European Journal of Chemistry 7 (3) (2016) 352-356

European Journal of Chemistry

Journal webpage: www.eurjchem.com

Tensile strength and dynamic mechanical analysis of new IPNs based on epoxy resin-polysulphide elastomer

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ARTICLE INFORMATION

DOI: 10.5155/eurjchem.7.3.352-356.1459

Received: 18 May 2016
Received in revised form: 15 July 2016
Accepted: 25 July 2016
Published online: 30 September 2016
Printed: 30 September 2016

KEYWORDS
DMA
Epoxy resin
Polysulphide
Impact strength
Tensile strength
IPNs preparation
Interpenetrating polymer networks

ABSTRACT

The toughness of diglycidyl ether of bisphenol, an epoxy resin with polysulphide was investigated. Several interpenetrating polymer networks based on epoxy resin and different weight percentage of polysulphide were prepared and characterized by dynamic mechanical analysis technique. From the result, the glass transition temperature of these systems was lower than glass transition temperature of epoxy alone and also the impact strength was increase with increasing percentage of polysulphide.

Cite this: *Eur. J. Chem.* **2016**, *7(3)*, 352-356

1. Introduction

Thermosetting polymers have number of advantages over thermoplastic polymers such as, elevated heat distortion temperature, good solvent resistance and high modulus, which result in their use in a wide range of commodity, engineering and especially application [1]. Optimization of the properties of thermosetting polymers for specific application has been achieved by modifying the structure of the monomer unit. For example, the addition of the aromatic structure which improves the rigidity of the polymer backbone and leads to improved mechanical properties [2,3]. Other property enhancement can be achieved by rubber or thermoplastic toughening, blending of thermoset to form interpenetrating polymer networks (IPNs), it is an entirely different route to extend the range of properties and hence increase the number of application of the products.

As first proposed by Sperling *et al.* [4], IPNs are ideally composition of two or more chemically distinct polymer networks held together exclusively by their permanent mutual entanglement. IPNs can formed by one of two methods, first a sequential IPNs is one where the first network is formed and then swollen with a second crosslinking system, which is polymerized. The second type is the simultaneones IPNs in which the two components are polymerized together, and this type that is investigated in the present study.

There are a number of factors that could leads to complication in that curing of IPNs, first the interaction between the component of one network and the initiators of other component may accelerate the reaction. As an example, in the study of epoxy resin-polyester IPNs, Dean *et al.* [5], observed an interaction between the cobalt salt catalyst of the polyester and diamine curative for the epoxy resin. Second factor, the rate of reaction of one component might be expected to be reducing due to the dilution effect by the other component.

Some times in an IPNs the first component reacts more slowly than the second component, the former may acts as plasticizer to the cure of the latter, allowing faster reaction of the second component and full cure without verification. Evidence for this has been reported by Lin *et al.* [6]. Epoxy resin are a major class of thermosetting polymers which are widely used as binder for fiber reinforced composite materials, adhesives and coating as well as other engineering materials [7,8].

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.7.3.352-356.1459

Table 1. The quantities of the reactant used in the preparation of IPNs.

First component (Polysulphide)			Second component (Epoxy resin)	
Polysulphide %	**Polysulphide content (g)**	**MnO_2 content (g)**	**Epoxy resin content (g)**	**TETA content (g)**
0 (epoxy alone)	0.00	0.000	3.00	1.00
10	0.30	0.006	2.70	0.90
20	0.60	0.012	2.40	0.80
30	0.90	0.018	2.10	0.70
40	1.20	0.024	1.80	0.60
50	1.50	0.030	1.50	0.50

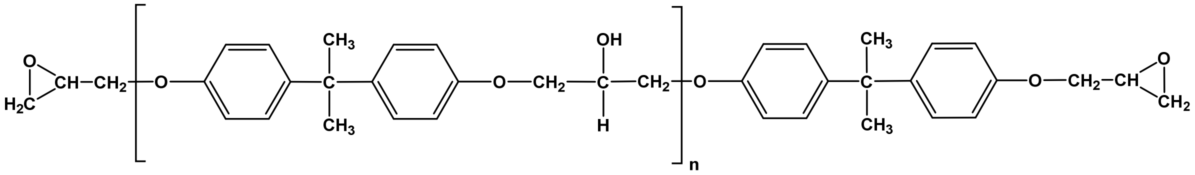


Figure 1. Chemical structure of bisphenol A diglycidyl ether (Epoxy resin).

But when being cured, epoxy resin typically possess a high crosslink density which leads to a low ductility and poor fracture toughness and low impact resistance, so many efforts have made to improve the toughness of cured epoxy resin [9-11]. Also, the toughness of epoxy will be improve by introduce some polymers in their network of the epoxy resin which leads to increase flexibility of the final network structure [12-14].

On the other hand, polysulphide are widely used as flexible sealants for joints, building, sewage pipes and road surfacing [15,16], also polysulphide show a number of remarkable properties like rapid curing at ambient temperature, good adhesion on many materials high impact resistance and chemically resistance to a number of dilute acids, alkalies and organic solvents.

The main objective of the present work is to synthesis of simultaneous IPNs formed from epoxy resin and liquid polysulphide in order to improve the toughness of the epoxy resin and study the effect of polysulphide on the glass transition temperature of epoxy resin.

2. Experimental

2.1. Materials

The epoxy oligomer was bisphenol A diglycidyl ether (DGEPA) (Figure 1) (n = 1.5, number of repeating units; type Araldite GY-9708-1) supplied by Ciba Geigy Company and was reported to have an average equivalent weight of 190 g/mol. This epoxy resin was cured with stoichiometric amount of amine curing agent (Triethylenetetraamine, TETA).

While the liquid polysulphide used in this study, the mercaptan terminated (SH), having the formula ($HS-CH_2CH_2-O-CH_2O-CH_2CH_2-(S-S-CH_2CH_2-)_n-SH$) was supplied from AkzoNobel, Giza, Egypt. With the following specification, viscosity was 35,000 cps at 25 °C, density 1.404 g/cm^3, molecular weight was 1000 g/mol, SH-content 1.75%, average viscosity 25 °C was 1.15 Pa.s, and trichloropropane cross-link agent 2%, this polysulphide was cured by commercial grade MnO_2.

2.2. Instrumentations

Dynamic mechanical measurement were made on dynamic mechanical analyzer 6100 (DMA) by Seiko Instrument were used to estimate the glass transition temperature (Tg) of the prepared IPNs and also to estimate the storage modulus (E') and loss modulus (E''). The tensile strength was determined by using dumb-bell shaped specimen conforming to ASTM-D412 with the instrument universal testing machine Instron-5582 (100KN), Model 122 (Canada). Izod impact strength was determined by using a ZWICK model impact tester type machine (5120), equipped with hammer (Zwick Co., Germany). Differential scanning calorimetry (DSC) model Q 20 TA was used to study the thermal behavior of these polymers by using inert atmosphere this instruments presence in Misan University, Scientific College, Chemistry Department, Misan, Iraq. Flexural strength was performed by using Tinus Olenutm fitted with three point binding fixture at cross-head of 5 mm/min and the test was done according to ASTM D 790. Izode impact strength was determined by using Zwick model impact tester type machine (5102), equipped with a hummer (Zwick Co. Germany) and the specimens were conforming according to ASTM (D256). These two instruments presence in the Basra University, Scientific College, Chemistry Department, Basrah, Iraq.

2.3. Synthesis

2.3.1. Synthesis of IPNs

The IPNs consider in this study based on epoxy resin and polysulphide were prepared by efficient mixing of different quantities show in Table 1, for a period of 2 min at room temperature, then crosslinking agents (MnO_2) and tetra-ethylenetriamine (TETA), were added and mixed gently in order to homogenize. The samples were left overnight for curing at room temperature, then at 100 °C for 6 hr, and finally 4-5 hr post cure at 130 °C.

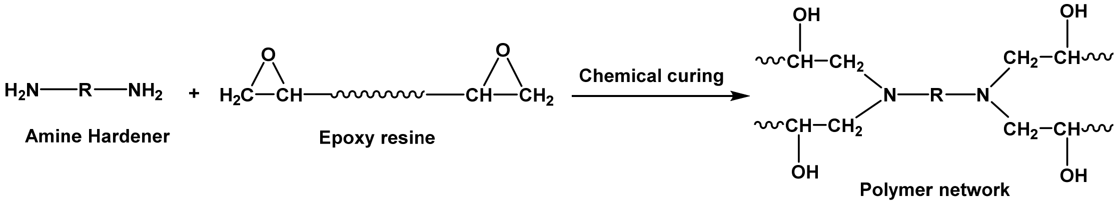
3. Result and discussion

3.1. Synthesis

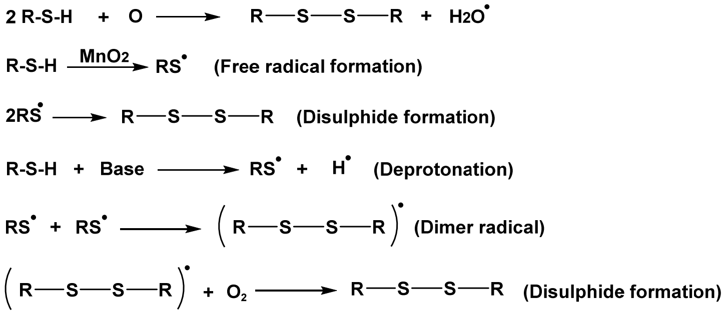
The epoxy resin used in this study was cured by aliphatic amine, the polymerization sequence illustrated in Scheme 1. Epoxy resins are converted into 3-dimensional networks held together by covalent bonds as a result of crosslinking reaction. This conversion of liquid or friable brittle solids into tough cross-linked polymer is called curing and achieved by the addition of curing agent which serves as initiators for resin homo-polymerization. While polysulphide oligomers have no workable applications in their liquid state so they are further polymerized or cured to higher molecular weight elastomers, so the curing process involves the addition of an oxidizing agent (MnO_2), which allows the terminal thiol groups to form disulphide bridges. The general oxidation process can be shown in Scheme 2. On the other hand, polysulphide also react with epoxy resin through the -SH group leading to opining of the oxirane ring [17,18], as shown in Scheme 3.

Table 2. Effect of polysulphide content on the tensile properties of epoxy resin.

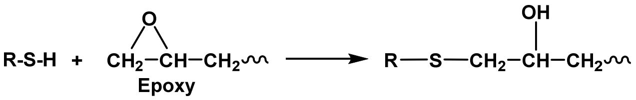
Polysulphide (%)	E (GPa)	Tensile strength (MPa)	Elongation at break (%)
0 (Epoxy alone)	2.32	29.72	3.46
10	2.13	27.31	5.10
20	2.01	26.63	6.31
30	1.83	25.01	8.76
40	1.68	23.12	14.96
50	1.13	22.01	18.45



Scheme 1



Scheme 2



Scheme 3

The characteristic bands display a strong broad band in the 3600-3200 cm^{-1} region assigned to O-H stretching vibrations in the FT-IR spectrum of uncured epoxy. A strong bands at 1605, 1580, 1510 and 1455 cm^{-1} are assigned for Ar-C=C-H stretching vibrations. Bands at 729 and 693 cm^{-1} may be attributed to out of plan bending of aromatic rings. Also bands at 912 and 1042 cm^{-1} due to epoxy ring, which is disappear after curing with amine. The absorption bands at 672 cm^{-1} and 558.5 cm^{-1} in the FT-IR spectrum of epoxy/ polysulphide IPNs can be ascribed to C-S group and S-S group of polysulphide.Also the absorption band at 1428 cm^{-1} is due to formation of -S-CH$_2$ linkage between -SH group of polysulphide and epoxide group of DGEPA. On the other hand , the broad absorption band at 3450 cm^{-1} might indicated the OH group formed due to reaction between the -SH group of polysulphide and epoxide group.

3.2. Mechanical properties

3.2.1. Tensile behavior

The load-elongation properties were obtained using an axial extensometer coupled to a mechanical tester. All tests were performed at room temperature according to ASTM D638 method. The results showed in Table 2, and the value of tensile strength a while the elongation increases. On the other hand, as expected, the tensile modulus gradually decreases due to increase the flexibility of the formulation samples.

3.2.2. Izod impact strength

Izod impact strength was evaluated using notched specimen. The rectangular specimens of 80×10×4 mm were taken according to ASTM D-256-88. The tests were carried out at room temperature and the values were taken from an average of at least five specimens. The Izod impact values are calculated with the Equation 1.

$$\mathrm{Is} = \frac{u1-u2}{(w-a)t} \qquad (1)$$

where, u1: the impact energy (KJ); u2: the residual energy (KJ); w: the specimen width (m); and a: the notch length (m).

The impact strength results for the prepared IPNs have been summarized in Table 3. The results shown that the impact value was increase with increasing percentage of polysulphide due to the increasing toughness and elastic behavior of prepared IPNs. So, there are several methods used to improve the toughness of epoxy resin [19,20].

3.3.3. Dynamic mechanical analysis (DMA) (Viscoelasticity data)

DMA was performed and evaluated using as sample of approximately 50 mm (L) × 10 mm (w) × 1.5 mm (t) under bending mode and the data were obtained at 1 Hz on at temperature from 25 to 130 °C, at heating rate 5 °C/min.

Table 3. Impact strength value of the prepared IPNs.

Polysulphide %	Impact strength (Kj/m²)
0 (Epoxy alone)	9.32
10	10.73
20	12.04
30	14.21
40	15.11
50	18.33

Table 4. Storage modulus E' (GPa) data of the prepared IPNs.

Temperature (°C)	Polysulphide (%)					
	0 (Epoxy alone)	10	20	30	40	50
40	16.101	13.780	6.496	2.438	0.992	0.206
60	13.911	3.939	0.864	0.163	0.111	0.035
80	6.322	0.132	0.105	0.030	0.023	0.017
100	1.213	0.057	0.032	0.027	0.012	0.022

Table 5. The loss modulus E''(GPa) data of the prepared IPNs.

Temperature (°C)	Polysulphide (%)					
	0 (Epoxy alone)	10	20	30	40	50
40	1.657	1.052	0.948	0.857	0.544	0.142
60	1.283	0.812	0.539	0.107	0.056	0.018
80	0.352	0.089	0.047	0.012	0.006	0.003
100	0.052	0.004	0.003	0.001	0.001	0.001

The properties obtained from these analysis are storage modulus (E'), loss modulus (E'') and tan δ that is recorded as a function of temperature. The result was obtained and showed in Figures 2-6, from the data on Table 4 and 5.

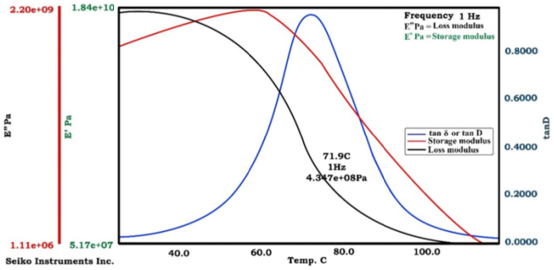


Figure 2. Inset of storage (E') and loss modulus (E'') curves as function of temperature for IPNs containing 10% polysulphide.

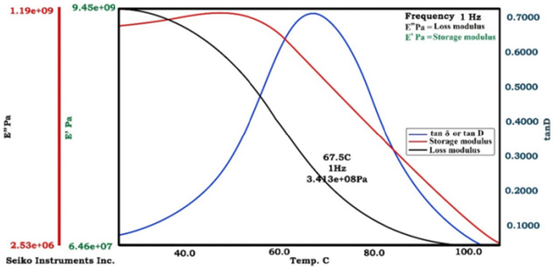


Figure 3. Inset of storage (E') and loss modulus (E'') curves as function of temperature for IPNs containing 20% polysulphide.

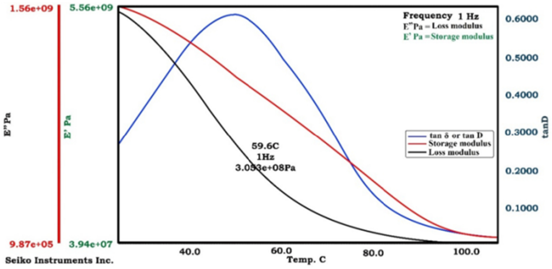


Figure 4. Inset of storage (E') and loss modulus (E'') curves as function of temperature for IPNs containing 30% polysulphide.

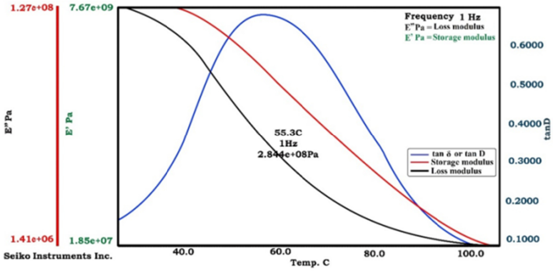


Figure 5. Inset of storage (E') and loss modulus (E'') curves as function of temperature for IPNs containing 40% polysulphide

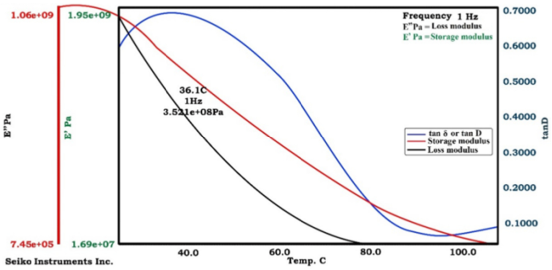


Figure 6. Inset of storage (E') and loss modulus (E'') curves as function of temperature for IPNs containing 50% polysulphide.

There is drop in the storage modulus with temperature and also with increasing percentage of polysulphide, also the same behavior in the case of loss modulus, but there is some deviation occurred at temperature of 60 °C in the case of 10 and 20% polysulphide, the value of E' increase at this temperature and then decrease Figures 2-6. The damping property tan δ as the ratio of the dynamic loss modulus to the dynamic storage modulus is related to the molecular motion and phase transition. It is sensitive to all molecular movement occurring in polymer. The glass transition temperature (Tg) of the epoxy-polysulphide IPNs is determined by the tan delta maximum [21], and the result shown that the Tg decreased with increasing polysulphide weight percent in composition (Table 6). It can be resulted from the figures the decreasing of the temperature of tan delta and this was attributed to the more elastic behaviour.

Table 6. Tg of prepared IPNs at different percentage of polysulphide.

Polysulphide (%)	Glass transition temperature (°C)
0 (Epoxy alone)	86
10	71
20	67
30	55
40	49
50	36

4. Conclusions

IPNs were prepared in this study by variation percentage of polysulphide in the presence of epoxy resin, after complete curing the final product was evaluated by some mechanical properties. The result shown that the properties of epoxy resin was improved by introducing polysulphide in there structure network due to increase flexibility, also glass transition temperature was decrease through the addition of polysulphide.

Acknowledgements

The authors would like to thank Anis Abdol Wahab Al-Najar for more support, and also gratefully acknowledged to Moayd Naim Galaf and Ali Kareem Al-Lami for the mechanical and thermal analysis, respectively.

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