Efficient graft-from functionalization of ethylene-propylene-diene rubber (EPDM) dissolved in hexane

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Received 7 September 2004; received in revised form 12 April 2005; accepted 14 May 2005
Available online 5 July 2005

Abstract

A facile and commercially applicable method to modify the polarity of ethylene-propylene-diene rubber (EPDM) by reacting with simple metal salts was described. Firstly, a brominated EPDM was produced by reacting EPDM solution in hexane that was sampled directly from commercial plant with N-bromosuccinimide, and then the brominated EPDM was further reacted with sodium acetate or sodium chlorodifluoroacetate in the presence of phase transfer catalyst to yield the functionalized EPDM. The effectiveness of the functionalization method was demonstrated by estimating contact angle, work of adhesion, and lap shear strength after characterizing the polymers by various spectroscopies.

Keywords: Bromination; EPDM; Functionalization; Graft-from reaction

1. Introduction

Functionalization of the ethylene-propylene-diene terpolymer (EPDM) with the introduction of polar groups increases the adhesion of EPDM to a broad range of materials, resulting in the expansion of the EPDM applications. The functionalized EPDM derivatives can also be used as a compatibilizer for polymer blends and composites.

All prior attempts to functionalize EPDM were made through graft copolymerization by free radical [1–3] or radiation [4–6] mechanism. The resulting graft copolymers produced by both “graft-from” [7] and “graft-onto” [8] techniques resulted in ill-defined products as a result of gel formation, backbone degradation, or simultaneous formation of homopolymer. Cationic pathway might be a candidate to yield well-defined product; however, stringent reaction conditions that are hardly achieved in a commercial viewpoint, are required and only a limited type of monomer is applicable [9]. Atom transfer radical
polymerization seemed to be a good tool to get well-controlled structure; however, very tedious purification steps are needed to remove the transition metal catalyst and ligand, which can be a major obstacle of this technique to be commercialized [10]. The objective of this study was to introduce a facile pathway to produce functionalized EPDM with well-defined structure. In order to maximize the increase of polarity of EPDM, we grafted simple molecules, not polymers, onto the polymer chain. Here we utilized EPDM sample, which is dissolved in hexane solution before stripping, collected directly from the plant process. An achievement of the aim of this study makes it possible to commercialize the EPDM functionalization process in a facile way.

2. Experimental

2.1. Materials

All reactions were performed under a purified nitrogen atmosphere using standard Schlenk technique. EPDM product was donated by Kumho Polychem Co., Korea as 6 wt% solution in hexane. Commercial production of EPDM at Kumho Polychem Co., is carried out by solution process in hexane, using soluble vanadium catalyst in the presence of alkyl aluminum cocatalyst. Immediately downstream of the reactor, the catalyst is quenched with a small amount of water. The resulting EPDM polymer solution goes then catalyst removal and polymer separation procedures. We utilized the EPDM solution directly collected after quenching the catalyst active sites for our further study. This EPDM has its viscosity average molecular weight of $3.0 \times 10^5$ g/mol and is comprised of 59 wt% of ethylene, 32.1 wt% of propylene and 8.9 wt% of ethylidienenorbornene (ENB). Dibenzoyl peroxide (BPO), N-bromosuccinimide (NBS), sodium acetate (Ac), and sodium chlorodifluoroacetate (CDFAc) were obtained from Aldrich and recrystallized before use. Various quaternary ammonium salts, tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrahexylammonium chloride (THAC), and tetraoctylammonium chloride (TOAC), were obtained from Fluka and used as received.

2.2. Bromination of EPDM

The allylic bromination was performed in a 3-neck round bottom flask (1000 ml) equipped with a reflux condenser, a thermometer, and a mechanical stirrer. After increasing the temperature of EPDM solution (200 ml, 6 wt% in hexane) to 70 °C, 0.2 g of BPO was added. To this mixture a solution of NBS (1.08 g, [ENB]/[NBS] = 1.0) in acetone (50 ml) was added drop wise for 30 min. The resulting homogeneous mixture was stirred for 1 h under reflux. The homogeneous solution was kept during the reaction, demonstrating the likely crosslinking reaction of EPDM in the presence of BPO was not so significant. After finishing this reaction, the brominated polymer was separated by routine procedure or further graft-from reaction (vide infra) was proceeded. For the separation, the reaction was quenched and precipitated by adding excess amount of methanol. The polymer was collected by filtration, extracted with boiling acetone by using Soxhlet extractor for 24 h, dried (60 °C, vacuum oven, overnight), and weighed.

2.3. Graft-from reaction by using phase transfer catalyst (PTC)

For a facile grafting of the simple metal salts such as sodium acetate and sodium chlorodifluoroacetate to the brominated EPDM in hexane solution, various quaternary ammonium salts were used as a solid–liquid phase-transfer catalyst, since the salts (Ac, CDFAc) were insoluble in hexane. In a typical procedure, 0.057 g (5 mmol) of TOAC and 1.63 g (0.2 mol) of sodium acetate was introduced into the EPDM solution resulting from the bromination (vide supra). The resulting slurry was stirred for 5 h at 70 °C. The reaction was quenched and precipitated by adding excess amount of methanol. The polymer was collected by filtration, extracted with boiling acetone by using Soxhlet extractor for 24 h, dried (60 °C, vacuum oven, overnight), and weighed. The graft-
from reactions by using different metal salt and phase transfer catalysts were carried out with similar procedures.

2.4. Characterization

All $^1$H-NMR spectra were recorded on a Varian Unity Plus 300 spectrometer in CDCl$_3$ at 25 °C, using tetramethylsilane as an internal reference. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer with thin polymer films. Samples were prepared for IR examination by using hot press equipped with a film maker (Graseby Specac). The contact angles ($\theta$) were determined using a contact angle meter (Kernco, model GII). The sessile drop method, using water as probe liquids, was used for contact angle measurements. Each contact angle quoted is the mean of at least five measurements with a maximum error in $\theta$ within 1°. All investigations were carried out using a polymer film in vapor-saturated air at 20 °C in a closed sample box. In order to understand surface energies of functionalized EPDM, work of adhesion ($W_A$) was estimated according to the famous equation of Young and Dupré derived for liquid droplets on surface exposed to vapor [11–14]

$$W_A = \lambda_i(1 + \cos \theta)$$  \hspace{1cm} (1)

where $\lambda_i$ is the surface free energy of liquid droplets (72.8 mJ/cm$^2$ for in water) [14].

For lap shear measurements strips of functionalized EPDM (20 $\times$ 10 $\times$ 0.9 mm) films were cut from the standard films. The test assembly was made by sandwiching the test films with Mylar® sheet made of poly(ethylene terephthalate) in a hot press at 180 °C for 5 min. The lap shear test was performed in a Zwick UTM (model 1445) at room temperature at a crosshead speed of 50 mm/min [ISO-813-1986(E)].

3. Results and discussion

A very useful way to carry out allylic bromination is to use the reagent NBS in carbon tetrachloride or aromatic hydrocarbon solvents initiated by peroxide and AIBN initiators or light. A solution of EPDM polymer dissolved in hexane used in this study was obtained from Kumho Polychem Co., Brominations of EPDM were carried out in hexane solvent, changing the molar ratio of [ENB]/[NBS] from 0.5 to 2.0 in the presence of BPO at 70 °C. Fig. 1 shows the FTIR spectra in the 2000–400 cm$^{-1}$ region for pure EPDM and brominated polymers. The characteristic signals in the spectra (Fig. 1(b)–(e)) are found in the range of 1075–1030 cm$^{-1}$ for the allylic C–Br stretching vibrations and 1250–1190 cm$^{-1}$ for C–Br bending vibrations. The graft yield was determined by $^1$H NMR by comparing the relative amount of alkenyl H bearing methyl groups and bromomethyl groups [15–17].

For a further functionalization the brominated EPDM solution was reacted with acid metal salts in the presence of various quaternary ammonium salts as PTC (Scheme 1). The reactions of the brominated EPDM with metal salts in the absence of PTC were not effective at all due to the insolubility of the metal salt in hexane [18]. In addition the yield of the same reaction was not so high when
short chain quaternary ammonium salts such as TBAB, TBAC, TBAI, and THAC were used as PTC. TOAC containing long alkyl chains showed the best performance as a solid–liquid PTC in our system. Fig. 2 shows the FTIR spectra of the functionalized polymers in the 2000–400 cm$^{-1}$ region. Comparing the spectra of the pure EPDM, brominated EPDM, and functionalized EPDM polymers by sodium acetate (Fig. 2(c)) and sodium chlorodifluoroacetate (Fig. 2(d)), the functionalized polymers show C=O stretching vibrations at 1760 and 1778 cm$^{-1}$, respectively. These results show that the metal salts insoluble in hexane react with bromine groups in EPDM effectively by using TOAC as solid–liquid PTC. It is interesting to note that the reactions are directly carried out in brominated EPDM solution.

The results of the graft-from reactions and the equilibrium contact angles for EPDM, brominated EPDM, and functionalized EPDM are tabulated in Table 1. The reaction of EPDM with an excess amount of NBS (say $[\text{NBS}]/[\text{ENB}] = 1.5$) in hexane in the presence of BPO at 70 °C resulted in a conversion of 77% of allylic hydride in ENB to allylic bromide. The reaction of the brominated EPDM
in hexane with sodium acetate and sodium chlorodifluoroacetate in the presence of TOAC as a PTC resulted in conversions of 82% and 65%, respectively, to yield corresponding acetate (Ac) and chlorodifluoroacetate (CDFAc) groups. These results demonstrate that direct graft-from reactions of the EPDM solution in hexane with NBS, followed by metal salts are a facile method for the production of functionalized EPDM with a defined structure.

The values of thermodynamic work of adhesion ($W_A$) calculated from Eq. (1) are also included in Table 1. The functionalization of the polymers decreases the equilibrium contact angle for water considerably. For example, the contact angles of water for brominated EPDM decreases from 94° to 77° (Entry 4, in Table 1), for functionalized EPDM with acetate groups from 94° to 76°, and for functionalized EPDM with chlorodifluoroacetate groups from 94° to 74°, respectively. The contact angle decreases due to several factors, of which surface polarity is an important one. Thus the more polar chlorodifluoroacetate groups yield lower contact angle. The work of adhesion calculated from the contact angle value increases when the contact angle decreases. Table 1 indicates that the functionalization by polar groups enhances the work of adhesion: $W_A$ of EPDM goes up from 68 to 93 mJ/m$^2$ on grafting with chlorodifluoroacetate groups. The polarity of the polymer surface might play an important role in increasing the work of adhesion.

The effect of wetting behavior is further understood from the measurement of lap shear strength test of pure and modified joints. For example, brominated EPDM rubber film and Mylar sheet joined together by hot pressing shows lap shear strength of 510 Pa (Table 1), which is much high value than pure EPDM film and Mylar sheet joint by 10 times. The values increase further to 650 Pa for acetate functionalized EPDM film and to 900 Pa for EPDM films with chlorodifluoroacetate groups. Even though these values have no significant absolute meaning, they are informative in that the relative increase in strength is due to the increased polar component of the surface energy, which gives rise to increased interaction through the interface.

### 4. Conclusions

The allylic bromination of the EPDM solution in hexane that was taken directly from the commercial plant was successfully carried out by reacting with NBS in the presence of BPO. About 77% of allylic hydride in ENB units was transformed to allylic bromide at 70 °C at [NBS]/[ENB] = 1.5. Addition of metal salts of polar

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>$[[\text{NBS}]/[\text{ENB}]]$ in feed</th>
<th>$[[\text{ENB}]<em>{\text{Br}}]/[\text{ENB}]</em>{\text{d}}$ in polymer</th>
<th>$[[\text{ENB}]<em>{\text{Ac}}]/[\text{ENB}]</em>{\text{br}}$ in polymer</th>
<th>$\theta$ (°)</th>
<th>$W_A$ (mJ/m$^2$)</th>
<th>Lap shear strength (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EPDM</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>94</td>
<td>68</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>EPDM-Br$^a$</td>
<td>0.5</td>
<td>0.23</td>
<td>–</td>
<td>79</td>
<td>86</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>EPDM-Br</td>
<td>1</td>
<td>0.51</td>
<td>–</td>
<td>77</td>
<td>89</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>EPDM-Br</td>
<td>1.5</td>
<td>0.77</td>
<td>–</td>
<td>77</td>
<td>89</td>
<td>510</td>
</tr>
<tr>
<td>5</td>
<td>EPDM-Br</td>
<td>2</td>
<td>0.79</td>
<td>–</td>
<td>77</td>
<td>89</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>EPDM-g-Ac$^b$</td>
<td>1.5</td>
<td>0.77</td>
<td>0.63</td>
<td>76</td>
<td>90</td>
<td>650</td>
</tr>
<tr>
<td>7</td>
<td>EPDM-g-CDFAc$^c$</td>
<td>1.5</td>
<td>0.77</td>
<td>0.50</td>
<td>74</td>
<td>93</td>
<td>900</td>
</tr>
</tbody>
</table>

* EPDM polymer obtained by allylic bromination.
* EPDM polymer obtained by reacting EPDM-Br (Entry 4) with sodium acetate.
* EPDM polymer obtained by reacting EPDM-Br (Entry 4) with sodium chlorodifluoro-acetate.
* Molar ratio of brominated ENB unit to total ENB unit (brominated ENB + unreacted ENB) determined by $^1$H NMR [15–17].
* Molar ratio of acetate functionalized ENB unit to total ENB unit (acetated ENB + brominated ENB + unreacted ENB) determined by $^1$H NMR [15–17].
compounds which are not soluble in hexane to this mixture together with quaternary ammonium salt as solid–liquid PTC yielded functionalized EPDM polymers. The effectiveness of the functionalization of EPDM employed in this study was demonstrated by the decrease of contact angle, the increase of the work of adhesion, and the increase of lap shear strength.

Acknowledgements

This work was supported by Grant No. R01-2003-000-10020-0 from the Basic Research Program of the Korea Science & Engineering Foundation and the Brain Korea 21 Project (2003). The authors also thanks the Center for Ultramicrochemical Process Systems (ERC), and NRL for partial financial support.

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