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FUNCTIONALISATION OF ETHYLENE-PROPYLENE COPOLYMER (EPM) BY MELT GRAFTING OF MALEIC ANHYDRIDE (MAH) USING HIGH SHEAR INTERNAL MIXER

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MAH grafted EPM is a highly potential compatibiliser in EPDM based blend. This study is focusing on synthesizing peroxide-initiated MAH-g-EPM via melt grafting using a Haake internal mixer at high shear rate. The effect of MAH and dicumyl (DCP) percentage on the grafting efficiency of MAH onto EPM chains was carried out through a 2-level factorial experimental design using the Design Expert 6.0.5 software. The MAH and DCP content were varied in the range of 1-5 phr and 0.1-0.3 phr, respectively. The grafting parameters were fixed at temperature of 180°C, rotor speed of 60 rpm for 5 minutes. The grafting efficiency was determined by Fourier Transform Infrared spectroscopy analysis based on cumulative absorbance of anhydrides characteristic peaks. It was observed to be highly influenced by the amount of MAH and DCP and the optimum functionalisation was achieved at 5 phr MAH and 0.3 phr peroxide addition.

Keywords: Ethylene-Propylene Copolymer (EPM), melt functionalisation, maleic anhydride, grafting parameters, rubber blends incompatibility.

Introduction

Blending of two or more polymers produces material with improved properties, better processibility and superior⁹ compared to its original phases at⁹ very minimal cost^{1,2,3}. For instance, rubber blends are widely utilised in automobile parts like springs and snubbers, hose and belting, seals and bearing⁴, engine mounts⁵, gears gaskets, pneumatic tires and tubes³. Previous research works have reported some attractive elastomers blends such as NR/EPDM^{6,7}, BR/EPDM⁸, NBR/EPDM^{7,8}, NR/BR/EPDM⁹, NR/ENR¹⁰, NR/SBR/BR¹¹, NR/IIR¹² and NR/EPM^{1,13,14}. Among these blends, NR/EPDM shows great potential in outdoor-application due to excellent thermal, chemical and ozone resistance, as well as attractive dynamic properties^{6,13}. For example, poor outdoor properties of high unsaturated rubbers such as NR can be significantly improved by the incorporation of EPDM without sacrificing their unique mechanical properties⁹.

According to Kothandaraman², a successful NR/SBR blend may exhibits discrete areas of each elastomers in the range of ~ 0.5 microns². However, in most cases elastomers are immiscible due to their high molecular weight chains, viscosity mismatch, differences in cure rate, different saturation level, and polarity mismatch^{9,13}. Immiscibility produce blends with poor mechanical properties. Due to that, compatibilisation is required to improve compatibility of the blends¹⁵. In El-Sabbagh⁶ and Zhang⁹ findings, the incorporation of a small amount of compatibiliser reduces the domain size of the dispersed phase, and thus enhances the compatibility and rheological properties of the blend.

Generally, compatibilisation can be conducted either physically or chemically. Physical compatibilisation is achieved by the addition of third polymer into the elastomers blends to form a block or grafted copolymers⁶. The third polymer acts as surfactant where the high polar component of the blend will attract to the high polar part of the compatibiliser and vice versa. The third polymer can be polybutadiene rubber (BR)⁶, chlorinated rubber or SBR⁶ and ENR^{16,17}. Due to Mohamad¹⁶, ENR is frequently used as compatibilizer in producing natural rubber nanocomposites due to its high polarity. On the other hand, chemical compatibilisation is achieved by addition of reactive or functional compound into the blends in order to induce in-situ chemical reaction between the blends components¹⁸. For chemical compatibilisation, maleic anhydride (MAH) from vinyl monomers group is often used to be grafted onto a polymer either through free radical copolymerisation or melt grafting. The anhydride group will grafted to polar polymer and form functionalised compound^{2,14,15}. According to Stuart¹⁹ and Segneanu et al.²⁰, MAH grafting is identified by a distinctive

carbonyl band region at several characteristic infrared bands; (1840-1800), (1780-1740) and (1300-1100) cm^{-1} which correspond to anhydrides stretching regions (-CO-O-CO-). In addition, a strong C-O stretching band of open-chain and cyclic anhydrides structures may be observed near 1150 cm^{-1} or ranging around 1150-1300 cm^{-1} , respectively. Furthermore, based on Ismail et al.²¹, the grafting of MAH is also indicated by the presence of band at (1710-1719) and (1770-1792) cm^{-1} which attributed to C=O symmetric stretching bonds. Examples of functionalised compatibiliser for EPDM based blend are EPDM-g-PVAc¹⁴, MMA-g-EPDM¹³, EVA-g-MAH, mercapto-functionalised EVA, mercapto-modified EPDM and MAH-g-EPDM^{9,22}.

MAH-g-EPM is a potential compatibiliser and similar with MAH-g-EPDM in term of structure except for the double bond. Referring to Zhang⁹, addition of MAH-g-EPM in NR/BR/EPDM blends increases the chemical reactivity of the blends due to the increase in polarity of the EPDM. This is due to the presence of maleic anhydride group which provides extra polarity to the EPDM and be well linked to high polar double bond of NR diene rubber phase.

Melt compounding via internal mixer is a widely used technique to prepare for polymer compounds and blends¹⁷. Uniform compounding is achieved when the materials are sheared between two rotors that are circulating in an opposite manner in the mixer chamber. High shear forces are needed for a blending process in order to overcome the high viscosity of melted elastomers². Nevertheless, melt grafting via internal mixer is a rarely use technique to produce MAH-g-EPM compatibiliser.

This study is an effort to measure the efficiency of melt grafting through high shear melts compounding using a Haake internal mixer. It is aimed to prepare MAH-g-EPM via peroxide-initiated melt grafting of anhydride onto EPM backbone as well as to detect the optimum formulation of MAH-g-EPM using a mathematical and statistical technique. Response Surface Methodology is selected due to less time consuming and has the ability of detecting the true optimum of the factor²³. Incorporation of low molecular weight peroxide is expected to activate the inert polyolefin and thus induce functionalisation of EPM with MAH.

Experiments

Ethylene Propylene Copolymer (EPM) with propylene content of 80%, melt flow index of 1.3 g/10 min, and density of 0.862 g/cm^3 was supplied by Exxon Mobil Chemical. Maleic anhydride ($\text{C}_4\text{H}_2\text{O}_3$) with purity of 99% and weight average molecular weight, M_w of 98.06 g/mol was supplied by Scharlau. Bis(α,α -dimethylbenzyl)peroxide (DCP) as free radical

initiator and crosslinking agent with purity of 98%, M_w of 27037 g/mol and density of 102 g/cm³ was supplied by Merck.

MAH grafted EPM compounds were prepared by blending 100 phr EPM, 1-5 phr varied amount of MAH and 0.1-0.3 phr varied amount of DCP in a Haake internal mixer at temperature of 180°C, rotor speed of 60 rpm and mixing period of 5 minutes. The internal mixer used was equipped with a Banbury-type rotor blade and a mixing chamber capable of 78 cm³ volume, with fill factor of 0.70. Equation 1 was applied to calculate the total mass of ingredients capable by the mixing chamber;

$$m_{\text{total}} = \rho \times V_{\text{chamber}} \times 0.7 \text{ fill factor} \quad \text{----- Equation 1}$$

(1)
re-write

All the three components were initially dry mixed in a weighing tray before immediately being introduced into the mixing chamber. The mixing was performed until 5 minutes for a complete peroxide reaction and to produce homogenous blend. The generated compounds were then conditioned for FTIR analysis.

The experiment for this study implemented 2-level factorial design using Design Expert software. The 2-level factorial design for two independent variables, with three replications at centre point leads to a total of seven set of experiments. In this experiment, the contents of MAH and DCP were varied in the range of 1-5 phr and 0.1-0.3 phr, respectively; whereas content of EPM was kept constant.

MAH grafting efficiency characterisation through FTIR spectroscopy

MAH-g-EPM thin films of 200-250 μm thickness were prepared by compression moulding using a laboratory hydraulic hot moulding. Machine parameters for hot pressing were set at 150°C temperature, 5MPa (or equivalent to 51 kg/cm²) pressure and 10 min. The films were then dried in an air drying oven for 10 hours at 75°C in order to draw off the unreacted MAH from the thin films. The possible interaction of MAH with EPM was determined using JASCO FTIR 6100 Spectrometer machine through thin film-FTIR approach. The FTIR spectra were collected from the MAH-g-EPM thin films in the transmission mode, and were recorded in a range of between 2000-400 cm⁻¹ with a 4cm⁻¹ resolution and 50 scans. Different functional groups and structural features which present in the molecules of MAH-g-EPM absorbed energy at the characteristic frequencies. The intensity of absorption is the indication of the bond strength and structural geometry in the molecules²⁴. In this experiment, FTIR spectra were used to identify the functional groups present on EPM backbone after the

grafting. At least five different spectra were generated for every sample to ensure high confident level.

Previous research on anhydride grafting efficiency analysis was conducted through qualitative approach, which is based on the presence or occurrence of new characteristic peaks^{25,21}. However for this study, the FTIR analysis has been conducted quantitatively by which the internal standard method was applied on the recovered spectra in order to build an equation that can be used to quantify anhydride through standard calculation. The approach is based on Lambert-Beer law theory¹¹.

After the grafting efficiency was confirmed and quantified by FTIR, the next evaluation on statistical reliability was then performed by Design Expert Statistical software. Then, ANOVA was applied to show the statistical significance of the MAH grafting to the EPM. From the experimental findings, the effect of independent variables on the grafting efficiency was studied using a half-normal graph, effect-list and regression model.

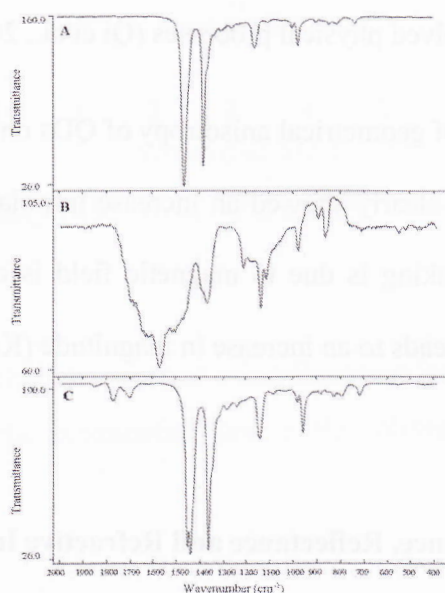
Result and Discussion

FTIR-quantitative analysis of MAH-g-EPM

Figure 1 shows the FTIR spectra of pure EPM (spectrum A), maleic anhydride (spectrum B) and MAH-g-EPM (spectrum C) in the region of 2000-400 cm^{-1} . Referring to Figure1, there were obvious differences between infrared spectrum of MAH-g-EPM if compared to pure EPM as well as pure MAH. The MAH-g-EPM spectrum shows the presence of few new peaks, increase absorbance in few MAH characteristic peaks and strong peaks identification to ethylene propylene structure except for minor broadening due to peaks overlapping. By taking into consideration the increment of absorbance at typical anhydride characteristic peaks; (1840-1800), (1780-1740), (1300-1100), (1710-1719) and (1770-1792)^{21,19,20}, the grafting of MAH onto EPM backbones was confirmed. However, it is important to ensure that the peak height of absorbance values for each selected band were measured by employing an appropriate baseline in order to get a reliable and accurate infrared data¹¹.

Based on the FTIR peak absorbance intensity data of each MAH-g-EPM samples, all samples exhibit an increment in intensity of anhydrides characteristic peaks as compared to the peak intensity of pure MAH. It was proven when cumulative intensity of anhydride of all MAH-g-EPM samples increases in comparison with the absorbance intensity of control/pure EPM sample. The increment demonstrated that all samples had experienced chemical modification and alteration in its functional group. Due to the utilisation of absorbance ratio

approach for quantitative grafting efficiency analysis, the internal standard is required to perform quantification process; this approach follows the Lambert-Beer law theory¹¹. Decision on internal standard was referred at a selected range in between 1456-1460 cm^{-1} (6.85 μm) where the intensity is at maximum ~ 99.00 , which referring to strong band of polyethylene and polypropylene monomers of EPM rubber.



1 FTIR spectra of A) pure EPM, B) pure MAH, and C) MAH-g-EPM

The anhydride content of MAH-g-EPM was then determined from the ratio of peaks heights of the absorbance peaks at 1712.48 to 1456.96 cm^{-1} , which correspond to anhydrides and polyethylene/polypropylene functional groups, respectively. Anhydride characteristic peak at the 1712.48 cm^{-1} region were selected for the absorbance ratio approach due to its high confirmation of anhydride grafting based on the presence of a new peak on MAH-g-EPM spectrum as compared to the pure EPM spectrum. Finally, a calibration curve of absorbance ratio (1712.48/1456.96 cm^{-1}) versus MAH in phr was built and generated an exponential curve with $R^2=0.900$ (Figure 2). There were only three points selected to represent the contribution of various MAH addition during the grafting process with EPM.

2	3	0.2	3.82	2.38
3	3	0.2	3.81	2.32
4	1	0.3	4.54	4.57
5	3	0.2	3.66	2.00
6	1	0.1	3.59	1.53
7	5	0.1	1.33	0.00

^aRelative to that of the 1456.96cm⁻¹ peak

Regression model of the functionalisation of MAH into EPM using RSM

Where is the plot

The experimental result was further proved by RSM statistical tools. In the generated half normal plot, it shows that variable A (MAH content), B (DCP content) and interaction point of AB were positioned away from the straight line. These plots show that all variables, A and B were significant model terms. However, variable B was distance away from the straight line when compared to variable A and interaction point AB. This indicates that variable B was the most significant term. By selecting significant model term in half normal plot, a regression model for grafting yield, Y (Equation 3) and an effect list were generated. By using the Equation 3, the predicted grafting yield at each experimental point was obtained. This result was supported by the effect list which stated that the variable B to be the most significant factor with 88.02% contribution to grafting yield than 0.37% contribution by variable A.

$$Y = 2.91 - 0.14 A + 2.14 B + 0.62 AB$$

Table 2 Effect List of all model terms for the screening experiments

Term	Sum of Square (SS)	F-value	P-value	Percentage of contribution (%)
A	0.078	1.92	0.3002	0.37
B	18.40	452.19	0.0022	88.02
AB	1.56	38.28	0.0251	7.45

ANOVA produces value such as mean of square (MS), sum of square (SS), F value, P value and coefficient of multiple determinations (R²). Variables B and interaction point AB were selected as significant model terms because their P values were lower than 0.05.

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