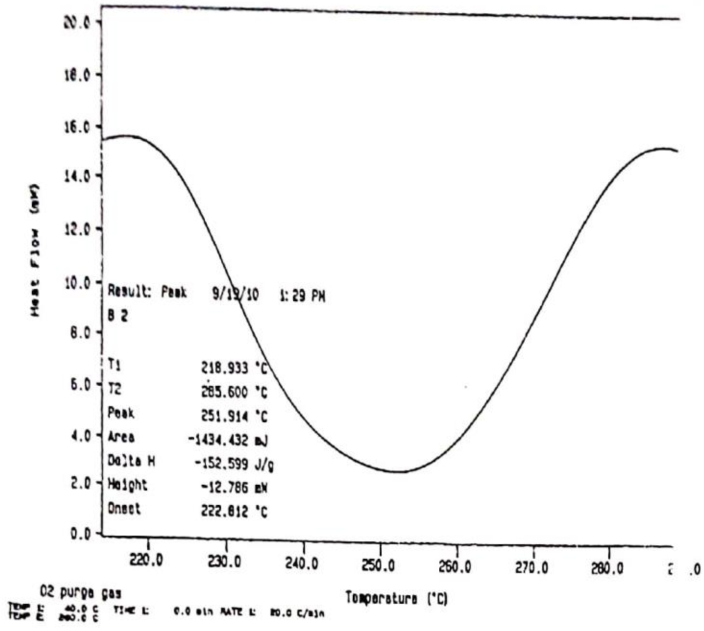

Fig. (3) DSC curve for MMA/ PMMA

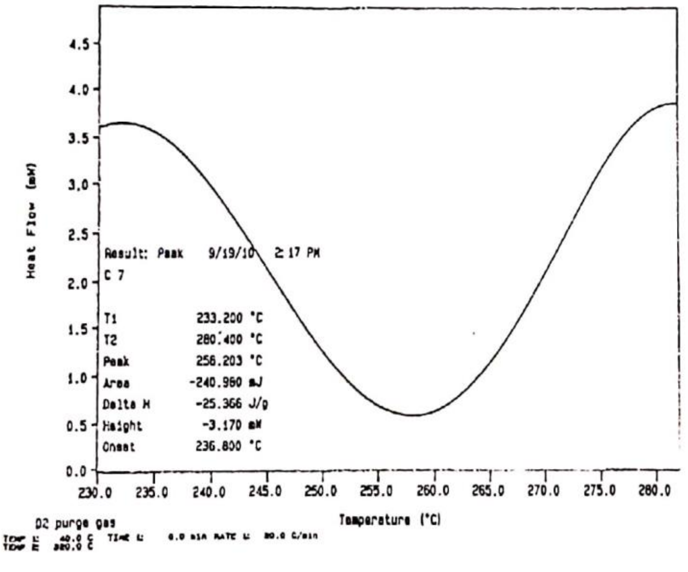

Fig. (4) DSC curve for epoxy/ MMA

تحوير راتنجات الايبوكسي باستخدام مواد مطاوعة للحرارة

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الخلاصة

تم تحوير راتنجات الايبوكسي باستخدام مواد مطاوعة للحرارة مثل البولي ستايرين والبولي مثيل ميثاكريلات او من خلال بلمرة مونيميراتها في الموقع، اعطت عملية التحوير نتائج جيدة ولاسيما عند استخدام (PMMA). تم دراسة الخواص الحرارية للبموليمرات المحضرة باستخدام تقنية (DSC) وكذلك تمت دراسة خواصها الفيزيو- ميكانيكية.