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Synthesis and Characterization of Glycidyl Methacrylate-Grafted Ethylene-Propylene Diene Terpolymer Employing Styrene as a Comonomer

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ABSTRACT

Melt free-radical grafting reactions between ethylene-propylene-diene terpolymer (EPDM) and glycidyl methacrylate (GMA) were studied in a batch mixer at 170°C and 60rpm, with and without styrene (St) comonomer. Effect of dicumyl peroxide (DCP) initiator, GMA and styrene concentrations were studied on the grafted EPDM characteristics. Titration results indicated an increase in the graft degree (GD) and gel content (GC) values with increasing DCP concentration. Whereas, introduction of St led to 132% increase in GD and 39% decrease in GC which might be ascribed to its effect on restricting crosslinking side-reaction. FTIR spectrums confirmed that GMA has been successfully grafted onto EPDM.

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1. Introduction

The inert nature of most polymers is the key characteristic allowing for their considerable use in variety of applications, but at the same time a disadvantage for applications in which surface wettability or interaction with polar components is required (Oxley, Gaffney, 2022, Passaglia, Coiai, 2009, Sun, Liu, 2020). In order to obviate this problem, several studies have been conducted on the functionalization of polymers (e.g. polyolefins, polyesters, etc.) through free-radical grafting of functional monomers onto the polymer backbone.

Free-radical grafting of functional monomers onto polyolefins is always accompanied with side reactions depending on the nature of macro-radicals and the polyolefin. Chain branching/crosslinking and chain scission are the most common side reactions detected for polyethylene and polypropylene, respectively (Marsilla and Verbeek, 2015). Introducing a second monomer such as styrene (Ma, Cai, 2014), divinyl benzene (DVB) (Doudin, Ahmad, 2009) and trimethylolpropanetriacrylate (Tris) (Al-Malaika and Kong, 2001) to the grafting reactions as “comonomer” or “co-agent” is suggested to control undesirable side reactions. Comonomer are shown to decrease the gel content dramatically where a little effect on the grafting degree have been reported (Li, Zhang, 2003). However, there are no reports on the compatibilization of EPDM using styrene as a comonomer or co-agent. According to the mentioned gap in the grafting process of EPDM, styrene-assissted free-radical grafting reactions at different dicumylperoxide initiator and GMA concentrations were investigated in the present study. Grafting degree and gel content of EPDM rubber samples functionalized at the absence and presence of styrene comonomer were analyzed through FTIR and titration techniques.

2. Experimental

2.1. Materials

Materials used in this research were ethylene propylene diene monomer (EPDM), KEP 270 supplied by KumhoPolychem (Korea)with mooney viscosity ML (1 + 4) 125 °C: 71M, ethylene content: 57%, termonomer content: 4.5 ENB%, density: 0.86 g/cm^3; glycidyl methacrylate monomer (GMA, 97%, Aldrich Chemical Co., Japan); dicumyl peroxide (DCP, 98%, Merck Millipore, Germany) and styrene monomer (st., 99%, Merck Millipore, Germany). Xylene, acetone, ethanol, trichloroacetic acid (TCA), phenolphthalein and potassium hydroxide used for titration and purification were all of analytical grade obtained from Merck Millipore.

2.2. Preparation

Melt grafting reactions were conducted using an internal mixer (Brabender W50, Duisburg, Germany) preheated to 170 °C. Regarding the volatility of GMA at the processing temperature, twenty minutes prior to the mixing, GMA, DCP initiator and styrene chain-transfer agent (for styrene-assisted batches) were physically poured on EPDM in a closed container. Impregnated EPDM was then melt mixed for 8 minutes at 60 rpm. This process can be seen in (Figure 1). All EPDM-g-GMA samples were prepared according to (Table 1) (Jazani, Rastin, 2017).

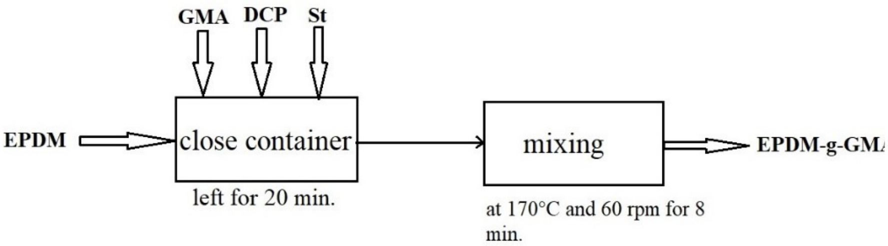

Figure 1. Melt Free-Radical Grafting Process

Table1. Melt Free-Radical Grafting Components: Concentrations and Nomencalture

Sample Code	DCP, phr	GMA, phr	St, phr
E-St-1	0.5	3	2.25
E-St-2	0.5	5	3.75
E-St-3	0.5	7	5.25
Blank1	0	5	0
E1	0.5	5	0
E2	0.3	5	0
Blank2	0	3	0
E3	0.3	3	0
E4	0.15	3	0

2.3. Characterization

Gel content and graft degree measurements- A few grams of each EPDM-g-GMA sample was put in 100 ml boiling xylene for one hour. The remaining solid filtrate was dried in vacuum oven at 80 °C for 24 hours. Gel content was then calculated according to the following Equation:

$$GC = \frac{w_1}{w_0} \times 100 \qquad (1)$$

Where w_0 and w_1 are sample weights before and after xylene solution, respectively.

Graft degree was calculated according to Eq. (2) (Alidadi-Shamsabadi, Arefazar, 2020):

$$GD = \frac{142.15 \times (C_0V_0 - C_2V_2)}{W} \times 100 \qquad (2)$$

Where C_0 and C_2 are TCA and KOH standard solution concentration, respectively. V_0 and V_2 are TCA standard solution volume and KOH standard solution volume used through titration, respectively. Windicates the initial sample weight. Fourier transform infrared (FTIR) spectroscope (Bomem-102, Canada) was used to track the expected reactions. Samples were purified with boiling xylene and acetone/ethanol anti-solvent before acetone rinsing to prepare the test sample:

3. Results and Discussion

3.1.Gel Contact and Degree of Grafting

(Figure 2) compares the variations observed in gel content and GMA graft degree with increasing DCP amount at fixed GMA contents, for those samples prepared with no styrene. At both GMA contents studied here (i.e. 3 and 5 phr); a similarly increasing trend is observed for graft degree values versus DCP content. This is attributed to the accelerated formation of free-radicals and consequently macro-radicals along the polymer chain at the presence of DCP. In fact, the DCP initiator undergoes a homolytic decomposition upon thermomechanical heating to yield a pair of primary free radicals which can abstract a tertiary hydrogen from the EPDM chain to form a macromolecular radical (Brito, Xin, 2014).

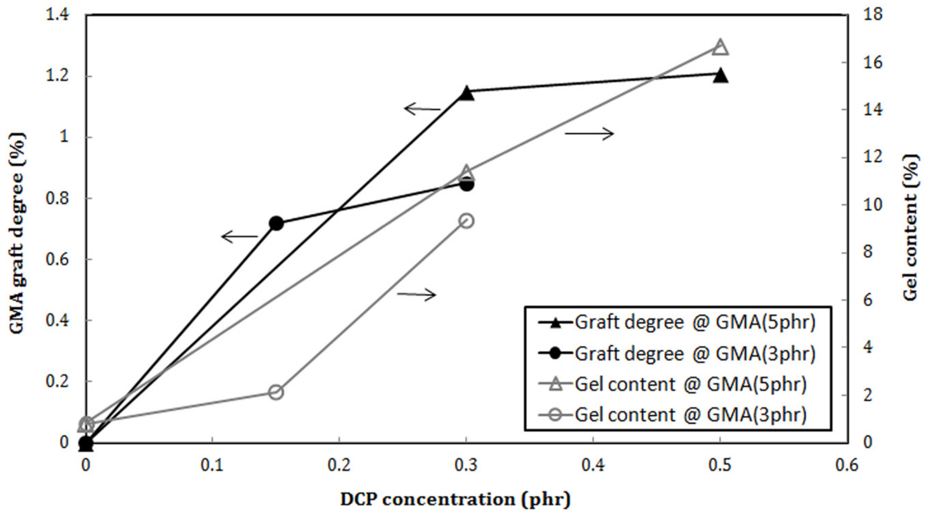

Figure 2. GMA Grafted EPDM, Graft Degree and Gel Content Versus DCP Concentration at Different GMA Concentrations

Gel content has also increased with DCP content at the same time with the graft degree but the trend is somehow different. At GMA content of 5 phr, the increasing rate is almost uniform along all DCP contents studied here, since crosslinking competing reactions would be more contingent at the presence of higher concentrations of macro-radicals. This would produce more gel-like structures in the sample bulk. At GMA contents of 5 phr, the increasing rate was observed to be unaffected by DCP concentration which might be due to the homo-polymerization of GMA molecules beside the crosslinking reactions. In such circumstances, a portion of the free-radicals present in the reaction media are involved in the GMA homo-polymerization. This would suppress the expected crosslinking reactions. Limited solubility of monomer in the polymer, yielding high local concentration, has also known to be responsible for oligo(GMA) grafts (Gross, Schneider, 2018).

Comparing the values presented in (Figure 2) and (Table 2) for E-St-1, E-St-2 and E-St-3 with those of E1, E2, E3, E4, Blank1 and Blank2 shows that the graft degree and gel content of the samples prepared at the presence of styrene chain-transfer agent are respectively greater and smaller than the samples prepared without styrene.

Table2. Graft Degree and Gel Content of EPDM Samples Grafted at the Presence of Styrene (DCP=0.5 phr)

Sample Code	Graft Degree,%	Graft Efficiency,%	Gel Content,%
E-St-1	1.93	64.3	8.51
E-St-2	2.81	56.2	10.12
E-St-3	3.04	43.4	10.68

It should be noted that the direct attack of the macroradicals to GMA is significantly hindered by the steric effect of polymer chains where in the presence of styrene comonomer; the EPDM macroradicals preferably attack styrene due to its less steric effect. Produced styryl radicals, then, are copolymerized with GMA monomers easily. On the other hands, styrene could progress a reaction with EPDM macro-radicals much faster than GMA and this would prevent the macroradicals to be involved in the crosslinking competing pathways. The resulting styryl macroradicals are also stabilized by resonance of styrene. This procedure would cause an increase in the graft degree (Bansod, Kapgate, 2018).

According to (Table 2), a moderate increase can be seen in the gel content by simultaneously increasing equimolar amounts of GMA and St, as well the graft efficiency has decreased. While GMA (positive on GD, negative on GC) and St (positive on GD and GC) effects have been individually investigated, the equimolar amount of GMA introduced to the reaction seems to negatively affect the reaction. Accordingly, to achieve acceptable gel contents and graft efficiencies, St/GMA molar ratios greater than 1 seem to be more sensible. Considering that styrene, besides the direct reaction with macroradicals, could activate the graft monomer (i.e. GMA) by forming a charge-transfer complex;(Brito, Xin, 2014) introducing St/GMA molar ratios smaller than 1 might restrict the styrene comonomer roles. Flat(Hu, Flat, 2012) correspondingly showed that grafting yield does not always increase with styrene content but it goes through a maximum when St/GMA molar ratio is between 1 and 2.

3.2. FTIR Spectroscopy

(Figure 3a) compares the FTIR spectroscopy results of pure EPDM and the EPDM samples grafted by GMA in the absence of styrene comonomer. As expected, the main characteristic peak confirming the formation of C = O carbonyl groups during the grafting reaction, has appeared at 1730 cm-1 for samples E1, E2, E3 and E4. Although Bray (Bray, Damiris, 1998) believed that formation of oligo(maleic anhydride) grafts would shift the characteristic peak of simple alkyl succinates; no evidence reliable enough to claim the formation of graft length was detected here. The epoxy group, responsible for the compatibilizing features of GMA-grafted polymers, was detected as a shoulder at 990 cm-1.

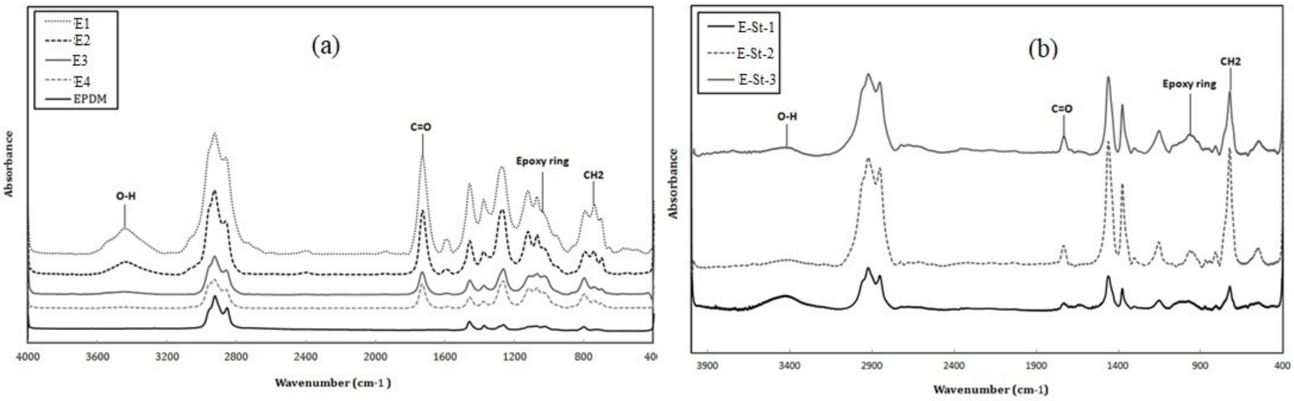

Figure 3. FTIR results of pure EPDM and the EPDM-g-GMA samples in the (a) absence and (b) presence of styrene

FTIR spectroscopy results of EPDM-g-GMA samples prepared in the presence of styrene comonomer are illustrated in (Figure 3b). Peaks appeared at 721, 972, 1734 and 3433 respectively correspond to stretching CH_2, epoxide, carbonyl and hydroxyl functions confirming the functionalization of EPDM chains by GMA.

4. Conclusion

Glycidylmethacrylate was grafted onto ethylene-propylene-dieneterpolymer through melt free-radical grafting process in the absence and presence of styrene chain-transfer agent. Graft degree and gel content results obtained by titration indicated that styrene improves the graft degree by preventing the unfavorable crosslinking reactions. The decrease in gel content values confirms this observation. Comparing the results published on the application of trimethylolpropanetriacrylate shows that styrene shows a better performance decreasing the gel content besides its positive effect on the graft degree. In the absence of styrene, increasing the concentration of DCP can improve the graft degree as well as the gel content. Analyzing the graft degree and gel content results showed that sample E4 (DCP = 0.15 phr, GMA = 3 phr) with grafting degree of 0.72 wt% and gel content of 2.12 wt% could be selected as the best sample to use as a compatibilizer in polymer blends. FTIR results confirmed the conclusions based on titration technique.

List of Abbreviation

DCP	Dicumyl peroxide
EPDM	Ethylene-propylene-diene terpolymer
EPDM-g-GMA	Glycidyl methacrylate grafted Ethylene-propylene-diene terpolymer
FTIR	Fourier transform infrared
GC	Gel content
GD	Graft degree
GMA	Glycidyl methacrylate

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سنتز و مشخصه‌یابی اتیلن پروپیلن‌دی ان مونومر پیوند خورده با گلایسیدیل‌متاکریلات از طریق کومونومر استایرن

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چکیـــــــده

واکنش پیوند رادیکال آزاد مذاب بین اتیلن-پروپیلن-دی ان مونومر (EPDM) و گلیسیدیل متااکریلیت (GMA) در حضور و غیاب کومونومر استایرن (St) در مخلوط‌کن داخلی (۱۷۰ سیلسیوس، ۶۰ دور بر دقیقه) بررسی شد. اثر غلظت آغازگر دی کیومیل پراکساید (DCP)، GMA و St بر پیوند بین EPDM و GMA مطالعه شد. نتایج تیتراسیون افزایش مقادیر درجه پیوند (GD) و میزان ژل (GC) را با افزایش غلظت DCP نشان داد. در حالی که کاربرد St، با جلوگیری از ورود ماکرورادیکال‌ها به واکنش جانبی ژل شدن، منجر به افزایش ۱۳۹درصد برای GD و کاهش ۳۹درصد برای GC شد. نتایج FTIR پیوند GMA بر روی زنجیره‌های EPDM را تائید کرد.

واژگان کلیدی: پیوند رادیکال آزاد، گلایسیدیل متاکریلات، اتیلن-پروپیلن-دی ان مونومر، کومونومر، میزان ژل