SYNTHESIS AND CHARACTERIZATION OF SOME MODIFIED EPOXY RESINS WITH FATTY ACIDS

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Abstract :

Some modified epoxy resins were prepared from the reaction of epoxy resin with some fatty acids(palmitic acid, stearic acid, oleic acid)in the presence of para-toluene Sulfonicacid at low temperature ranging between 70,90C◦ and at high temperature ranging between 280,300C◦

All the epoxy modifier were characterised by IR and acid value AV.
The mechanical properties (Hardness, Impact strength, Elongation, Tensile strength) and thermal stability (TGA)were studied.

The mechanical properties of modified are lower than unmodified polymers, but Oleic acid was the best of all. The thermal stability was decreased according to

below.(Stearic acid>Palmatic acid>Oleic acid).

INTRODUCTION:

The epoxy resin are of the most familiar thermosetting resins due to their wide range application mainly as electrical insulation, protective coating and binder for compositing materials with different types of reinforcing fibers as glass fibers, carbon fibers…etc.[1]

Thousands of patent have been registered in the field of epoxy resins modification[2] .e.g. increasing the reactivity(enhancing the epoxy equivalent),improving the curing characteristics developing new photo cationic curing agent…etc. [3]

The curing of epoxy resins is often brittle with poor resistance to crack propagation.[4]

The toughness of epoxy resins has been prepared as flexible epoxy resins or flexible curing agents for epoxy resins. [5]

Epoxy resins reactant with fatty acids were used increasingly popularly as synthetic coating for both air-drying and baking finishes. However, almostly no thing published on using epoxy resins ester has had hard tough plastic material. [6]

The aim of the present work is to study the possibility, improving the toughness of epoxy resins through its reactions with fatty acids.

EXPERIMENTAL:

I-Instruments

1- Infra-red spectra photometer (IR)

The IR spectra of the modified and unmodified epoxy resins were recorded by Unicom sp3-100 spectra photometer.

2-Thermogravemetric analysis (TGA).

Stanton record ft TG-760 series to obtain the above thermo grams.

The rate of heating was 20°C/ min and the atmosphere was oxygen

3-Hardeness

The hardness tester used was H.B Brinell, west Germany. The specimen dimension is as fallows:

Cylinder of length = 2.5Cm

Diameter = 1.25Cm

4-Impact Strength.

Sharpe Impact tester,:

II-materials:

1-Epoxy resin

Was a commercial Bis phenol A Araldite GY 216 (Ciba-Gig) with a weight per equivalent, WPE = 187 gm/eq, the hardener

2- (K. F) Kevlar fibers- PR16; formulated aromatic amine: D-49-woven Roving. DuPont

III-preparation

preparation of esterified of fatty acids with epoxy resins:

In erlenmeyer flask was put 10gm of epoxy resin with (2- 10gm) of fatty acids,0.2gm p-toluene sulfonic acid was used as catalyst.The mixture was heated on water bath for 3-5 hrs. The esterified was prepared at high temperature (180-200C°) in the same way as low temperature.

Determination of gelation time (manual method)[7]:

This method has been carried out according to the direction of the British plastic standards committee. It is one of a series of methods of determination of gelation time of resins.

To (2.25) gm of reacting mixture was added, to a calculated a mount initiator and. Maintain the test tube content at the prescribed temperature, place the stirring rod in the resin mixture and stir it by moving the rod one complete revolution of the diameter of the tube every 15 mins until gelation occurs.

Determination of acetone unextractable material(8):

The method used for the determination of acetone unextractable matter is the soxhlet method adopted in ASTM standard method. The apparatus is made entirely of glass and

designed so that the condensed extraction, solvent in contact with the sample at a temperature not much below its boiling point, atypical amply.

Accurately weight (0.2gm) samples were placed in a filter paper basket and then introduced in the siphon cup of the soxhlet and extracted with acetone for 8hr to separate experiments

The sample was dried after extraction in vacuum oven at 50C°. Constant weight is attained. The acetone unextractable value (X) was calculated by the fallowing equation.

$$X\% = \frac{A}{B} \times 100$$

where

A=Wight of sample dry after extraction

B=weigh sample before extraction.

IR Spectrophotometer:

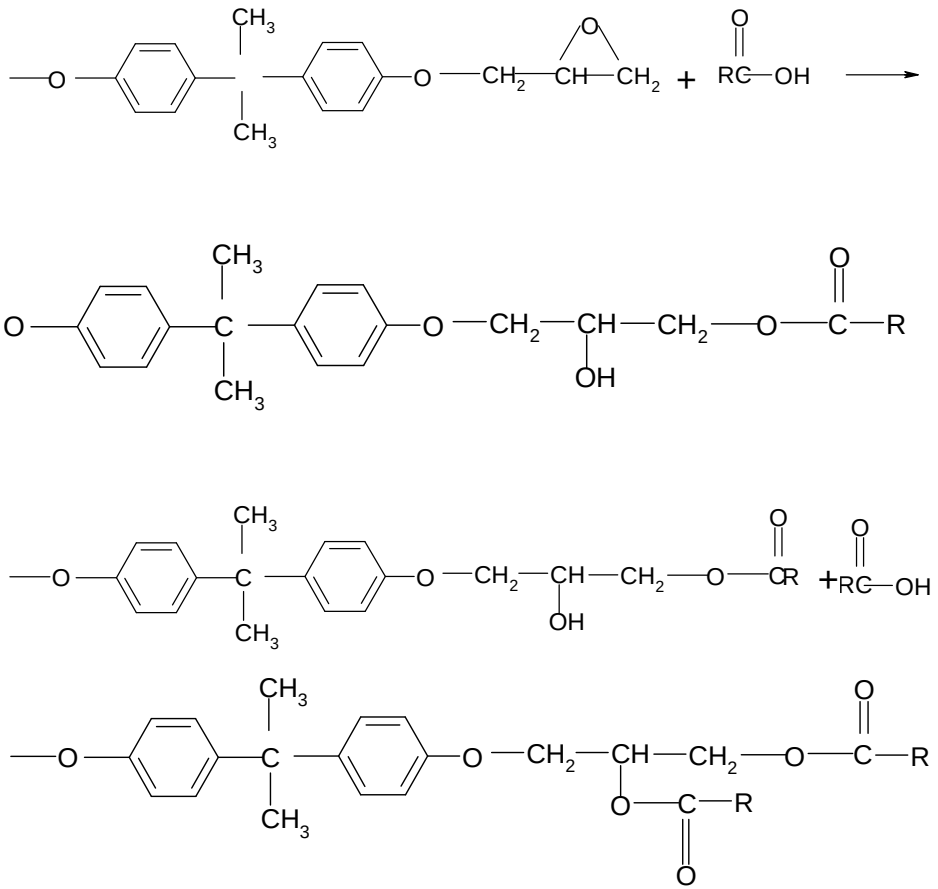
The IR spectra of the modifier and unmodifier epoxy resins were recorded the most important characteristic bands observed in the spectra are listed in Table(9)And Figs(1,2)

Acid Value(AV):

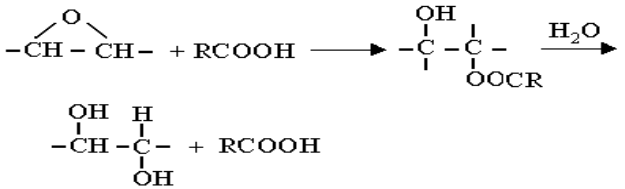
The acid value of modifier epoxy resins which represent the degree of esterificition to acids was recorded. The data of A V are listed in Table(10)

RESULT AND DISCUSSION

The esterified of fatty acids with the epoxy resins terminal groups or pendant hydroxyl sits on the polymer chain can be expressed by the equations[9]:



An important secondary reaction is the acid catalyzed opening of epoxide groups [11]



Esterification of epoxy resins were carried out using Palmatic acid, Stearic acid, and Oleic acid in the presence of P-toluenesulfonic acid at low temperatures 70,90 C◦ with or without initiator.

Gelatin time and acetone in extracted materials were measured in the presence of hardener.

Effect initiators(12)

At addition of initiators to reactions, acetone unextracted materials was increased profoundly and gelatin time was decreased, when using Palmatic acid and this is due to cross-linking initiated by peroxide free radicals. The data obtained are listed in Table(I). Runs carried out in presence of peroxide initiator at temperature less than 90C°, do not give rise to sensible increase in acetone unextracted materials but in the oleic acid. The gelatin time increased because reaction of oxygen with unsaturated bounds gives rise to cyclic peroxide. These cyclic peroxides are relatively stable at the temperature at which the reaction is carried out and will minimize cross-linking reaction and hence decrease percentage acetone unextrated material. The data obtained for oleic acids are listed in Tables(4,5)

Effect of Temperature:

In palmatic acid when temperature increased the gelatin time was increasing and percentage acetone unextracted material was decreasing this attributed to secondary reaction Table(1) . In oleic acid, increase 0f temperature was decreasing gelatin time and increasing acetone un extracted materials, that attributed to cyclic peroxide was formed. These cyclic peroxides are relatively stable at the temperature at which the reaction is carried out and will minimize crosslinking reaction and hence decrease percentage acetone unextrated material.The data for oleic acid are listed in Tables(4,5) Put at high temperature between (280-300C°).In Table(3) the solidification occurs irrespective to the absence of hardener and initiator. However, it is difficult to accept the product for application since the resin color was very dark.

Thermal analysis[12] :

The thermal analysis characterization of modified and unmodified epoxy resins were investigated on StanTom Redecorate TG-790Series, on heating war rate of 200c°/min in presence oxygen. The typicals of thermo grams are shown in Fig(3,4) and the result are shown in Table (8). The Table (8)showed that the stability to modified and unmodified of epoxy resins increased while chain length of the modified were increasing and decreasing percentage of fatty acids but in the unsaturated of fatty acids decreased stability of the modified epoxy resins .

Mechanical properties[14] :

The mechanical properties of modified and unmodified epoxy resins were investigated by measurhng of (tensile strength,

elongation, Impact strength and hardens) according to the Society of Plastic Industry (SPI). These properties were measured with ore without used the Kevlar fiber

Tables(6,7) show that physico mechanical properties of modified are lower than unmodified epoxy resins. This was attributed to secondary reactions but the modified with oleic acid which is along chain unsaturated fatty acid and give rise to best modification properties, owing to its flexibility and ability of cross-linking. These properties were improved when using kevlar fiber as reinforcement because reinforcement improve the ratio of strength to density, and stiffness to density, increase resistance to corrosion, fatigue, creep and reduce the coefficient of thermal expansion

Table (1): reaction of epoxy resin with Palmitic acid in absence of initiator.

sample	N.O	Wt of palmitic Acid, gm	Wt of epoxy resin, gm	Wt of hardener, gm	Gelation time, hr	TC°	Acetone unextracted materials wt%
I	1	0.2	0.5	0.125	7	70	74.75
	2	0.2	0.5	0.150	7	70	68.26
	3	0.2	0.5	0.175	7	70	44.87
II	4	0.3	0.5	0.125	7	70	53.43
	5	0.3	0.5	0.150	7	70	72.82
	6	0.3	0.5	0.175	7	70	66.02
I	1	0.2	0.5	0.125	4	90	65.68
	2	0.2	0.5	0.150	4	90	54.63
	3	0.2	0.5	0.175	4	90	89.95
II	4	0.3	0.5	0.125	4	90	53.58
	5	0.3	0.5	0.150	4	90	56.65
	6	0.3	0.5	0.175	4	90	65.00

Table (2): reaction of epoxy resin with palmitic acid in presence of initiator at 90C°

Weight of Epoxy, gm	Weight of acid, gm	Weight of hardener, gm	Weight of initiator, gm	Gelation time, hr	Aceton unextracted material wt %
0.2	0.5	0.150	0.010	2.5	99.916
0.2	0.5	0.150	0.015	2.5	99.514
0.2	0.5	0.150	0.02	2.5	85.14
0.2	0.5	0.150	0.025	2.5	90.19
0.2	0.5	0.150	0.03	2.5	91.00
0.2	0.5	0.150	0.035	2.5	92.78

Table (3): reaction of epoxy resin with Stearic acid at high temperature.

NO.	Wt of stearic acid, gm	Wt of epoxy resin, gm	TC°	Gelation time, hr	Acetone un extracted materials wt%
1	0.1	0.5	280-300	4	90
2	0.2	0.5	280-300	4	72
3	0.3	0.5	280-300	4	46
4	0.4	0.5	280-300	4	35
5	0.5	0.5	280-300	4	-

Table (4): reaction of oleic acid with epoxy at 70Cº time of esterification = 5hrs

No	Wt of Oleic acid	Wt of epoxy, gm	Wt of hardener, gm	Wt of initiator, gm	TCº	Gelation time, hr	Acetone unextraxted materials wt%
1	0.11	0.5	0.175	0	90	1.5	97.964
2	0.22	=	=	0	=	2	84.519

3	0.33	=	=	0	=	3	63.00
4	0.44	=	=	0	=	3	52.195
5	0.55	=	=	0	=	3	61.057
6	0.11	=	=	0.020	=	1.5	97.044
7	0.22	=	=	=	=	2	83.30
8	0.33	=	=	=	=	3	77.722
9	0.44	=	=	=	=	3	47.722
10	0.55	=	=	=	=	3	54.761

Table (5): reaction of epoxy resin with oleic acid at different temperature.

No	Wt of epoxy resin, gm	Wt of oleic acid	Wt of hardener, gm	TC°	Gelation time, hr	Acetone unextraxted materials wt%
1	0.5	0.11	0.175	90	4	100
2	0.5	0.22	0.175	90	4	98.03
3	0.5	0.33	0.175	90	4	65.17
4	0.5	0.44	0.175	90	4	62.17
5	0.5	0.55	0.175	90	4	55.77
1	0.5	0.11	0.175	70	4	100
2	0.5	0.22	0.175	70	4	95.02
3	0.5	0.33	0.175	70	4	66.66
4	0.5	0.44	0.175	70	4	59.40
5	0.5	0.55	0.175	70	4	41.37
1	0.5	0.11	0.175	60	6.5	97.02
2	0.5	0.22	0.175	60	6.5	66.91
3	0.5	0.33	0.175	60	6.5	65.91
4	0.5	0.44	0.175	60	6.5	57.63
5	0.5	0.55	0.175	60	6.5	40.53

Table (6): physico mechanical properties of epoxy resin and epoxy resin modified with fatty acids in absence Kevlar fibers.

Properties	Epoxy resin	Palmitic Acid 20%	Palmitic Acid 40%	Oleic Acid 20%	Oleic Acid 40%	Stearic Acid 20%
Impact Kg/cm	441.0	210.7	220.5	245	392	147
Hardeness HBR	174.7	89.13	52.02	41.93	109.43	45.164
Tensile strength Kg/Cm2	537.6	417.9	328.2	221.2	437.9	54.3
Elongation%	18	16.3	17.3	25	31.6	6.16

Table (7): physico mechanical properties of epoxy resin and epoxy resin modified with fatty acids in presence of Kevlar fibers

Properties	Epoxy resin	Palmitic Acid 20%	Palmitic Acid 40%	Oleic Acid 20%	Oleic Acid 40%	Stearic Acid 20%
Impact Keg/cm	7105	1078	1176	980	6468.0	2254.0
Hardness HBR	555.9	23802	305	127.4	103.86	190
Tensile strength Kg/Cm2	629.2	-.	515.8	515.3	534.5	-
Elongation%	18.5	-	20	20.8	25	-

Table (8): Thenmogravimetry of modified epoxy resin.

samples	Original weight	Weight loss%									
		1st		2nd		3d		4th		At Tmax	
		W_1%	TC^o	W_2%	TC^o	W_3%	TC^O	W_4%	TC^o	w_m%	T_m
Epoxy resin	6.44	2.42	114	13.04	309	65.2	622	-	-	99.2	1000
Stearic acid 20%	5.67	0.102	107	37.03	392	80.07	632	-	-	99.8	800
Oleic acid	5.15	0.97	107	25.24	325	75.84	680	-	-	100	800
Palmitic acid 20%	7.49	0.12	110	21.76	320	76.36	590	-	-	99.59	722

Palmatic acid 40%	6.46	0.99	107	7.85	248	27.36	320	80.94	593	96.6	713
Oleic acid 40%	5.42	0.99	107	32.65	320	78.53	597	-	-	92.6	685

Table (9): characteristic bands and their locations for the epoxy resin and modified.

umber) cm^{-1}				
	$-CH_2-$	C=C O	C-O-C	-C=O
———	2950-3050(sh)	———	1250	1680(sh)
550(br)	———	1470(sh)	1450	1720(sh)
———	2900-3100(sh)	1575(sh)	1210(sh)	1700(sh)
000(br)	2900-3050(sh)	1650(sh)	1300(sh)	1750(sh)
———	2980(sh)	1560(sh)	1200(sh)	———

Table (10): A.V of reaction of palmatic acid and oleic acid

Palmitic acid		**Oleic acid**	
Time, min	A.V	Time, min	A.V
15	140.27	120	117.83
30	132.44	180	112.22
45	112.22	240	109.41
60	100.99	300	106.61
75	84.1	360	103.803
90	81.35	-	-

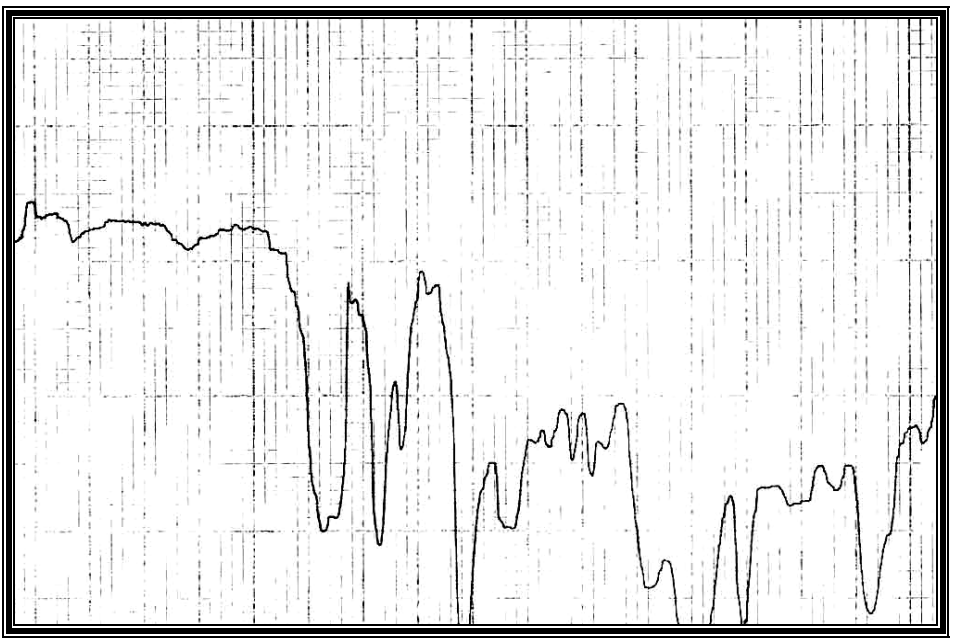


Fig.(1) IR Specrum of Modified Epoxy Resin With Oleic Acid

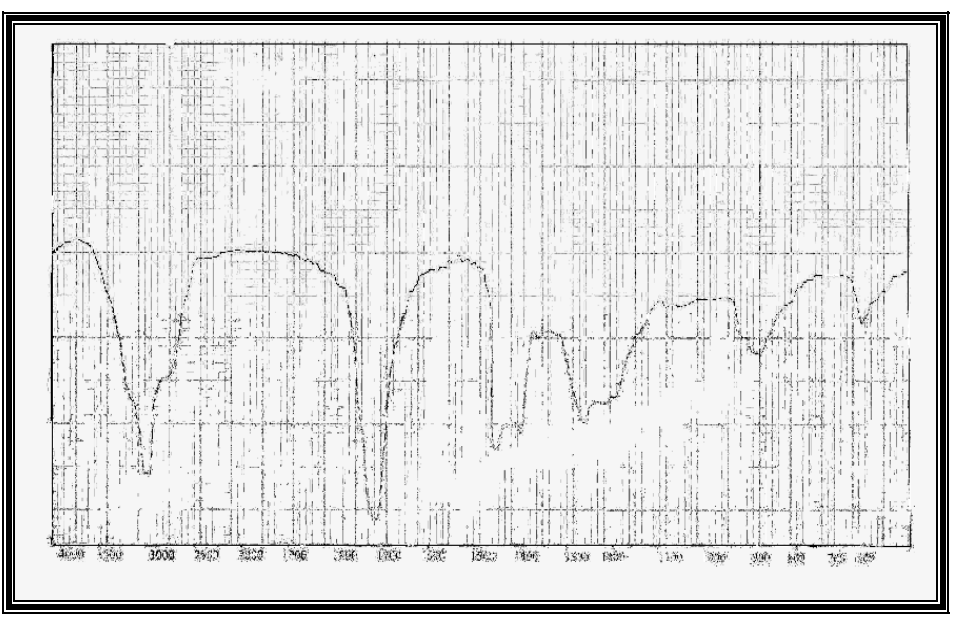


Fig.(2) IR Specrum of Oleic Acid

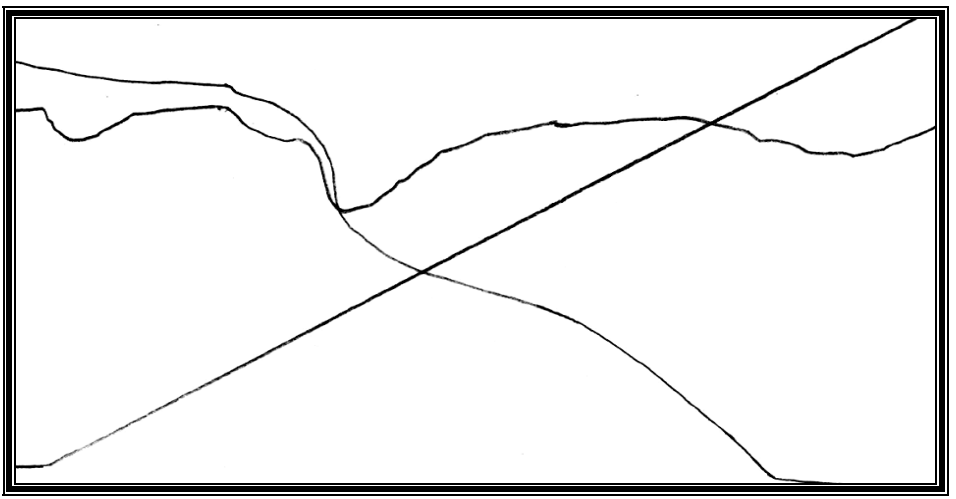


Fig (3) Thermogravimatry of Modified Epoxy Resin With palmatic Acid 20%

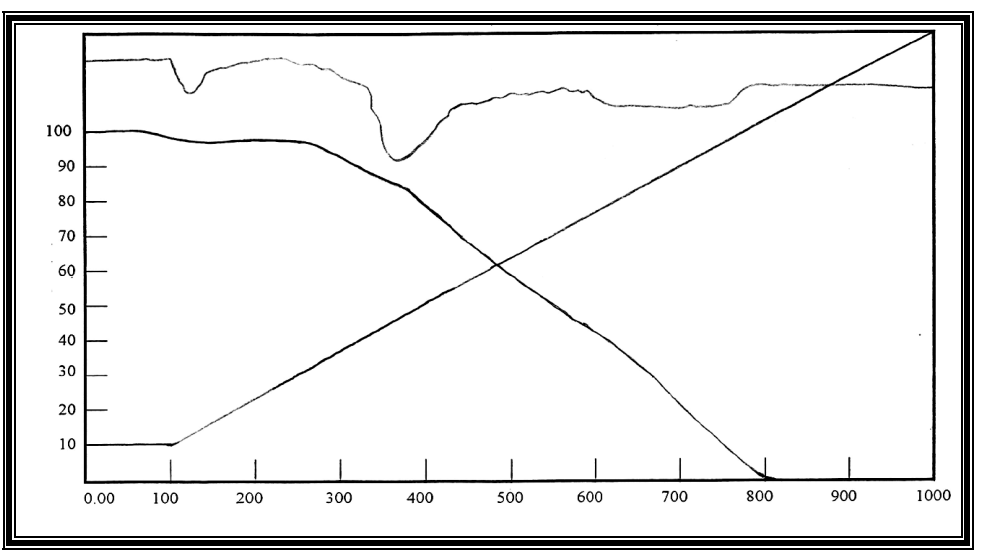


Fig (4) Thermogravimatry of Modified Epoxy Resin With Oleic Acid 20%

Conclusion:

1-Esterification of epoxy resins with fatty acids (palamatic,stearic, and oleic) were Studied in the presence of P-toluensulfonic acid as catalyst at low temp between(70,90c) and at high temp between(280,900c)

2-estrified epoxy resins with palmatic, oleic and stearic were giving increasing of gelation time an decreasing of acetone unextracted materials witch reversed at high temp(70-90c) . at high temp(208-300) the gelation time and acetone unextracted materials were getting without using of initiator or hardener but the product wase very dark

3-The initiator was decreasing gelation and increasing acetone unextracted materials with saturated fatty acids and but that reversing in oleic acid

3-The thermal stable for all acids modifier was increasing during the increase of chain length of acid and decreased percent of acid but it decreased was unsaturated of acid

4-The mechanical properties of oleic acid are better than of palmatic and stearic. This attributed to duple pond in oleic acid

5-Whenwe used the Kavelar fibers the mechanical properties were improving

الخلاصة :

تحضير ودراسة بوليمرات محورة من تفاعل راتنجات الايبوكسي مع بعض ألا حماض الدهنية . تم تحضر هذه الراتنجات من تفاعل راتنج الايبوكسي مع بعض الأحماض الدهنيية(حامض الاستيريك، البلمتيك،الاوليك، السيناميك)في وجود الباديات أو في غيابها،عند درجة حرارة منخفضة تتراوح بين (60,90درجة) ودرجة حرارة عالية تتراوح بين(280,300درجة).

تم تميز البوليمرات المحورة باستخدام أطياف الأشعة تحت الحمرا وكذلك قياس القيمة الحمضية لها تمت دراسة الخواص الميكانيكية باستخدام أليات الكفلر وبدون استخدامها، ولوحظ أن الخواص الميكانيكية للمحورات اقل منها للايبوكسي لكن التحوير بحامض الاوليك هوافضلها على الإطلاقوانه عند استخدام الياف الكفلر تتحسن الخواص الميكانيكية بدرجة كبيرة جدا .

تمت دراسة الاستقرار الحراري لهده البوليمرات ووجد أنها مستقرة حراريا وان الاستقرار يزداد بزيادة طول السلسلة ،قلة نسبة الحامض ألدهني ويقل بوجد الرابطة غير المشبعة

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