

Modification of epoxidised polydienes

III. Studies on the reaction between epoxidised polydienes and polypropylene glycol

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ABSTRACT

The optimum conditions for the reaction between epoxidised polydienes and polypropylene glycol have been studied. The reaction has been traced by consumption of epoxy groups, crosslinking density, i.r. analysis, and the new properties of the cured polymers. The thermal stability of the modified cured product has been studied employing differential thermal analysis (DTA) and thermogravimetric analysis (TGA) techniques. The results obtained by DTA and TGA support the occurrence of modifications in the cured polymer. The elasticity and flexibility of the cured epoxy polydienes are maintained for a longer period on using polypropylene glycol, indicating its usefulness as a flexibiliser and diluent for epoxidised polydienes. A mechanism for the reaction, based on the above studies, is proposed.

INTRODUCTION

The existence of epoxy groups in rubber molecules is of great importance in the applied field due to their high reactivity with various curing agents. Epoxy groups in polybutadiene enhance different reactions with some curing agents which are unable to react with the non-epoxide polybutadiene (e.g. dicarboxylic acids, their anhydrides, diamines, polyhydroxy compounds and phenolic resins (El-Fayoumi *et al.* 1972)).

More than fifty compounds react with epoxy groups to produce chemicals of broad scientific and industrial interest (Lee & Neville 1967). Curing of epoxy polymers depends principally on the chemical structure of the curing agent and the mechanism of polymerisation. Curing agents are polyfunctional reagents and the minimum functionality should be 2.

By the use of different curing agents, modified epoxy polydienes have been synthesised (Akhnookh & El-Fayoumi 1973). The same authors stated that some of these curing agents imparted greater flexibility and elasticity to epoxy elastomers and could be considered as flexibilisers of the epoxidised polydienes. Other curing agents were considered efficient diluents as they influenced crosslinking density, system functionality and system viscosity. The present work deals with the studies on the reaction between polypropylene glycol and epoxidised polydienes. A comparison is

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made between the effect of ethylene glycol and that of polypropylene glycol on epoxidised polydienes. Ethylene glycol is considered a flexibiliser for epoxidised elastomers. The optimum conditions for this reaction are determined by tracing the modification by means of chemical and i.r. spectral analyses. DTA and TGA studies are also used to support the proposed mechanism and to elucidate the role of polypropylene glycol as an excellent diluent for epoxidised polydienes as reported by Akhnookh & El-Fayoumi (1973).

EXPERIMENTAL

The elastomers used in this work are of the polybutadiene type. Three rubbers were employed: (1) Europrene cis 1-4, Italy, (η) = 2.45 dl/g, (2) Cariflex Br 11, Compagnie Française des Produits Chimique, Shell, France, (η) = 2.24 dl/g and (3) JSR BR 10, Synthetic Rubber Co., Japan, (η) = 3.00 dl/g. The rubbers were dissolved in dry toluene, precipitated with absolute alcohol and then dried at normal temperature under reduced pressure (1 mmHg).

Epoxidation of polydienes was carried out following the procedure of El-Fayoumi *et al.* (1972). Peracetic acid (PAA) (0.5 mol/l) was the epoxidising agent. Polypropylene glycol was obtained from BDH Chemicals Ltd., Poole, England.

The modified products of the reaction were isolated from the reaction medium, purified by washing with absolute ethanol followed by sodium ethoxide (three times). Samples were then treated with dil. HCl, washed several times with distilled water and dried at room temperature under reduced pressure. The cured samples were prepared as above for subsequent chemical and instrumental investigations by i.r., TGA and DTA techniques.

I.r. spectral analyses were carried out for both the starting polymers and cured products using a Beckman IR 4 Spectrophotometer (KBr tablet technique). DTA and TGA techniques were carried out as described by El-Fayoumi & Abou Ali (1978).

Determination of the optimum conditions for the reaction between epoxidised polybutadiene (EPB) and polypropylene glycol (PPG)

A series of round bottom flasks was fitted with condensers. In each flask 20 cm³ (1 g) of the prepared epoxidised polydiene stock solution were placed. Other constituents were:

Series I:

- (a) Polymer + polypropylene glycol (PPG) + piperidine.
- (b) Polymer + PPG + amm. acetate.
- (c) Polymer + PPG + NaOH.
- (d) Polymer + PPG + pyridine (10 drops).

The reactions were allowed to take place at 80°C for 4 hr.

Series II: Using different amounts of pyridine in the following order: 1, 5, 10 and 20 drops, and 1 mole EPB/mole PPG. The reaction continued for 4 hr at 80°C (Table 1).

Series III: Similar to Series I and II with the exception that only pyridine was used as a catalyst. 0.5, 1, 2, 5 and 7 moles PPG/mole EPB were allowed to react at 80°C for 4 hr in the presence of 5 drops of pyridine (Table 2).

Table 1. The effect of catalyst on the product yield and % α -epoxide

Catalyst	Quantity (mg)	Yield	% α -epoxide
Piperidine	250	None	7.3
Amm. acetate	100	None	7.3
NaOH	100	None	7.3
Pyridine	500	55.5	3.8
Pyridine	250	60.6	2.9
Pyridine	125	75.1	1.5
Pyridine	25	56.9	3.1

Note: The reaction was performed with equimolar concentrations of EPB and PPG at 80° for 4 hr (% α -epoxide at the start = 7.4).

Table 3. The influence of the reaction time on the product and α -epoxide content in the reaction between PPG and EPB

Time (hr)	Yield (%)	% α -epoxide
1.0	61.5	3.0
1.5	63.0	2.9
2.0	65.0	2.7
3.0	66.0	2.3
4.0	69.5	2.0

Note: The reaction was carried out with equimolar concentrations at 80° in the presence of 125 mg pyridine.

Series IV: The reaction was carried out using equimolar concentrations of EPB and PPG in the presence of 125 mg pyridine for 4 hr at 80°C. Reaction time was varied (Table 3).

Series V: The previous reaction was repeated at 20°, 50°, 60° and 80°C for 4 hr using equimolar concentrations of EPB and PPG in the presence of 125 mg pyridine (Table 4).

Table 2. The effect of PPG concentration on the yield product and epoxide consumption in the reaction between PPG and EPB

PPG concn. (mole/mol EPB)	Yield (%)	% α -epoxide
0.5	43.4	4.1
1	70.0	1.9
2	60.5	2.9
5	None	1.1
7	None	0.4

Note: The reaction was performed at 80° for 4 hr in the presence of 5 drops pyridine (% α -epoxide at the start = 7.4).

Table 4. The influence of temperature on the reaction between PPG and EPB

Temperature (°C)	Yield (%)	% α -epoxide
20	None	7.3
50	None	7.3
60	None	7.1
80	70.5	1.9

Note: The reaction was carried out for 4 hr. Equimolar concentrations of EPB and PPG were used, in the presence of 125 mg pyridine.

RESULTS AND DISCUSSION

The α -epoxide content of the epoxy polymers was estimated to be 7.4%. The epoxy polydienes were purified, dried and then used. Results (Table 1) show that pyridine (5 drops, i.e. 125 mg) is the most efficient catalyst. Tables 2 and 3 reveal that highest yield

Table 5. Comparison between the reaction conditions of PPG and EG as curing agents for epoxidised polydienes

Optimum cure conditions	PPG	EG
Pyridine (mg)	125	250
Concentration/mole polymer	1	10
Reaction time (hr)	4	4
Reaction temperature (°C)	80	80

is obtained when EPB and PPB are used in equimolar concentrations, and that the optimum reaction time is 4 hr. The optimum temperature is 80°C (Table 4). At this temperature, bulk precipitation takes place whereas none occurs at 20°, 50° or 60°C. Comparison between PPG and EG as curing agents for epoxidised polydienes is given in Table 5. It is clear that highest yield is obtained when 10 moles EG/1 mole EPB are used. It should be recalled (Table 2) that the use of 5 or 7 moles PPG/1 mole EPB inhibited precipitation of the product.

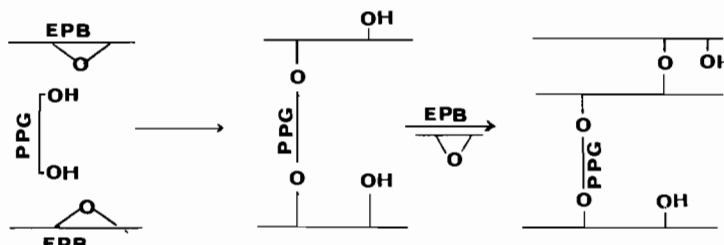
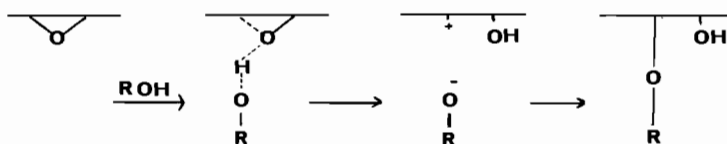
The modification in epoxidised polydiene structure was elucidated by different routes:

- (a) The consumption of epoxy groups which was studied qualitatively, quantitatively and by i.r. analyses.
- (b) The relation between epoxy group consumption and crosslinking density.
- (c) The new properties imparted to the product of the reaction between PPG and EPB, e.g. insolubility, chemical resistance and flexibility.
- (d) The effect of storage on both EPB and the reaction product.
- (e) DTA and TGA techniques.

(a) Consumption of epoxy groups

This is determined by quantitative, qualitative and i.r. analyses. Results (Table 2) reveal a drastic decrease in the α -epoxide content (from 7.4% to 0.41%) with the increase of PPG concentration, although no precipitate was obtained during polymerisation. This result could be interpreted on the basis that the large decrease in α -epoxide content is due to the huge number of available OH's capable of opening epoxy groups (Scheme 1). Precipitation does not occur because the probability of ethereal crosslink formation between two neighbouring EPB molecules is highly reduced, as the hydroxyl groups in PPG react preferentially with epoxy groups rather than with OH's implanted on the polymer backbone. The crosslinks in this case are represented by a PPG molecule connecting two EPB molecules (Scheme 2). The molecular distances between the EPB molecules are increased as the EPB molecules are put far away from each other by the increase in PPG concentration.

Qualitatively, the procedure of Kline (1959) was followed on both starting EPB and the cured product; a specific orange colour appeared with EPB. The failure to develop any colour with the cured product revealed the drastic decrease in the α -epoxide content.



I.r. spectral analyses for both starting EPB and the modified reaction product showed the appearance of new bands at 1100 cm^{-1} , 740 cm^{-1} and 1440 cm^{-1} which may indicate the presence of $-\text{C}-\text{O}-\text{C}-$, $-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_3$ respectively. The i.r. spectrum of the product has no distinctive band specific to epoxide groups at $3010\text{--}3060\text{ cm}^{-1}$, which was clear in the starting polymer. A specific band for $-\text{OH}$ at 3400 cm^{-1} was clear in both the starting polymer and the product.

(b) Epoxy group consumption and crosslinking density

When epoxy polymers are treated with certain agents, they are transformed into hard insoluble compounds, a reaction described as 'cure'. Kline (1961) distinguished between the two processes involved in cure: conversion and crosslinking. Conversion refers to the extent of the chemical reaction that occurs during cure and is expressed in terms of the disappearance of reactive groups. Crosslinking relates to the three-dimensional aspect that appears during the course of cure. The extent of crosslinking depends in part upon the progress of conversion and in part upon the functionality of the curing agents.

From the results given in Tables 1–4, it is clear that the best yields obtained are highly related to the high conversion, i.e. the higher the consumption of epoxy groups, the higher the percent yield. The cured products were precipitated in the reaction media, indicating their insolubility in the reaction solvent. This insolubility is due to the formation of crosslinked products.

As shown in Table 2, the use of 5 or more moles of PPG/mol EPB yielded no precipitates along the course of the reaction in comparison with the use of 1 mol/mol, although we observed a drastic decrease in epoxide content. This has already been interpreted.

Swelling values of the cured products were determined using the method of Kline (1961). Values of 46–47% indicate the existence of crosslinking. The use of EG as curing agent for EPB produced a polymer whose swelling value was 39%. Comparison between the two results may point to a higher degree of crosslinking on using EG as compared to PPG.

(c) The new properties imparted to the reaction product

(i) Insolubility of the products in either polar or non-polar solvents even after shaking for 72 hr.

(ii) The chemical resistance of the products to 18M H₂SO₄, 12M HCl, glacial acetic acid and 12M NaOH, indicated the existence of crosslinking.

Both aspects afford the occurrence of crosslinking. I.r. analyses of the reaction product and EPB revealed the existence of a band specific to ethereal crosslink at 1100 cm⁻¹ in the product only.

(iii) The flexibility imparted to EPB: exposure to direct and diffuse sunlight showed that EPB is stiffened and converted to a yellow hard resin after 2 months. Upon using PPG and EG as curing agents for EPB, the product kept its flexibility for more than 8 and 5 months respectively. The swelling value (39%) of the reaction product cured with EG indicates higher crosslinking density, whereas in case of PPG the swelling value (46–47%) refers to a lower crosslinking density.

(d) Thermal behaviour of the cured epoxidised polydienes using PPG as curing agent

DTA thermograms reveal both exothermic and/or endothermic degradation processes. As described by El-Fayoumi & Abou Ali (1978), the exothermic process included oxidation reactions. The melting, thermal crosslink bond scission and depolymerisation processes probably account for the endothermic reactions. DTA results (Table 6) reveal that the melting, thermal crosslink scission and depolymerisation processes occurred at moderate temperatures and may account for the role of PPG as diluent which increases the flexibility of EPB. PPG decreases the system viscosity, thus the gross mobility of the molecules is increased and the flow of the molecules past each other will occur at mild conditions, i.e. melting will take place at low temperatures. The available OH's in PPG molecules can attack the epoxy groups preferentially to hydroxyls on the EPB chain. PPG residue is grafted on EPB chain. Other hydroxyls in the same PPG residue have higher chances of attacking other epoxy groups in other EPB molecules. Thence the crosslinks between EPB are represented mostly by PPG (Scheme 2). This interpretation is supported by the flexibility of EPB cured with PPG. As the crosslinks are not so strong, they require lower energy to be

Table 6. Thermal degradation processes of cured epoxidised polydiene using PPG

Curing agent mole/mol	Endothermic processes					
	Melting		Thermal cross-link scission		Depolymerisation	
	Temp. range	Peak	Temp. range	Peak	Temp. range	Peak
EPB	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)
PPG	20–100	50	100–310	175–275*	300–650	400–582*

* Plateau.

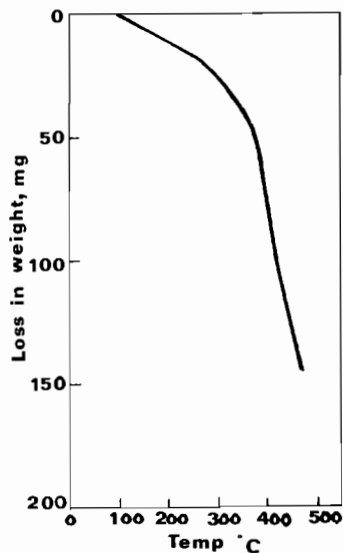


Fig. 1. TGA of the cured epoxidised polydiene using PPG (1:1 mol.).

disrupted. Thus the crosslink bond scission temperature should not be high (Table 6). Swelling value of the product showed, also, that crosslinking density is not so high. Depolymerisation occurred at mild conditions as the system viscosity is decreased by curing with PPG.

TGA results revealed that the activation energy (2.2 kcal/mol) is low which may indicate the weakness of crosslinks as they require low energy to be formed; the weight loss recorded by TGA may reveal that the flexibility imparted to epoxy polymers influences both initial and final weight loss. The range of weight loss was broadened by the decrease in flexibility. On using PPG as curing agent for EPB, the initial and final weight loss occurred at about 100° and 350° respectively (Fig. 1).

The activation energy for thermal degradation was derived from TGA curve using the equation of Bikales (1971):

$$\Delta \log R_t = n \Delta \log w - (E_a/2.303R) \cdot \Delta(1/T)$$

where w = weight of active material remaining and R_t = reaction rate (dw/dt) (mg/min).

The plot of $\Delta \log R_t$ against $\Delta \log w$ should be linear when $\Delta(1/T)$ is held constant. The slope of the resulting line will give a value for n (the reaction order) which is 2 for PPG/EPB reaction. The intercept will give a value for E_a for the degradation reactions between epoxidised polydiene and polypropylene glycol.

Proposed mechanism

On the basis of chemical analyses, i.r. spectra, the new properties obtained by the product (flexibility, insolubility, and chemical resistance), and DTA and TGA of the cured polymers, a mechanism for the reaction between EPB and PPG is given as follows:

The first stage involves the attack by —OH in PPG on one epoxy group yielding new —OH on the polymer backbone and grafting PPG residue on the polymer molecule. Scheme 1 represents the mechanism of —OH attack on the epoxy group.

The second stage involves ethereal bond formation between two polymer molecules via —OH implanted on the polymer chain with epoxy groups in neighbouring molecules. However, this stage occurs to a smaller extent and consumption of further epoxy groups takes place by the available OH in polypropylene glycol. Crosslinking between two polymer molecules takes place by PPG molecule as shown in Scheme 2. As PPG is a long-chain molecule, when it is grafted onto one EPB molecule and/or crosslinked with another EPB molecule, it will increase the intermolecular distance between EPB molecules providing a higher degree of mobility for the molecules and maintaining epoxy rubber flexibility for more than 8 months. PPG acts as an excellent diluent for EPB as it decreases the viscosity of the system.

CONCLUSION

Polypropylene glycol (PPG) is proved to behave as a diluent for epoxidised polydiene (EPB). The flexibility and elasticity of the cured epoxypolydienes are maintained for longer periods indicating the usefulness of PPG as flexibiliser for EPB. The results obtained by DTA and TGA techniques, new properties of the cured polymers, chemical analyses and i.r. spectral analyses revealed the existence of modifications in the structure of epoxy polydienes. They also supported the proposed mechanism of the reaction. The reaction between PPG and EPB indicates the reactivity of hydroxyl groups with the epoxy group and reveals its importance in the applied polymer field.

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دراسات على التفاعل بين الالبوكسي بولي داينيات وبولي بروبيلين جليكول

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قسم الكيمياء بكلية التربية ، جامعة عين شمس ، روكسي ، مصر الجديدة ، القاهرة .

خلاصة

لقد امكن اثبات دور مجموعة الهيدروكسيل مع مجموعة الالبوكسي من خلال تفاعل البولي بروبيلين جليكول مع بعض الالبوكسي بولي داينيات وتم وضع ميكانيكية التفاعل اعتمادا على التحليل الكيميائية والطيفية ودراسة درجة الثبات الحراري من خلال التحليل الحراري التفاضلي والتحليل الحراري الوزني . وهذه الدراسات اثبتت وفسرت حدوث التحور في تركيب بوليمرات الالبوكسي بولي داينيات .

وقد وضح تأثير البولي بروبيلين جليكول كعامل رابط في اكساب الالبوكسي بولي داينيات درجة اكبر من المرونة والليونة ، واستمرارهما لفترات زمنية اطول ، ولهذا فانه يمكن اعتبار البولي بروبيلين جليكول عاملا مخففا وملينا للالبوكسي داينيات . كذلك تم في هذا البحث تحديد افضل الظروف للتفاعل للحصول على اكبر ناتج .

