*Bulgarian Chemical Communications, Volume 49, Number 1, (pp. 26 – 30) 2017*

# Optimization of process conditions and characterization of ethylene-propylene-diene rubber with bismaleimide

M. Vadivel[1,*], S. Shobana[2], S.A. Narayan[3], L. Mitu[4], J. Dhaveethu Raja[1], M. Sankarganesh[1]

[1]*Department of Chemistry & Research Centre, Mohamed Sathak Engineering College, Kilakarai - 623 806, Ramanathapuram, Tamilnadu, India.*
[2]*Department of Chemistry and Research Centre, Aditanar College of Arts and Science, Virapandianpatnam, Tiruchendur–628 216, Thoothukudi, Tamilnadu, India.*
[3]*Department of Science and Humanities, Rohini College of Engineering & Technology, Anjugramam, Kanyakumari–629 851, Tamilnadu, India.*
[4] *Department of Physics and Chemistry, University of Pitesti, Pitesti–110040, Romania*

Received January 18, 2016; Revised May 18, 2016

The thermal and morphological properties of ethylene-propylene-diene rubber with bismaleimide (EPDM-g-BMI) were investigated. The effects of EPDM concentration, BMI concentration, reaction time and reaction temperature in terms of grafting efficiency (%) were examined. As the BMI concentration increases, the grafting efficiency increases. The FT-IR spectroscopy analysis of EPDM-g-BMI reveals that the C=C double bond in EPDM reacts with the maleimide double bond through a nucleophilic addition reaction. The SEM image of EPDM-g-BMI reveals a rough surface due to the formation of inter-crosslinked network between EPDM and BMI.

**Keywords:** Thermal properties, Ethylene-propylene-diene rubber, EPDM-g-BMI, DSC, SEM.

## INTRODUCTION

Ethylene-propylene-diene (EPDM) has excellent wear strength and superior mechanical resistance. It also has excellent tribological properties after chemical coupling [1]. Crosslinked EPDM is one of the major compounds commonly used as industrial polymers because of its marvelous resistance to wearing out and swelling, its thermal and flame retardant properties [2–4]. A number of graft copolymers, such as PS [5, 6], (POE)-graft-PS [7], EPDM-graft-POE [8] and (PE)-graft-PS [9–11] have been formed. These copolymers play an important role as compatibilizer at the interface of blends and decrease the interfacial tension between polymer phases.

Bismaleimides (BMI) are widely used as elevated performance composite matrices in aerospace industry. As compared with extra thermosetting polyimides, bismaleimides show both outstanding high performance and cost effectivity; thus they have been chosen as attractive candidates for advanced composite matrices [12]. Bismaleimides have outstanding solubility in the majority of the solvents like ethylene chloride, cyclohexanone, methylene chloride, etc. With the characteristics of both rigid rings and network forming ability, the final Tg of such systems can reach 400 ºC [13]. Therefore, the main challenges concerning the use of bismaleimides for composite applications are the improved processability and the crack toughness [14]. EPDM rubber has considerable marketable and technological importance and high research value. Though earlier investigations present a lot of useful information, however, no effort has been made to develop EPDM grafted bismaleimide.

## EXPERIMENTAL

### *Materials*

The EPDM (ENB type diene) terpolymer used in this study of a commercial grade Nordel IP 4750R was supplied by DuPont Dow elastomers, USA. (Ethylene/propylene/5-ethylidene-2-norbornene: 71/20/9 by wt. % and specific gravity 0.88). Dibutyltin dilaurate (DBTDL, Merck, Germany, density = 1.066 g.cm$^3$, freezing point >110 ºC, mw = 631.56). Maleic anhydride 99% (Otto Kemi, India, mw = 98.06, melting point = 53 ºC). Nickel acetate (HiMedia Laboratories Pvt Ltd, India, mw = 248.86). Triethyl amine (Fisher Chemic Ltd, India, mw = 101.19). Analytical grade toluene and n-hexane were used as received. Synthesis of bismaleimide (BMI) was already reported [15].

### *Methods*

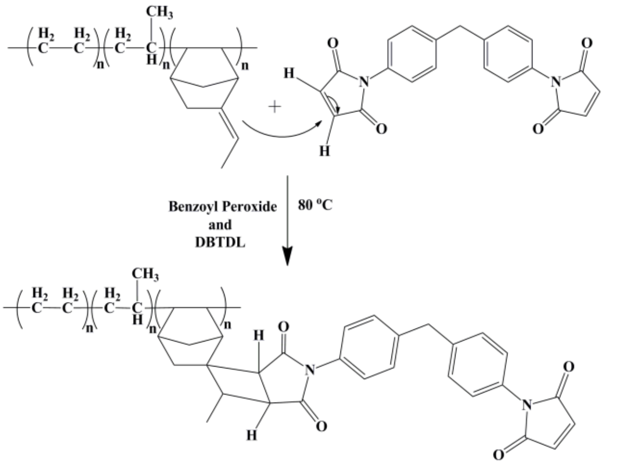
The FT-IR spectra of the samples were measured in KBr disks on a Shimadzu-1800S spectrometer. The samples were scanned from 4000 to 400 cm$^{-1}$. DSC (differential scanning calorimetry) was performed with a NETZSCH DSC 200 instrument. The sample (2 to 6 mg) was put in a sealed aluminum

---

* To whom all correspondence should be sent:
E-mail: vadivelche@gmail.com

pan and was heated at 10 $^{o}$C/min in the range of 0 - 500 $^{o}$C using an empty sealed pan as a reference. SEM (scanning electron microscope) micrographs of the composite materials were recorded using a Quanta-200, FEG scanning electron microscope (The Netherlands), and micrographs were taken at the required magnification. A working distance of 9.8 mm was maintained and the acceleration voltage used was 20.00 kV with the minor electron image as the detector.

### *Preparation of epdm grafted bismaleimide (EPDM-g-BMI)*



**Scheme 1**. Schematic presentation of EPDM-g-BMI preparation

EPDM (10 g/5 mM) was dissolved in 200 mL of toluene. Bismaleimide (0.025g/0.5 mM) was dissolved in 20 mL of toluene. The above two solutions were mixed in a 250 mL three-necked flask fitted with a condenser and nitrogen inlet. Benzoyl peroxide (0.05 g/0.01 mM) and DBTDL (0.005 g/0.0015 mM) were added to the above mixture and heated at 80 $^{o}$C for 5 h. The EPDM-g-BMI was precipitated by pouring the homogeneous mixture in excess amount of acetone where the unreacted BMI was removed. The precipitate was dried at 50 $^{o}$C for 48 h (Scheme 1).

### *Isolation of graft terpolymer*

After the synthesis, ungrafted EPDM, BMI and EPDM-g-BMI are present in the medium. The EPDM was separated from settled down products by extraction using n-hexane. The bismaleimide grafted EPDM (EPDM-g-BMI) was separated from BMI using DMF where the former is soluble and the latter is insoluble. The total conversion was calculated from the ratio of the total weight of crude products to the weight of EPDM charged. The grafting ratio and grafting efficiency were determined on the basis of the changes in polymer weight during the reaction development and the total amount of EPDM-g-BMI formed, respectively. The grafting ratio and grafting efficiency were calculated by the following equations:

$$\text{Total conversion (\%)} = \frac{\text{The weight of polymers formed}}{\text{Weight of EPDM charged}} \times 100$$

$$\text{Grafting ratio (\%)} = \frac{\text{Weight of EPDM - g - BMI}}{\text{Weight of EPDM charged}} \times 100$$

$$\text{Grafting effeciency (\%)} = \frac{\text{Weight of EPDM - g - BMI}}{\text{Total weight of polymers formed}} \times 100$$

The best grafting efficiency of BMI onto EPDM was achieved by the solution (grafting) polymerization method. All samples were dissolved in toluene followed by intense stirring for 10 min, till the mixture became homogeneous. Then, the solution was transferred into a glass mold and closed with Para film to permit the removal of small molecules of both the solvents, and those produced in the hydrolysis. Upon gradual ventilation over 10 days, translucent samples of hybrids were obtained without cracks. All samples are listed in Table 1.

**Table 1**. Conditions of graft copolymerization

| Conditions | Description | | | | |
|---|---|---|---|---|---|
| EPDM concentration (%) | 5.0 | 10 | 15 | 20 | 25 |
| BMI concentration (%) | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| Reaction time (h) | 2.0 | 4.0 | 6.0 | 8.0 | – |
| Reaction temperature ($^{o}$C) | 50 | 60 | 70 | 80 | – |

## RESULTS AND DISCUSSION

### *FT-IR spectroscopy*

The IR spectra of EPDM and EPDM-g-BMI exhibit ν(C–H) stretching, ν(CH$_2$) rocking ν(CH$_3$) symmetric bending (aliphatic) and ν(CH$_2$)$_n$ wagging vibrations at 2911, 1451, 1367 & 721 cm$^{-1}$ and 2918, 1464, 1375 & 719.15 cm$^{-1}$, respectively (Fig. 1).

In addition, EPDM shows vibrations at 2851 cm$^{-1}$ and 811 cm$^{-1}$ for ν(C–C) and ν(>C=CH–) stretching due to the presence of ENB. However, ν(C–H=) stretching vibration at 3090 cm$^{-1}$ is observed while ν(C=C) stretching vibration at 1627.99 cm$^{-1}$ of BMI has disappeared [15] due to the grafting reaction by a free radical mechanism which involves the allylic position of the ENB unit of the EPDM with addition across the α,β-unsaturated linkage [16] in the bismaleimide resin. Similar observations are made for bismaleimide toughened reactive rubbers [16]. A decrease in band intensity due to unsaturated ν(C=H) present in the side chain of ENB at 815 cm$^{-1}$ is observed which indicates that ν(C=C) is utilized for new chemical bond formation with BMI.

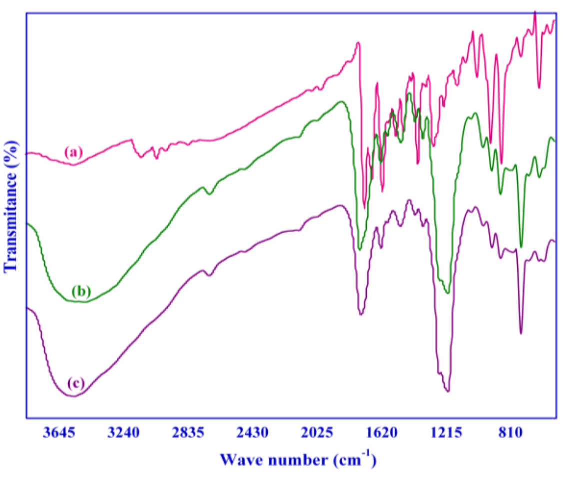


**Fig. 1.** FT-IR spectra of (a) EPDM, (b) BMI and (c) EPDM-g-BMI

## *Effect of reaction conditions on grafting*

### *Effect of EPDM content*

The effect of EPDM content on the graft copolymerization is presented in Fig. 2(a). The grafting reaction was carried out at 80 °C for 4 h with 2.5 wt% of BMI. The grafting efficiency increases linearly with the increase in concentration of EPDM, due to the availability of a double bond present in EPDM. The grafting efficiency for 10 wt% EPDM is 20% and that for 30 wt% is 30%. At higher concentrations of EPDM, additional active sites are created and thus the grafting efficiency increases. However, a smaller number of active sites are generated in the case of lower concentration of EPDM resulting in a decrease in grafting efficiency, which favors the enhanced homopolymerization of BMI.

### *Effect of BMI concentration*

The effect of BMI on the grafting efficiency is presented in Fig. 2(b). The grafting reactions were carried out at 80 °C for 4 h with 1, 1.5, 2, 2.5 and 3% of BMI on EPDM. The grafting efficiency increases with the increase in BMI concentration. The grafting efficiency for 2 wt% of BMI is 24.67, whereas the highest grafting efficiency of 28.01 is observed for 2.5 wt% of BMI. There is a sharp increase in grafting efficiency up to 2.5 wt% of BMI. Above 2.5 wt% of BMI no significant increase in grafting is observed. The higher concentration of BMI favors the formation of a larger number of active sites in the amine part of BMI, which favors the homopolymerization rather than grafting.

### *Effect of reaction time*

The efficiency of grafting of BMI onto EPDM as a function of reaction time is given in Fig. 2(c). The reactions were carried out at 80°C with 0.1wt% of

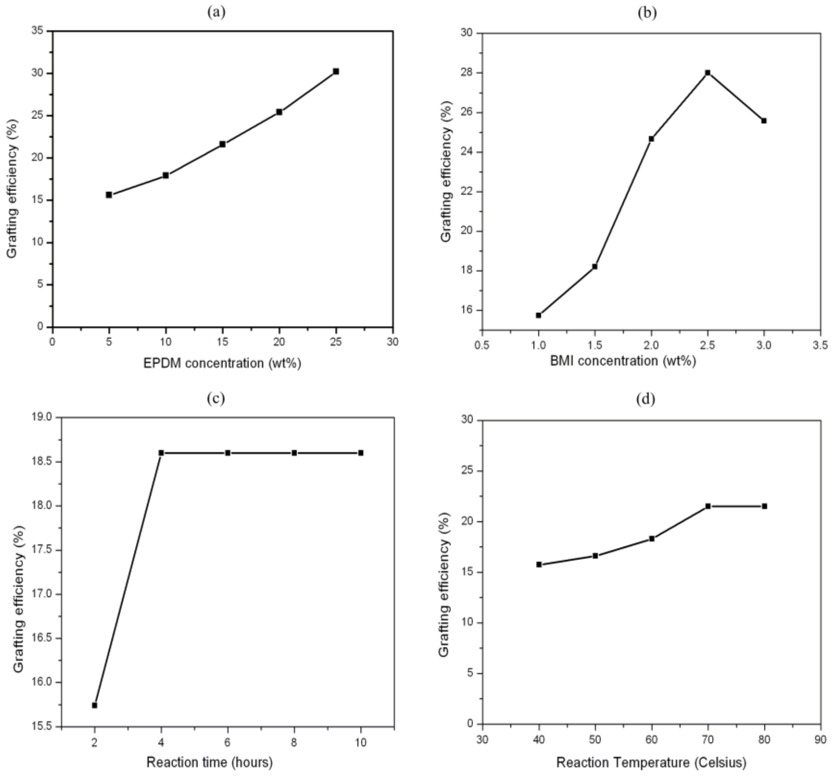


**Fig. 2**. Plot of grafting efficiency against (a) EPDM concentration; (b) BMI concentration; (c) reaction time; (d) reaction temperature.

benzoyl peroxide for periods of 2, 4, 6, 8 and 10 h. It was observed that the grafting efficiency increases with increase in reaction time up to 2 h, and beyond 4 h there was no appreciable effect on the grafting efficiency. However, the total conversion increases with increase in reaction time due to the formation of the homopolymer.

### *Effect of reaction temperature*

The influence of temperature on the grafting is presented in Fig. 2(d). The reaction was carried out with 2.5 wt% of BMI and 0.1 wt% of benzoyl peroxide at different temperatures, namely, 40, 50, 60, 70 and 80 °C. The grafting efficiency increases with increasing reaction temperature from 40 to 80 °C. However, beyond 80 °C, there was no significant change in the grafting efficiency which indicates the end of the reaction.

### *Calorimetric analysis*

A sharp endothermic peak at -52.1 °C indicates the simultaneous occurring of dehydrogenation and disproportionation of EPDM. DSC scans also show a sharp endothermic peak at 489 °C due to the curing of EPDM-g-BMI (Fig. 3).

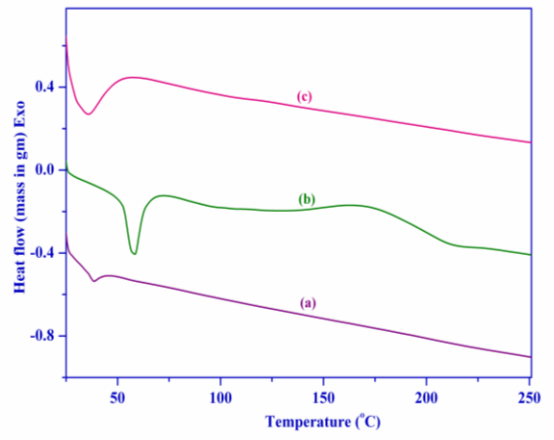


**Fig. 3.** DSC curves of (a) EPDM, (b) BMI and (c) EPDM-g-BMI.

The complex molecular structure of the grafted copolymer of bismaleimide and EPDM hinders the contribution of reactive sites for the curing reaction, which in turn increases the curing temperature of the system. The increase in endothermic peak temperature was also due to the steric hindrance produced by the EPDM particles between the two reacting sites, which necessitated a higher temperature to increase the reactivity of the crosslinking sites [17].

### *SEM analysis*

The SEM images of the EPDM, BMI and EPDM-g-BMI are shown in Figs. 4(a) to 4(c). The SEM micrograph of EPDM shows a smooth surface morphology. The SEM micrograph of the unmodified BMI reveals that crystallites with micropores are representative of the brittle phase.

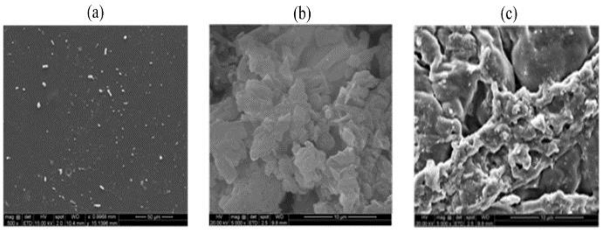


**Fig. 4**. SEM micrograph of (a) EPDM; (b) BMI; (c) EPDM-g-BMI.

The SEM micrograph of the EPDM-g-BMI system reveals that the minor component (BMI) is dispersed within a range of the major component (EPDM) with continuous morphology [18, 19]. Fig. 4a of pulled out traces of micrographic morphology depicts the poor adhesive nature of EPDM. Fig. 4b also shows a chunk of BMI agglomerate-like morphology. Figs. 4a and 4b explain their lower stiffness value / storage modulus. From Fig. 4c, a high interfacial tension between BMI and EPDM phases follows which leads to a bigger size of dispersed rubber phase (3.3 μm), which means enhanced stress transfer and higher impact on strength and supports the rubber wear concept by the process of plowing. It is obvious that it is a stratification phenomenon, if no segregation of the core and periphery exists, due to the configuration of inter-crosslinked network indicated by the active and rough surface. Moreover, Fig 4c implies that there is an influence on storage modulus and loss factor, separately.

## CONCLUSIONS

EPDM-g-BMI graft terpolymer was synthesized by a solution polymerization method. The following conclusions are made based on the data resulting from different experimental studies. The grafting of BMI onto EPDM reveals that the C=C double bond in EPDM reacts with the maleimide double bond through a nucleophilic (Michael) addition reaction which is confirmed by FTIR spectra. It was ascertained that the threshold grafting efficiency was maximum at 2.5 mol% of BMI. The grafting efficiency increases with the increase in temperature and EPDM content. The grafting of BMI onto EPDM increases Tg values. Hence the EPDM-g-BMI rubber may be used in cable insulation application for better performance. The morphology proved that EPDM-g-BMI rubber shows improved adhesion, better stress transfer, superior impact on strength and protective rubber wear.

## REFERENCES

1. M.S. Khan, D. Lehmann, G. Heinrich, U. Gohs, R. Franke, *Express. Polym. Letters*, **3**, 39 (2009).
2. J. He, X. Zhang, X. Li, R. Yang, *Plast. Rubber. Compos.*, **44**, 206 (2015).
3. R. Chen, S. Lu, C. Li, M. Li, S. Lo, *J. Therm. Anal. Calorim.*, **122**, 449 (2015).
4. H. Ismail, S. Ishak, Z. A. A. Hamid, *J .Vinyl. Addit. Techn.*, **21,** 1 (2014).
5. M. F. Diaz, S. E. Barbosa, N. J. Capiati, *Polymer*, **46**, 6096 (2005).
6. M. F. Diaz, S. E. Barbosa, N. J. Capiati, *Polym. Eng. Sci.*, **46**, 329 (2006).
7. Z. H. Guo, L. F. Tong, Z. P. Fang, *Polym. Int.*, **54**, 1647 (2005).
8. J. Su, J. Zhang, *J. Elastomers Plast.*, **46**, 368 (2013).
9. G. Zhang, Y. Wang, H. Xing, J. Qiu, J. Gong, K. Yao, H. Tan, Z. Jiang, T. Tang, *RSC. Advances*, **5**, 27181 (2015).
10. Y. Gao, H. Huang, Z. Yao, D. A. Shi, Z. K
11. M. F. Diaz, S. E. Barbosa, N. J. Capiati, *Polymer*, **48**, 1058 (2007).
12. R. Rajasekaran, M. Alagar, *J. Compos. Mater.*, **42**, 1031 (2008).
13. M.R. Tant, J.W. Connell, H.L.N. McManus, High-Temperature Properties and Applications of Polymeric Materials. American Chemical Society, Washington DC, 1995.
14. X.J. Hu, C.Y. Fan, G.Z. Yue, Liang. *J. Mater. Process. Technol.*, **89**, 544 (1999).
15. M. Vadivel, M. Suresh Chandra Kumar, V. Selvam, S. Shobana, S. Arvindnarayan, *Asian J. Chem.*, **26**, 7160 (2014).
16. S. Takeda, H Akiyama, H. Kakiuchi, *J. Appl. Polym. Sci.*, **35**, 1341 (1988).
17. Halimatuddahliana, H. Ismail, *Polymer Plast. Tech. Eng.*, **48**, 25 (2008).
18. S.S. Ray, M. Okamoto, *Prog. Polym. Sci.*, **28**, 1539 (2003).
19. K. Rajkumar, P. Thavamani, P. Jeyanthi, P. Pazhanisamy, *Chem. Sci. Trans.*, **2**, 1042 (2013).

# ОПТИМИЗАЦИЯ НА УСЛОВИЯТА НА ПРОЦЕСА И ОХАРАКТЕРИЗИРАНЕ НА КАУЧУК ОТ ЕТИЛЕН-ПРОПИЛЕН-ДИЕН С БИС-МАЛЕИНИМИД

М. Вадивел[1,*], С. Шобана[2], С.А. Нараян[3], Л. Миту[4], Дж. Дхавеетху Раджа[1], М. Санкарганеш[1]

[1]*Департамент по химия & Изследователски център, Колеж по инженерство „Мохамед Сатхак“, Килараи 623 806, Раматхапурам, Тамилнаду, Индия.*
[2]*Департамент по химия & Изследователски център, Колеж поизкуства и наука „Адинатар“, Вирапандианпатхам, Тиручендур-628 216, Тхоотхукуди, Тамилнаду, Индия*
[3]*Департамент по наука и хуманитарни знания, Колеж по инженерство и технология „Рохини“, Анджуграмам, Канякумари–629 851, Тамилнаду, Индия*
[4]*Департамент по физика и химия, Университет в Питещ, Питещ–110040, Румъния*

Постъпила на 18 януари, 2016 г.; коригирана на 18 май, 2016 г.

(Резюме)

Изследвани са термичните и морфологичните свойства на каучук от етилен-пропилен-диен с бис-малеимид (EPDM-g-BMI). Изучени са ефектите на концентрациите на EPDM и BMI, времето за реакцията и температурата в параметрите на графт-ефективността (%). С нарастване на концентрацията на BMI нараства и графт-ефективността. FT-IR спектроскопският анализ на EPDM-g-BMI показва, че C=C двойната връзка в EPDM реагира с двойната връзка в молекулата на малеинимида чрез нуклеофилна присъединителен механизъм. SEM-образите на полимера EPDM-g-BMI показват грапава повърхност поради образуването на вътрешни мрежи между EPDM и BMI.