The Iraqi Journal For Mechanical And Material Engineering, Vol.10, No.2, 2010

IMPACT MODIFIER OF EPOXY RESIN WITH CITRACONICIATED POLYBUTADIENE AS TOUGHENING AGENT

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ABSTRACT:

The impact strength of epoxy resin based on diglycidyl ether of bis phenol-A- with citraconiciated polybutadiene were investigated. The polybutadiene citraconiciated by reaction with citraconic anhydride and benzoyl peroxide as initiator. The percent citraconiciation was 10%.

In the present work citraconiciated polybutadiene was used as impact modifier for epoxy resin. The percentage of the blend between citraconiciated polybutadiene and epoxy resin was (5, 7.5, 12.5, and 20%) while the amine hardener of the epoxy resin was added at a ratio of 1 part amine to 3 part epoxy.

Keywords: epoxy resin citraconiciated polybutadiene, impact strength

الخلاصة:

تم في هذا البحث تحضير بولي بيوتاداين بمجاميع من الستراكونيك بنسبة 10% وذلك بمفاعلة البولي بيوتاداين مع الستراكونيك اللامائي بوجود بيروكسيد البنزويل كبادئ للتفاعل. تم أستخدام البولي بيوتاداين المطعم بالستراكونيك كمحسن لقوة الصدم للأيبوكسي بعد أن مزج مع اللأيبوكسي بالنسب (5 ، 7.5 ، 12.5 ، 20 %) بينما كانت نسبة المصلب الأميني الى اللأيبوكسي هي جزء واحد من الأمين وثلاثة أجزاء من الأيبوكسي.

أظهرت النتائج تحسنا" واضحا" في قوة الصدم للأيبوكسي بزيادة نسب البولي بيوتاداين المطعم بالستراكونيك بسبب زيادة التوافقية بين الراتنج الأيبوكسي و البولي بيوتاداين المطعم بمجاميع الستراكونيك الفعالة.

1- INTRODUCTION:

Epoxy resins are widely used as high-performance thermosetting resins for many industrial applications , but unfortunately some are characterized by a relatively low toughness. Many efforts have been made to improve the toughness of cured epoxy resins by the introduction of rigid particles , reactive rubbers , interpenetrating polymer networks , and thermoplastics within the matrix (Sumeera Ikram et al., 2003). The great majority of the studies involves the chemical modification with reactive liquid rubbers such as carboxy terminated polybutadiene co-acrylonitrile (CTBN). The microstructure formed consists of an elastomeric phase finely dispersed in the epoxy matrix and the impact behavior of the final material is highly dependent on the size of the elastomeric particales produced. Other studies involve modification of epoxy resin with kaolin as a toughning agent (S. Fellahi et al., 2001) and with hydroxy terminated polybutadiene (Payam Saadati et al., 2005). In the present work, a citraconiciated polybutadiene used as impact modifier to improve the toughness of epoxy resin with different percentage of citraconiciated polybutadiene. The infrared spectra of the polybutadiene and citraconiciated polybutadiene were measured and impact strength of modified epoxy resins was evaluated in terms of the Izod impact strength.

2- EXPERIMENTAL

2,1- Materials:

Polybutadiene a commercial adhesive material , liquid free epoxy resin and triethylene tetraamine as hardener supplied from Ciba-Geigy corporation , citraconic anhydride , and supplied from Fluka company , used without purification , acetone, and citric acid from Merck company, Benzoyl peroxide supplied from BDH company.

2,2- Preparation:

2,2,1-Preparation of Citraconiciated Polybutadiene

The citraconic anhydride was added and mixed with polybutadiene as a ratio of 10% from citraconic to polybutadiene in the presence of 0.5 % benzoyl peroxide as initiator at 110°C for 15 min (A. Benny Cherian and Eby T. Thachil, 2003). With vigorous stirring, then the product wash with large quantity of acetone and dried at vaccum oven at 50°C for 2 hrs. The grafting reaction was confirmed by FTIR spectroscopy and chemical testing.

2,2,2- Determination of the Degree of Citraconiciation

Standard procedure was adopted thus samples from the citraconiciated polybutadiene was dissolved under reflux in xylene at a concentration of (1% wt/vol), followed by the addition of an excess amount of (0.3 M) trichloroacetic acid solution in xylene. The mixture was reflux for (90 min) to drive the ring opening reaction of epoxy (with the acid) to completation. The hot solution was titrated immediately with (0.05 N) ethanolic KOH using three to four drops of (1%) thymol blue in DMF was added and the deep blue colour was back-titrated to a yellow end point against (0.05 N) isopropanolic HCl in the hot solution (A. A. Sultan 2007, Yasuharu Nakayama, 1973; Takayuki Okamura and Shobu Min atono, 1975). The acid number and the percent grafted citraconated anhydride content was determined from the following relationships (Payam Saadati et al. 2005).

$$\text{Acid Number (mg KOH / g Polymer)} = \frac{\text{ml KOH} * \text{N KOH} * 56.1}{\text{Polymer (g)}} \quad (1)$$

Therefore

$$\text{Cit – anhydride \%} = \frac{\text{Acid no.} * 98}{2 * 56.1}$$

2,2,3-Preparation of Blends

The blends were prepared by mixed the citraconiciated polybutadiene with epoxy resin at a ratio (5 , 7.5 , 12.5 , 20%) respectively , then the curing was done at room temperature for 24 hrs, followed by post curing at 120°C for 3 hrs.

2,3-Characterization Methods

Infrared Spectroscopy (FTIR)

FTIR Spectroscopy was used to characterized the polybutadiene Fig. 1 and the citraconic polybutadiene.

2,4- Impact Strength Evaluation

Izod Impact Strength

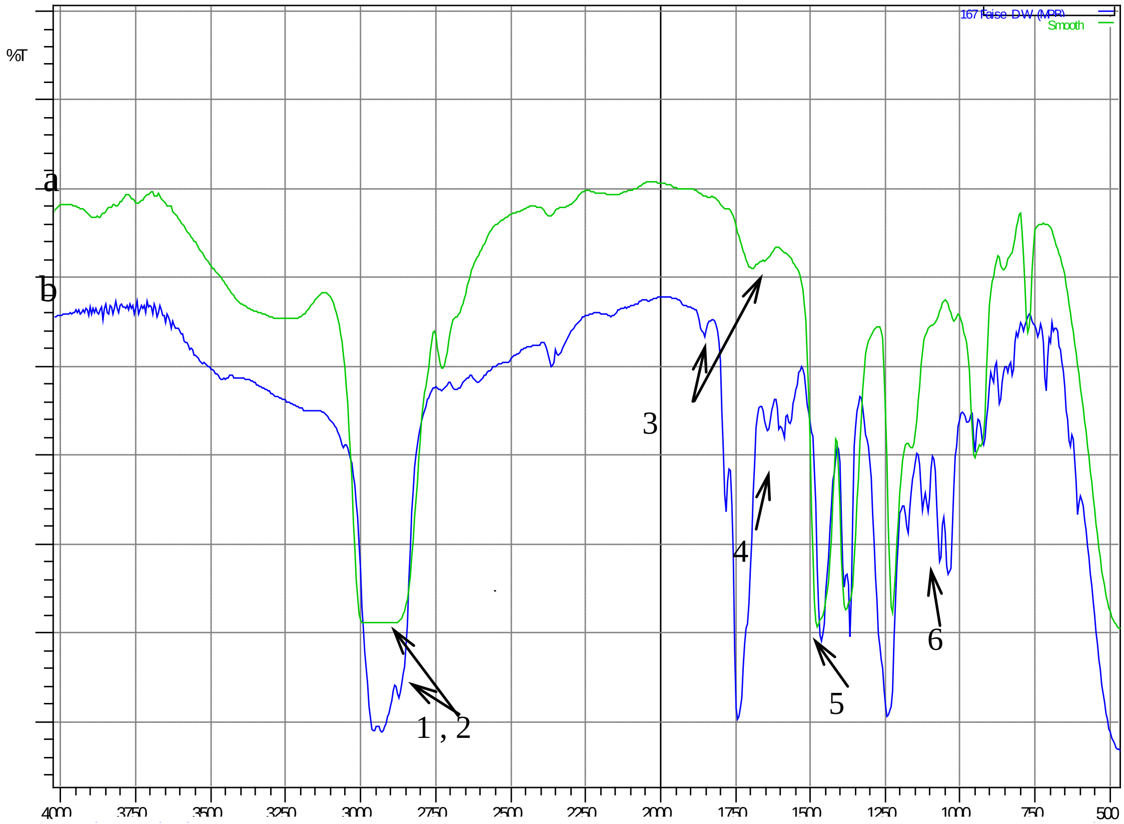
The Izod impact strength was evaluated according to ASTM D256 using a standard notched specimen. Five samples from each formulation were broken. Average impact strength values were reported and their Izod values are calculated in (J / cm^2) as follows:

$$IS = \frac{U_1 - U_2}{(W-a)t} \qquad (2)$$

The value Izod impact strength was measured of samples (epoxy alone and blends).

3- RESULTS AND DISCUSSION:

The grafting of citraconic anhydride onto polybutadiene characterized by FTIR spectra Fig. 1 which show the band at a region 1780 , 1856 cm^{-1} represents the symmetric and asymmetric stretching , 1140 cm^{-1} represent the C---O of anhydride(A. A. Sultan, 2007; Moayad N. Khalaf ,2005). The above bands are indicating the grafting of anhydride to the backbone of polybutadiene. Table 1 represent the wave number data of polybutadiene and citraconiciated polybutadiene.



(W/cm^{-1})

Fig. 1 . FTIR of a) PB and b) Citraconiciated PB

Table 1 . Characteristic Infrared Bands of Polybutadiene and Citraconiciated Polybutadiene

Band number	Band intensity	Wave number cm^{-1}	Absorption	Assignment
Polybutadiene 1 and 2	Strong	2950 , 2850	CH	Stretching vibration
3	Medium	1650	C==C	Stretching vibration
Citraconiciated Polybutadiene 1 and 2	Strong	2950 , 2850	CH	Stretching vibration
3	Medium	1856	C==O	Asymmetrical stretching
4	Strong	1780	C==O	Symmetrical stretching
5	Low	1707	C==O	Symmetrical stretching *
6	Strong	1140	C---O	Asymmetrical stretching

* due to acid form

The Izod impact strength results show increasing in the value of impact strength of epoxy resin with increased percentage of citraconic polybutadiene due to the increasing in the elastic behavior of epoxy resin. The funcatinilization of polybutadiene with citraconic increases compatibility between the citraconic polybutadiene and the epoxy resin, while the unfactinilized polybutadiene will not be compatable with epoxy and the impact strength of the epoxy will not improve as shown in the results. Table 2 and Fig. 2 show the value of impact strength.

Table 2 . The Values of Izod Impact Strenght Versus Percentage of Citraconic Polybutadiene to Epoxy Resin

Percentage of Citraconic Polybutadiene to Epoxy Resin	Izod Impact Strength for Notch Specimens (J/cm^2)
0	0.35
5	0.5
7.5	0.6
12.5	1.05
20	1.25

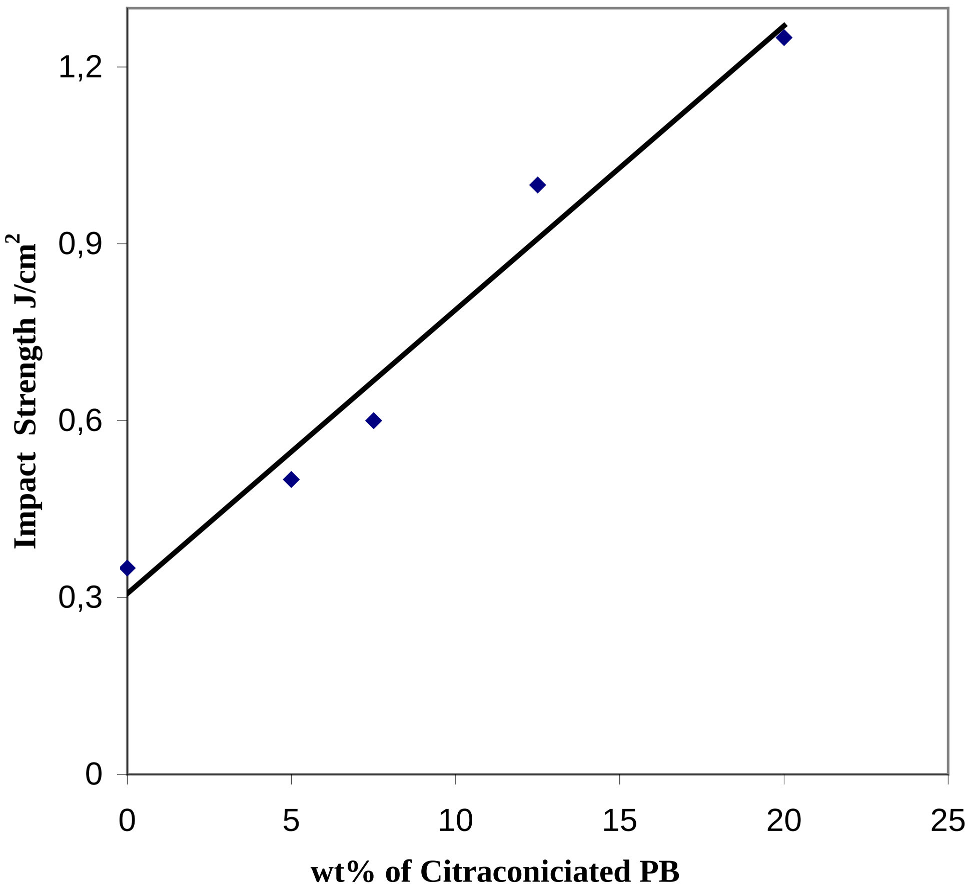


Fig. 2 Effect of wt% of Cirtraconiciated PB on the Impact of Epoxy Resin

CONCLUSIONS:

In the present work the fictionalization of polybutadiene with citraconic will increased the compatibility of the polybutadiene with the epoxy resin. The impact strength of modefied epoxy resin was increased with the increased percent of citraconiciated polybutadiene.

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Nomenclature

Symbols	Description	Unit
a	The notch length	cm
t	The specimen thickness	cm
U_1	The impact energy	J
U_2	Residual energy	J
W	The specimen width	cm