Epoxidation of Ethylene Propylene Diene Monomer (EPDM) Rubber by Using *In-Situ* Generated Dimethyldioxirane (DMD) and MoO$_3$

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Epoxidation of Ethylene Propylene Diene Monomer (EPDM) Rubber by Using *In-Situ* Generated Dimethyldioxirane (DMD) and MoO₃

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A method for functionalization of EPDM with in-situ generated dimethyldioxirane (DMD)/MoO₃ complex to a controlled increase in the functionality of the polymer was developed. For the evaluation of the oxygen transferring of in-situ generated DMD/ MoO₃ complex, the oxidation of EPDM using various ratios of Oxone® (the source of DMD) and MoO₃ were studied in detail at various reaction times and products were identified using ¹H-NMR, ¹³C-NMR and FT-IR spectroscopic methods. It was found that the in-situ generated DMD/MoO₃ complex is an effective and mild reagent for the oxidation of EPDM and the highest yields achieved without ring-opening of epoxy groups.

Keywords *in-situ* generated dimethyldioxirane (DMD)/MoO₃ complex, ethylene propylene diene monomer (EPDM), epoxidation, oxone® (2KHSO₅ · KHSO₄ · K₂SO₄), functionalization

Introduction

The introducing of epoxy groups, along the polymer backbone is one of the most promising methods of modifying olefinic double bonds containing polymers and has been known for a long time and all reported methods have their merits and drawbacks. The common disadvantages of previously reported procedures were the ring opening of produced oxirane rings in the oxidizing conditions. Historically, natural rubber was first epoxidized by Pummer and Burkhard as early as in 1922 (1). The epoxidation chemistry of unsaturated compounds and subsequent ring-opening reactions has been studied by Rosowsky and Swern (2). Swern and Witnauer showed that epoxidation is a stereospecific reaction and the rate of epoxidation is governed by the substituents on the double bond (3). The ease and positioning of ring-opening of epoxy groups is again

controlled by the neighboring groups (4). Peracids have been most commonly employed for the epoxidation reaction and the oxirane group has been utilized as a site for grafting or conversion to other functionalities on polymers. Upidi epoxidized SBS copolymers with peroxyformic acid generated *in situ* (5). The resulting polymers exhibit greatly improved solvent resistance. At conversion above 50% the oxirane ring undergoes significant amounts of ring opening to give formate esters and alcohols (5). Davies has epoxidized cis-1,4-polyisoprene to produce random copolymers with enhanced resistance to swelling by hydrocarbons while maintaining their high strength (6). Dreyfuss and co-workers used *m*-CPBA for the introduction of small amounts of oxirane groups into butyl and EPDM rubbers as sites for introducing polytetrahydrofuran grafts (7). Cameron studied the epoxidation of polybutadiene with *m*-CPBA (8). The resulting polymers, which were epoxidized to low levels, were converted to the chlorohydrins or used directly for the preparation of graft copolymers with THF. The reaction of epoxidized polyisoprene with 4-anilinoaniline has been used to synthesize a macromolecular antioxidant (9). Xigao and co-workers reported the epoxidation of unsaturated polymers with hydrogen peroxide (10). Pendant vinyl groups of a styrenic resin were epoxidized using *m*-CPBA to form poly (*p*-oxirane-styrene), with some ring opening of the epoxide group (11). Styrene-butadiene-styrene linear block co-polymer (SBS) was epoxidized using hydrogen peroxide (H_2O_2) and a phase transfer catalyst (12). This method was attempted with no success to epoxidize a block copolymer consisting of styrene and 1,2-butadiene units (13). Epoxidation of polybutadiene and styrene-butadiene-styrene block copolymers was also done using monoperphthalic acid (MPPA) (14). Poly (β-malic acid) with pendant allyl groups was epoxidized with *m*-CPBA or with an acetone solution of dimethyl dioxirane (DMD) (15). DMD has also been used in the oxidation of polymer containing silanes to form silanols (16) and to bleach Kraft pulps (17). Also, it is now generally accepted that the active species in epoxidation of alkenes by e.g. Bu^{t}OOH catalyzed by dioxomolybdenum (VI) complexes contains the Bu^{t}OOH co-ordinated to the metal *via* one of its oxygen atoms in a distorted octahedral complex (18). Gahagan and co-workers epoxidized polybutadiene using molybdenum/Bu^{t}OOH complex (19). Since most suitable catalyst precursors are to dissociate to create a vacant site for co-ordination of the Bu^{t}OOH. A possible strategy to obtaining high activity for such catalysts would be to employ a bidentate ligand in which molybdenum centre so that it stabilizes the catalyst precursor but readily deco-ordinates to allow co-ordination of the Bu^{t}OOH (19). The yields of the product from the *in situ* formed peracid route was good when the epoxidation level was less than 50%, but above the 50% level formation of the side products becomes a concern. Moreover, trace amounts of unreacted acid present in the rubber matrix becomes detrimental from a stability point of view. Thus, attempts have been made to epoxidize diene rubbers with hydrogen peroxide in the presence of a basic or an organomethalic catalyst. The Nippon Zeon Company, Ltd. Patended, in 1981, the process of epoxidizing BR with H_2O_2 at 40 to 70°C in the presence of $Ce(SO_4)_2 \cdot 4H_2O$ and an organic compound of the following type: glycerol, $RO(CH_2CH_2O)_nH$, $RCO_2(CH_2CH_2O)_nH$, and $RCO_2(CH_2CH_2O)_nCOR$, where n = 1 to 200. It was claimed that this process produced a byproduct-free epoxidized BR (20). An unsuccessful attempt was made by Burfield, et al. to epoxidize NR with hydrogen peroxide in the presence of acetonitrile and sodium tungstate separately (21). However, NR has been epoxidized using ethyl-N-phenylcarbamoyl azoformate (22). Very recently, Jian and Hay reported successful use of a nobel catalyst, viz., methyltrioctyl ammonium tetrakis (diperoxotungsto) phosphate (3-), $[(C_8H_{17})_3NCH_3]_3[PO_4[W(O)(O_2)_2]_4$ with hydrogen peroxide to produce side-product-free epoxidized SBR, SBS, EPDM,

and IIR rubbers (10). Some other attempts have been made to epoxidize polydienes using systems based on transition metals, such as V (23), and Mn (24). In the continuation of our research in the oxidation of organic materials using Oxone[®] and *in-situ* generated DMD we decided to examine the ability of *in-situ* generated DMD/MoO_3 complex for the oxidation of EPDM (25). Generation of DMD from Oxone[®] oxidation of acetone is well known in the literature and it is also known that DMD is much more reactive than Oxone[®] for epoxidation of unfunctionalized alkenes (26). In spite of many studies, to the best of our knowledge, there are no reports which used *in-situ* generated DMD in addition MoO_3 as a source of oxygen for the oxidation of EPDM.

Experimental

Oxone[®] ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), MoO_3 and other chemicals were purchased from Merck and used without further purification. Ethylene Propylene Diene Monomer (EPDM) was used in this study, namely Keltan 4802 is an EPDM from DSM (ethylene content: 52 wt%; termonomer: ENB 4.5 wt%; narrow molecular weight distribution). Products are known and were characterized by comparison of spectroscopic data with those of authentic samples. ^{1}H-NMR and ^{13}C-NMR structure confirmation were obtained using a Bruker DRX-500 Avance, FT-IR spectra was obtained using a Bomem MB-100 instrument and found to be comparable with those reported. All reactions were carried out at specified temperature in a 250 ml flask with a stirring bar. In a typical reaction, the Keltan 4802 (0.5 g) was dissolved in 35 ml of toluene. Then, 3.5 ml of acetone was added to the solution. 0.04 g MoO_3 and 0.312 g Oxone[®] dissolved in 2.3 ml distilled water and 2.3 of potassium bicarbonate buffer solution (containing 0.43 g potassium bicarbonate in 3.3 ml distilled water) were added to the reaction mixture. After a specific time, the polymer was precipitated in 20 ml methanol and dried under vacuum at 40°C for 24 ho. Finally, the sample was provided, obtaining the FT-IR spectrum in toluene and ^{1}H-NMR, ^{13}C-NMR in $CDCl_3$.

Results and Discussion

Molybdenum based systems are known as very active and selective catalysts for the epoxidation of C=C double bonds (19). Using this complex, the epoxidation of EPDM could be advantageous since the epoxy groups of the polymer could help the strong adhesion of the polymer to polar and slightly polar substrates. In order to better understand the increased epoxidation rates in some solvents we have done the reactions in various solvent mixtures. The results obtained for the EPDM are shown in Table 1.

As can be seen, under the investigated conditions when the reaction is carried in dichloromethane/acetone mixture, only unepoxidized EPDM recovered from the reaction mixture (run 1) and the oxidation reaction was started by increasing toluene and decreasing dichloromethane in solvent mixture (2–7). Maximum conversion was obtained with 35 ml toluene and 3.5 ml acetone (run 8) and dropped when the acetone solvent decreased (runs 9–13). Although, the concentration of Oxone[®] was selected constant in all reactions, but decreasing of acetone affected the amounts of produced DMD. In other words, this observation probably occurs due to decreasing in oxidant concentration as dimethyl dioxirane (DMD) that is produced from the reaction of acetone and Oxone[®] and acts as reactive oxidant in the oxidation process (15). Also, it was observed from Table 1 that increment of acetone and decrement of toluene, decreases the Epoxidation yields probably due to unsuccessful dissolving of EPDM in

Table 1
The influence of acetone, toluene and dichloromethane solvents on the epoxidation yields of EPDM

Run[a]	Acetone (ml)	Toluene (ml)	Dichloromethane (ml)	Epoxidation (%)
1	3.5	0	35	0.0
2	3.5	5	30	1.2
3	3.5	10	25	4.2
4	3.5	15	20	4.8
5	3.5	20	15	5.2
6	3.5	25	10	6.1
7	3.5	30	5	6.7
8	3.5	35	0	13.2
9	2.5	35	0	9.5
10	2.5	40	0	9.6
11	2.5	45	0	9.6
12	2.5	50	0	9.6
13	2.5	55	0	9.7
14	5	20	0	8.7
15	5	25	0	8.7
16	5	30	0	9.0
17	5	35	0	9.3
18	5	40	0	10.1

[a]EPDM Keltan 4802 (0.5 g), MoO_3 (0.04 g), Oxone[®] (0.312 g in 2.3 ml distilled water), potassium bicarbonate buffer solution (containing 0.43 g potassium bicarbonate in 3.3 ml distilled water), reaction times 12 h, all reactions were done at reflux temperature of solvent mixture.

the mixed solvents (runs 14–18). Mass recovery of the epoxidized polymer at the end of the reaction was a problem and only 80–90% could be recovered. It was even more difficult when the reaction was carried out either in dichloromethane/acetone solvent system or with longer reaction time or with higher reaction temperatures. Such behavior can be explained by the strong modification of the polymer solubility due to chain degradation, to the change in the polymer polarity, caused by the introducing of the epoxy groups in polymer chain or the crosslinking reaction of EPDM which appear as a side reaction.

In the other experiments for the evaluation of the MoO_3 effects in the epoxidation yield, various reactions was handled by the sampling at selected times from the reaction mixtures in various concentrations of MoO_3 catalyst at constant reaction temperatures (Figure 1).

As indicated in Figure 1, the decreasing and increasing of MoO_3 concentration affected the epoxidation yield and the maximum epoxidation yield was obtained at 0.04 g of MoO_3 concentration. On the other hand the minimum epoxidation yield was observed at 0.01 g of MoO_3 concentration, probably due to unsuccessfully formation of dimethyl dioxirane/MoO_3 complex.

Another important observation in this reaction was the dependence of the epoxidation yields to the concentration of Oxone[®]. In the series of the reactions the effects of Oxone[®] in the reaction yields was monitored by applying various amounts of Oxone[®] in constant
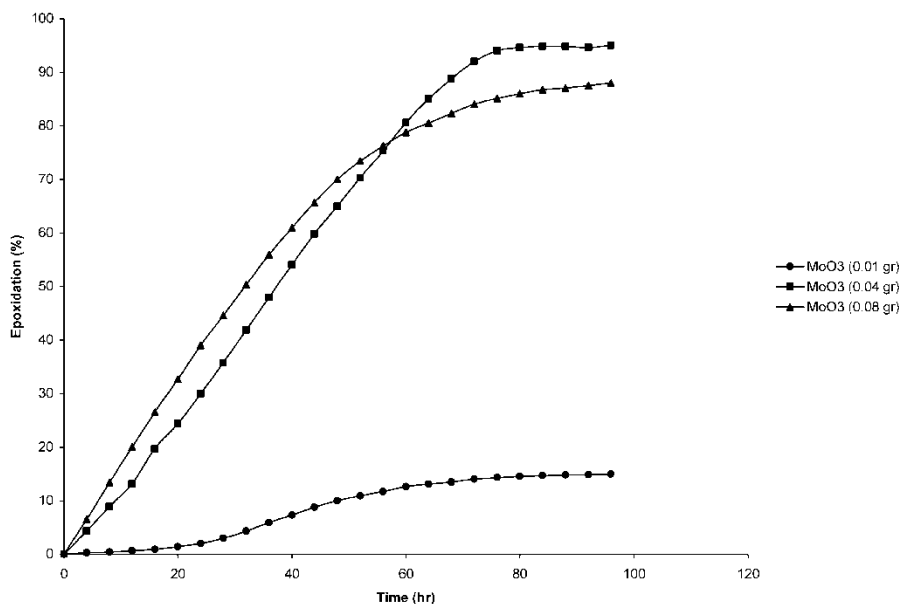
Figure 1. The influence of MoO$_3$ concentration on epoxidation yields.

amounts of other reactants and conditions (Figure 2). As shown in Figure 2, the maximum yield was observed for 0.64 g of Oxone® at 24 h reaction time.

We also observed that when the reactions are done in high temperatures, the mass recovery of the epoxidized polymer at the end of the reaction was a problem and only
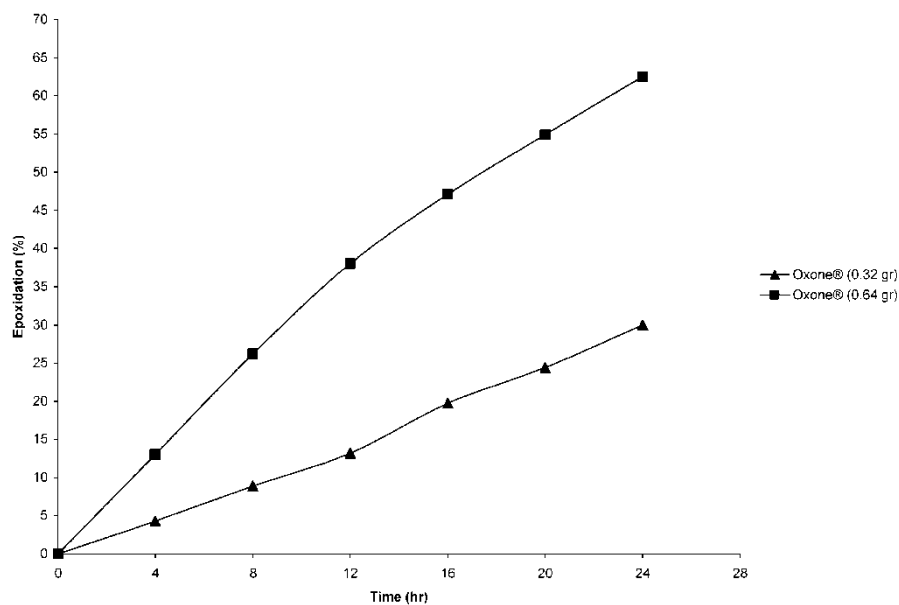

Figure 2. The effect of Oxone® concentration (parallel to DMD concentration) on epoxidation yields at various reaction times.

60% could be recovered, probably due to crosslinking reaction of EPDM which appear as side reaction. On the other hand, any side products due to epoxy ring opening or other over oxidation reactions was observed, when the reaction was handled in room temperature. The undesirable secondary reaction groups are detectable by spectroscopic techniques.

The ^{1}H-NMR was used for the calculation of epoxidation yields. Dubertaki and Miles first developed the method for the analysis of epoxy compounds by ^{1}H-NMR technique (27). Figure 3, shows ^{1}H-NMR spectrum of the epoxidized EPDM. In EPDM

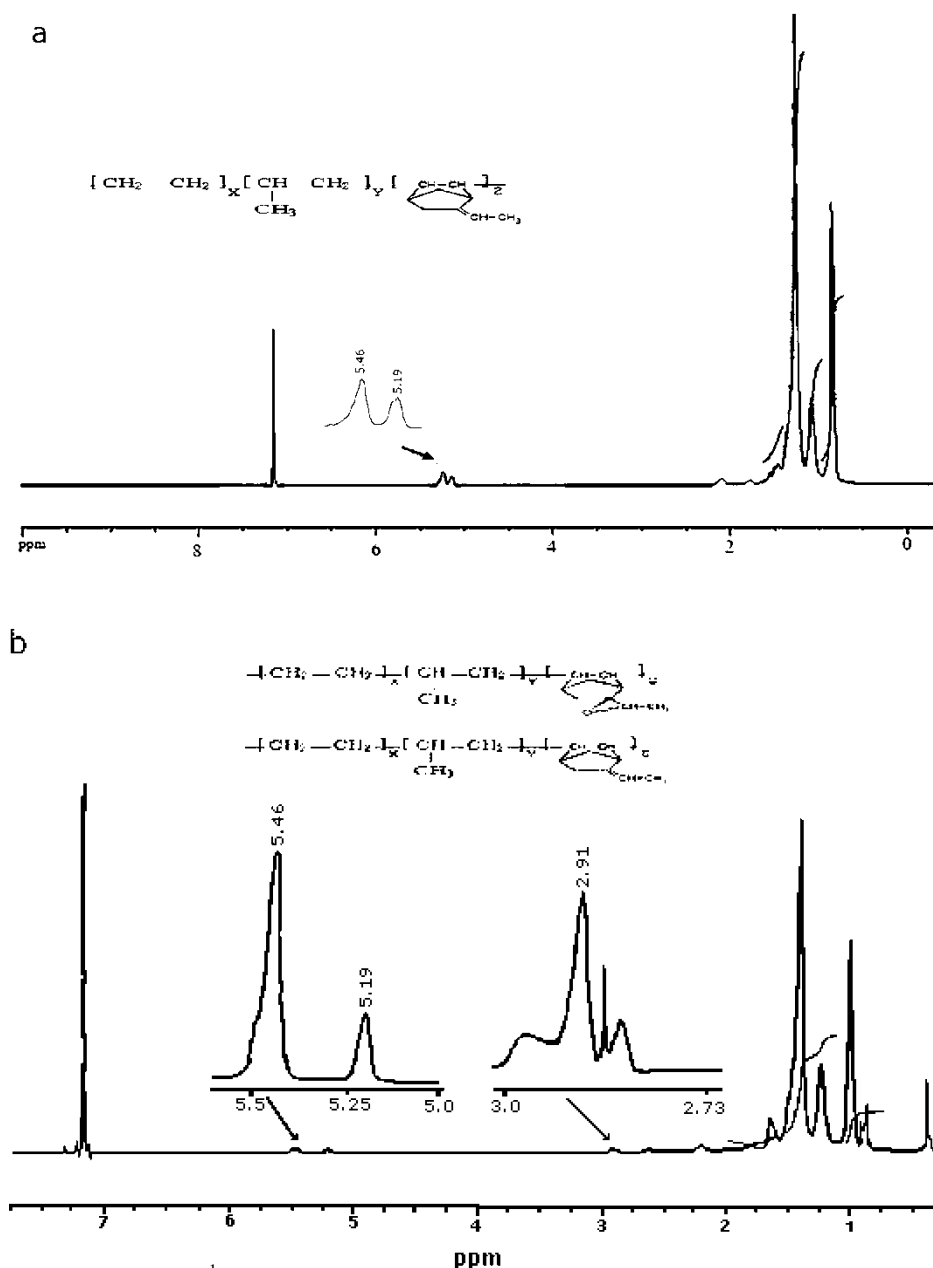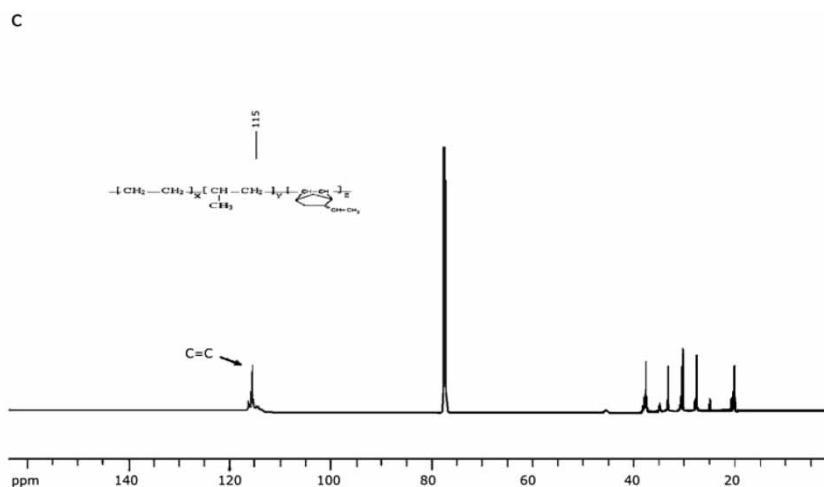**Figure 3.** ^{1}H-NMR spectra of unepoxidized (a) and epoxidized (b) EPDM.

polymersthe olefinic proton resonance appears at 5.19–5.46 ppm rangewhich on epoxidation disappears and a new signal around 2.61–2.91 ppm is created (28). This was assigned by Golub to the epoxy methane proton resonance (29).The epoxy content can be determined from the integrated area methane proton resonance divided by the sum of the area of the epoxy and olefinic methane proton resonances, by the following formula:

$$Mol\% \text{ epoxy} = \frac{A_{2.91}}{A_{2.91} + A_{5.46}}$$

where $A_{2.91}$ and $A_{5.46}$ represent the integrated area under the signal at 2.91 and 5.46 ppm, respectively.

The ^{13}C-NMR was used for the assigning of epoxy group carbons. Figure 4 displays the ^{13}C-NMR spectrum of unepoxidized and epoxidized product, respectively. In ^{13}C-NMR, the olefinic double bond carbons resonance appears at 115–116 ppm, which on epoxidation a new resonance grows at 57 ppm that assigned to epoxy ring carbons.

Figure 4. ^{13}C-NMR spectra of unepoxidized (c) and epoxidized (d) EPDM.

In order to understand the epoxidation process, the course of the reaction was monitored by FT-IR spectroscopy (Figure 5). As the reaction proceeds, the absorption band of epoxy group emerges and its intensity gradually increases while the absorbance at 806 cm^{-1}, typical of a carbon-hydrogen bond of —CH=CH—, coordinately decreases. Oxirane oxygen bands appear at 800 to 950 and 1270 cm^{-1}, depending upon the backbone structure of the parent diene polymer (30).

The chemical structure of ethylene propylene diene monomer (EPDM) and epoxidized EPDM are shown in Scheme 1, respectively.

Also, the *in-situ* generation of DMD and the schematic mechanism of oxidation process of EPDM are shown in Schemes 1 and 2, respectively.

The first step of the reaction mechanism is the formation of DMD that followed by the formation of *in-situ* generated DMD/MoO$_3$ complex. Furthermore, the *in-situ* generated DMD/MoO$_3$ complex intermediate is much more reactive than DMD, probably due to coordination of oxygen lone pairs with molybdenum atom.
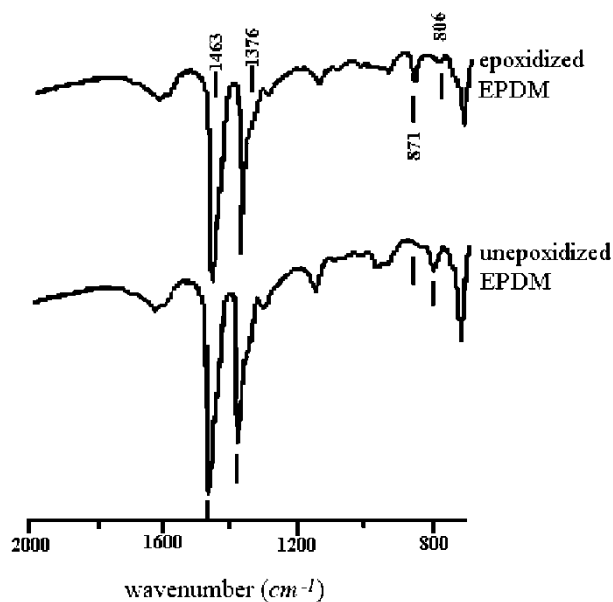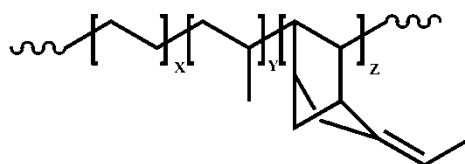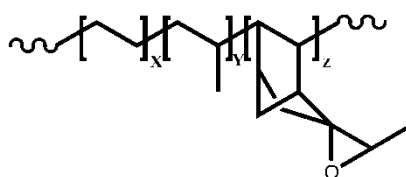
Figure 5. FT-IR spectra of unepoxidized and epoxidized EPDM.

Ethylene propylene diene monomer (EPDM)

Epoxidized ethylene propylene diene monomer (epoxidized EPDM)

Scheme 1. Chemical structure of ethylene propylene diene monomer (EPDM) and epoxidized EPDM.

Conclusions

Epoxidation of EPDM was achieved by using in-situ generated DMD/MoO_3 complex. The reaction doesn't proceed without MoO_3. The results show that there is a potential system for the epoxidation of EPDM and can be used for the other polydiene polymers. The results obtained in this study similar to the other previously

$$2KHSO_5.K_2SO_4.KHSO_4 + ACETONE \xrightarrow[\text{distilled water}]{KHCO_3}$$

in-situ generated dimethyldioxirane(DMD)
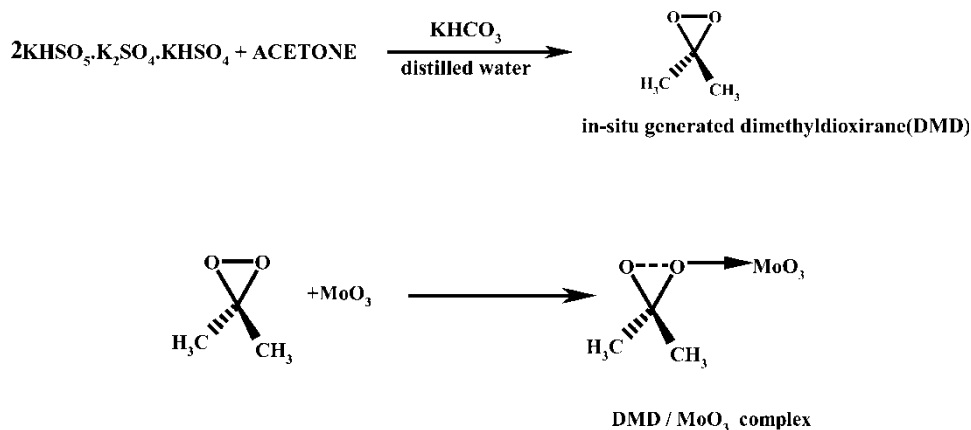
Scheme 2. Schematic formation of DMD/MoO₃ complex.

reported methods. Exception is the absence of side products due to epoxy ring opening or degradation reactions which can be attributed to the mild and selective reaction conditions.

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