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Efficient Functionalisation of Ethylene-propylene Rubber in the Presence of Comonomer

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The main aim of this work was two fold, firstly to investigate the effect of a highly reactive comonomer, divinylbenzene (DVB), on the extent of melt grafting of glycidyl methacrylate (GMA) on ethylene-propylene rubber (EPR) using 2,5-dimethyl-2,5-bis-(tert-butyl peroxy) hexane (Trigonox 101, T101) as a free radical initiator, and to compare the results with a conventional grafting of the same monomer on EPR. To achieve this, the effect of processing conditions and chemical composition including the concentration of peroxide, GMA and DVB on the extent of grafting was investigated. The presence of the comonomer (DVB) in the grafting process resulted in a significant increase in the extent of the grafting using only a small concentration of peroxide. It was also found that the extent of grafting increased drastically with the increasing DVB concentration. Interestingly, in the comonomer system, the extent of the undesired side reaction, normally the homopolymerisation of GMA (polyGMA) was shown to have reduced tremendously and in most cases the level of polyGMA was immeasurable in the samples. In contrast, the extent of grafting in conventional system increased with increasing the peroxide concentration but the level of grafting was much lower than in the case of DVB. Homopolymerisation of GMA and excessive crosslinking of EPR became dominant at high peroxide concentration and this reflects that the side reactions were favourable in the conventional grafting system.

Keywords: comonomer; ethylene-propylene rubber; Trigonox 101; functionalisation; grafted GMA

Studies on functionalisation of polyolefins by reactive processing have been carried out widely[1–9]. During this process, functional groups can be incorporated into the polymer backbone by a free radical melt grafting process. The term reactive processing refers to the use of suitable reactive modifiers with polymers and the adoption of conventional polymer processing machinery *e.g*. a batch mixer or an extruder, as a chemical reactor to perform *in situ* targeted reactions for chemical modification of preformed polymers[1]. The major feature of reactive processing is that it is carried out in the melt without a solvent in the presence of shear at high temperatures, using a high viscosity and heterogeneous polymers. This gives rise to tremendous challenges to melt free radical grafting in terms of reactivity,

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selectivity and process control. In a typical polymer functionalisation reaction, at least three reactants would be involved including a polymer, functional modifier, *e.g*. a vinyl-containing monomer, and a free radical initiator. The free radicals formed from the initiator react with the functional monomer to form propagating radicals, which would graft onto the polymer backbone. The efficiency of the grafting reaction depends largely on the reactivity of the free radicals formed as well as the reaction process conditions (temperature, time, shear). The major advantages of using reactive processing methods are relatively low output costs and is a rapid way of obtaining new polymers without having to search for new monomers. Furthermore, there is no need to use solvents in the melt reactions which would provide post processing cost advantages in terms of solvent recovery[1]. However, several limitations have been reported[10] including the use of high temperatures typically required for melt reactions which may promote polymer degradation or crosslinking that would subsequently affect the ultimate product quality and performance.

A number of functional monomers such as glycidyl methacrylate (GMA)[11–14], maleic anhydride (MA)[15–17], and oxazoline[18] have been grafted onto polyolefins by free radical grafting reactions. One of the main problems, however, in grafting these monomers on polymer backbones is the fact that in addition to grafting, they can also homopolymerise, a reaction that competes directly with the grafting process and often results in low grafting[9]. GMA (*Figure 1*) is a highly reactive bifunctional monomer, containing an unsaturated group capable of free radical grafting on hydrocarbon polymers, and an epoxy group that can react further with different functional groups *e.g*. carboxylic, hydroxide and amine group. The use of GMA in reactive processing for polymer functionalisation has gained a great attention from many researchers[2,9,19–21].

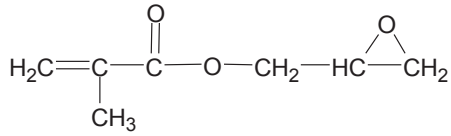


Figure 1. Chemical structure of glycidyl methacrylate (GMA).

The melt free radical grafting reactions are generally complicated due to the influence of various factors including high temperature, high viscosity and heterogeneity of the reacting medium as well as the formation of unwanted reactions of the monomer and the polymer which would compromise the level of grafting[10] including radical or shear induced crosslinking or chain scission of the polymer, as well as homopolymerisation of the monomer[22]. It was shown that, generally, addition of high concentration of the initial monomer or the initiator would result in an increase in the extent of homopolymerisation of the monomer[9]. Monomers such as GMA and MA have low reactivity toward 2,5- dimethyl 2,5-bis(t-butylperoxy)hexane, macroradicals[9], hence low extent of grafting can be expected. To improve the extent of grafting yield both the chemical composition and the processing conditions must be controlled to minimise the extent of the unwanted side reactions. Another approach would be to use a more reactive comonomer that will result in enhanced grafting efficiency.

Efforts have been made by many authors to improve the grafting yield of less reactive functional monomers by the use of more reactive comonomers (sometimes referred to as coagents)[9,11,23–25]. For example, to enhance the free radical grafting efficiency of GMA on polymers, various comomomers *e.g*. styrene[11,24], trimethylol propane triacrylate

(TRIS)[9,23] and acrylamide is another example of comonomer[14] have been used. Work in the Polymer Research Unit (PPP) (Aston University) by Al-Malaika *et. al*[9] showed that the presence of the highly reactive comonomer TRIS results in significant improvement in the grafting degree of GMA onto ethylene propylene rubber (EPR) with minimum extent of polymer degradation and with no GMA homopolymer formation. The use of TRIS in grafting of GMA onto ethylene propylene diene terpolymer (EPDM) has also been shown to give an improved grafting level[23]. Furthermore, the addition of divinyl benzene DVB and TRIS as comonomers in melt free radical grafting of GMA onto PP were also shown to greatly enhance the level of grafting reaction and reduction of the extent of side reactions[26]. The grafting reactions in the presence of the comonomers TRIS and DVB on PP were achieved at much lower peroxide concentration and consequently resulting in a negligible extent of PP degradation with very small amount of polyGMA formation[26]. Examination of the kinetic of the grafting reactions in the comomoner systems showed that TRIS led to shorter complete grafting reactions time compared to DVB[26]. It was also reported[26] that DVB was more reactive towards PP macroradicals and resulted in formation of PP-DVB-PP crosslinks which occurred before the copolymerisation with GMA. In contrast, in the GMA/TRIS system, TRIS appeared to be less reactive towards the PP macroradicals but more reactive towards GMA and copolymerised with GMA before the formation of TRIS assisted PP crosslinking.

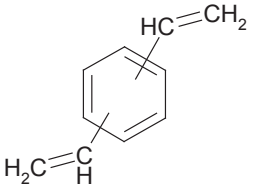


Figure 2. Divinyl benzene, DVB

The aim of this study was to investigate and optimise the grafting reaction of GMA on EPR in the presence of a highly reactive comonomer, and divinyl benzene (DVB) was chosen for this purpose. The *in-situ* melt free radical grafting of GMA in the presence of the reactive comonomer DVB was carried out using a novel approach developed by Aston University PPP research group[3,9,23,27]. The effect of the comonomer DVB on the grafting of GMA onto EPR was conducted using α,α- dimethyl 2,5-bis(t-butylperoxy) hexane (Trigonox T101) as an initiator. The investigation examined the effect of chemical composition and the processing conditions on the grafting reaction. The functionalised polymer products were characterised using various techniques including Fourier Transform Infrared (FTIR) spectroscopy and melt flow index (MFI). The grafting level was determined after purification of the reaction products to remove all side reaction products and the grafting extent was then measured using a calibration curve developed through titration and FITR methods. The overall performance of the functionalised rubber in the presence of DVB (*f*-EPR_{DVB}) was then compared with performance of conventionally functionalised EPR (*f*-EPR_{CONV}) in absence of DVB.

Materials

Ethylene-propylene rubber (EPR): Commercial grade Tafmer P-0280, pellet, supplied by Mitsui Chemical. Glycidyl methacrylate (GMA) (97% purity) and divinylbenzene (DVB) (80% purity) were purchased from Aldrich Chemical Co. Ltd and used as received. The peroxide, 2,5-dimethyl 2,5-bis(t-butylperoxy)hexane, Trigonox 101 (T101) was provided by Akzo Nobel and used without further purification. The initiator 2,2- azoisobisbutyronitrile (AIBN) was supplied by Ventron and used

without further purification. Trichloroacetic acid (TCA) and 1.0 N potassium hydroxide (KOH) standard solution in methanol were of analytical grade and were supplied by Aldrich Chemical Co.

Homopolymerisation of GMA in Chloroform

Homopolymerisation of GMA was carried out using AIBN as an initiator in 120 cm^3 chloroform. 8.53 g GMA was mixed with 0.1 molar ratio (AIBN/GMA) of the initiator AIBN to GMA in a 250 cm^3 three-neck round bottom flask. After assembling with thermometer, condenser and purging with nitrogen gas, it was refluxed for 4 hours at 70ºC. After cooling to room temperature, the solution was precipitated into 400 cm^3 methanol, filtered and washed thoroughly with methanol. After the filtration, the polyGMA (in powder form) was dried in vacuum oven at 70ºC for 24 hours.

Functionalisation of EPR with GMA in Absence and Presence of the Comonomer Divinyl benzene (DVB)

The reactive processing was carried out using a Thermo-Haake (Rheomix 600) internal mixer using roller rotors. The mixing (using roller rotor) was carried out for 15 minutes at the required temperature using rotor speed of 65 r.p.m. with the ram down offering a closed chamber condition. In the absence of DVB, the polymer was first charged into the chamber and processed for one minute followed by injection in the melt of a mixture of neat GMA and peroxide T101 (mixed at different molar ratios) using a syringe. In the presence of DVB, the polymer was tumble mixed with the DVB before charging into the chamber.

Purification of Functionalised EPR

Three g of grafted EPR (small film pieces) was placed in a paper thimble (weight known) and Soxhlet extracted for 24 hour with 120 cm^3 xylene under oxygen free nitrogen atmosphere. The crosslinked polymer was separated out as xylene insoluble. The xylene soluble fraction was precipitated in 7 time excess volume of acetone to give a soluble fraction containing the unreacted (free) GMA and polyGMA while the insoluble fraction contained the GMA-grafted-polymer. When the soluble xylene fraction was precipitated in methanol, the unreacted (free) GMA was soluble while the grafted GMA and polyGMA precipitated out. In the presence of DVB, the homopolymer of DVB (polyDVB), the copolymer of DVB with GMA (DVB-co-GMA) and any crosslinked polymer were separated out as xylene insolubles (stayed in the thimble). The soluble fraction was precipitated in acetone or methanol as described above. The precipitated polymers obtained from both routes were then dried for 24 hr in a vacuum oven at 50ºC.

Determination of GMA Grafting Degree by Titration and Calibration Against IR

The grafting parameters were calculated from the mass of purified reaction products before and after grafting. The grafting degree is defined as the weight percentage of grafted monomer onto a polymer backbone (*Equation 1*).

$$\text{Grafting Degree (\%) (by titration)} = \frac{M\,(V\text{-}V_1)\,M.W \times 100}{1000 \times W} \quad \ldots 1$$

Where;

M= molar concentration of KOH

V= Volume of KOH consumed by the blank sample

V_1 = Volume of KOH consumed by the purified sample
W = weight of sample
$M.W$ = molecular weight of GMA

About 1.0 g of a purified GMA functionalised polymers was completely dissolved in 75 cm^3 hot toluene (around 110ºC). 5.0 mL of 0.3M trichloroacetic acid (TCA) was then added into the dissolved polymer. The mixture was stirred continuously for over 90 minute at temperature of 100ºC–110ºC to drive the ring opening reaction of the epoxy group with the acid. The solution was then precipitated into 100 cm^3 ethyl acetate with continuous stirring at ambient temperature. The filtrate containing the residual trichloroacetic acid after reacting with the epoxy group of GMA was then titrated with 0.1M KOH solution in methanol until the first permanent pink end point was achieved (pink color must stay for at least 1 min.) 0.3% phenolphthalein in methanol was used as an indicator.

For a reference (blank), 1.0 g of unmodified processed polymer was also titrated using a similar procedure. The amount of 0.1M KOH consumed to react with TCA until permanent pink end point achieved was recorded and the degree of grafted GMA onto EPR was determined using *Equation 1*.

To confirm that the reaction of the epoxy group with the acid has occurred, the precipitated polymer was dried in vacuum oven for 24 hours at 70ºC. FTIR spectroscopic characterisation of the samples was carried out and it was shown that the epoxy absorption peaks at 909 cm^{-1} and 845 cm^{-1} have completely disappeared (*Figure 3*). Furthermore, a new absorption peak at 1772 cm-1 was observed due to tricholoro ester group (*Figure 4*) and a new absorption peak at 3432 cm^{-1} corresponding to –OH group formed during the ring open reaction was also observed (*Figure 5*). This confirms the reaction of epoxy group with tricholoroacetic has taken place.

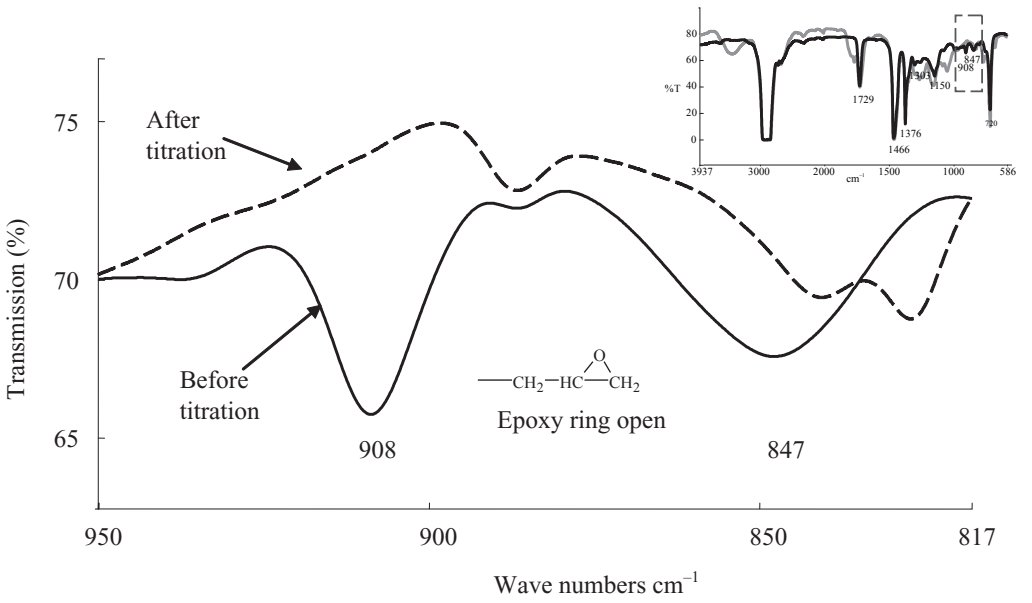


Figure 3. FTIR spectrum of pressed film of purified EPR-g-GMA before and after titration.

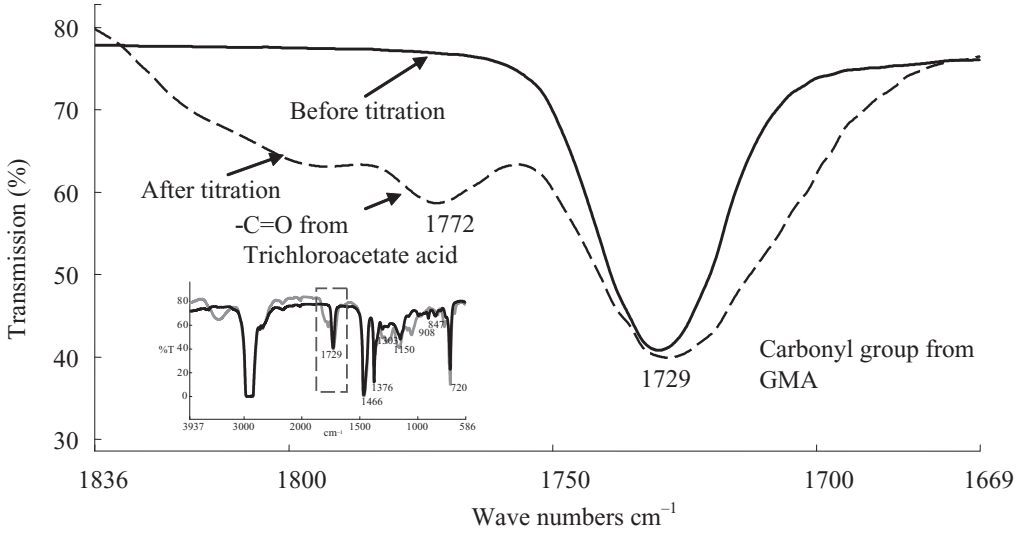


Figure 4. FTIR spectrum of pressed film of EPR-g-GMA before and after reaction with tricholoroacetic acid.

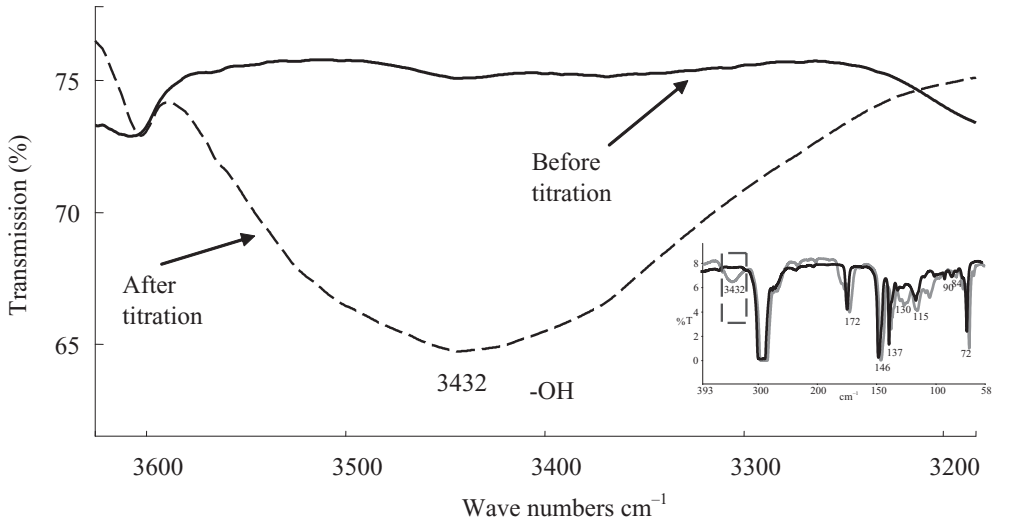


Figure 5. FTIR spectrum of pressed film of purified EPR-g-GMA before and after titration.

To determine the degree of grafting of GMA by IR spectroscopy, a calibration curve between IR spectroscopy and titration had to be constructed. For the IR spectroscopy, the carbonyl absorption at 1729 cm^{-1} was used in the modified and purified polymer along with a reference peak at 719 cm^{-1} corresponding to [~(CH2)n (n>4) rocking absorption of EPR]. The carbonyl absorption peak area boundaries were defined from 1786 cm^{-1} to 1662 cm^{-1} for peak maximum at 1729 cm^{-1} and the boundaries for the reference peak were defined from 680–781 cm^{-1}, (*Figure 6*). The amount of grafted GMA was calculated from absorption area ratio of 1729 cm^{-1} to 719 cm^{-1} according to *Equation 2*.

$$\text{Index Area Ratio (Y)} = \frac{\text{Peak Area of Carbonyl Absorption}}{\text{Peak Area of Reference Peak}} = \frac{A_{1662–1786\ cm^{-1}}}{A_{680–781\ cm^{-1}}} \quad \ldots 2$$

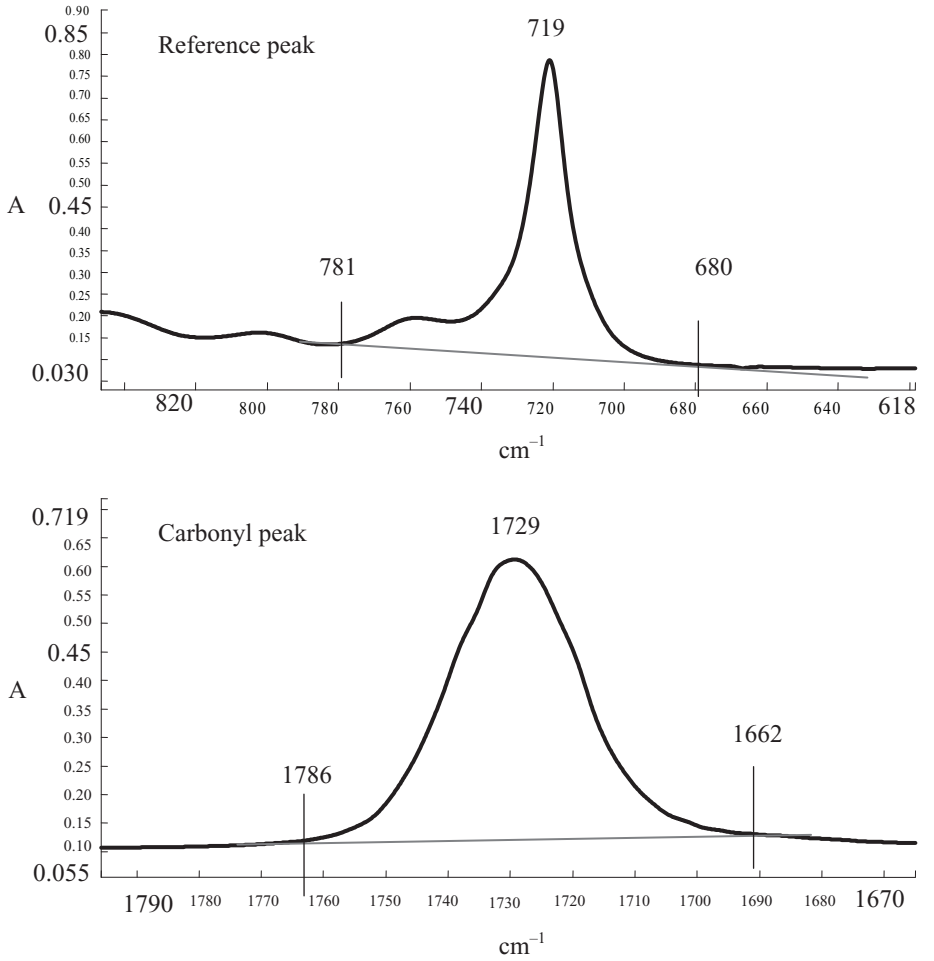


Figure 6. Area boundaries for absorption peak area calculation of GMA in functionalised EPR. Reference peak at 719 cm^{-1} (b) Carbonyl group peak at 1729 cm^{-1}.

A calibration curve (*Figure 7*) was established based on a correlation between the grafting degree measured by titration (*Equation 1*) and the carbonyl absorption area ratio determined by FTIR from a set of purified EPR-g-GMA samples *Equation 2*. From the calibration curve, the degree of grafting was calculated using *Equation 3*.

$$Y = M X$$
$$X = \frac{Y}{M} \quad \text{(value of slope of the curve)} \qquad \ldots 3$$

Where,

X = Grafted GMA (%)
Y = Peak Area Index from FTIR measurement ($A_{1662–1786\ cm^{-1}}/ A_{680–781cm^{-1}}$) (*Equation 2*)
M = Value of slope obtained from the calibration curve (*Figure 7*)

The total amount of grafted GMA and polyGMA was determined from extracted purified samples (precipitate in methanol) using FTIR spectroscopy and titration methods. The GMA grafting level was determined from purified samples precipitated in acetone. Thus, the concentration of polyGMA in the purified samples was calculated by subtraction from the total values of grafted GMA and polyGMA. (*Equation 4*).

$$PolyGMA\ (\%) = (PolyGMA + Grafted\ GMA) - Grafted\ GMA \qquad \ldots 4$$

Determination of Melt Index

MFI of GMA functionalised EPR samples were measured using a Ray Ran Melt Flow Indexer at a constant extrusion temperature of 230ºC and 2.16 kg load in accordance with *ASTM D 1238*. A standard die of 1 mm diameter was used for all samples. After the samples were granulated, 3 g of each sample was charged into the barrel within one minute. The sample was then preheated for 4 min before placing the load to drive the molten polymer through the die. The time interval for the cut off was 1 to 4 minutes depending on the flow rate of each sample. In this measurement, five samples per each measurement were taken and their averages calculated as shown in *Equation 5*.

$$MFI\ (g/10\ min) = \frac{m \times 10}{t\ (min)} \qquad \ldots 5$$

Where,

m = the average weight of extrudates (g)
t = time of extrusion (min)=10 min

RESULTS AND DISCUSSION

Films of the purified GMA-grafted polymer were prepared for characterisation by FTIR. *Figure 8* shows a comparison of FTIR spectra of EPR-g-GMA_{DVB} (functionalised EPR) and neat GMA. The shift in the ester carbonyl absorption from 1721 cm^{-1} to 1729 cm^{-1} is clearly seen and this is due to the formation of saturated ester groups whereas the acrylic double bond at 1638 cm^{-1} has completely disappeared. Furthermore, the absorption peaks of the epoxy group remained unchanged as shown at 908 cm^{-1} and 847 cm^{-1} confirming the grafting of GMA onto EPR. The structure of EPR-g-GMA-DVB was confirmed by NMR analysis and was well described in the previous work[28].

Characterisation of PolyGMA

Figure 9 shows the FTIR spectra of neat GMA and synthesised polyGMA. The formation of a saturated carbonyl group in polyGMA is evident from the observed shift from unsaturated carbonyl absorption at 1721

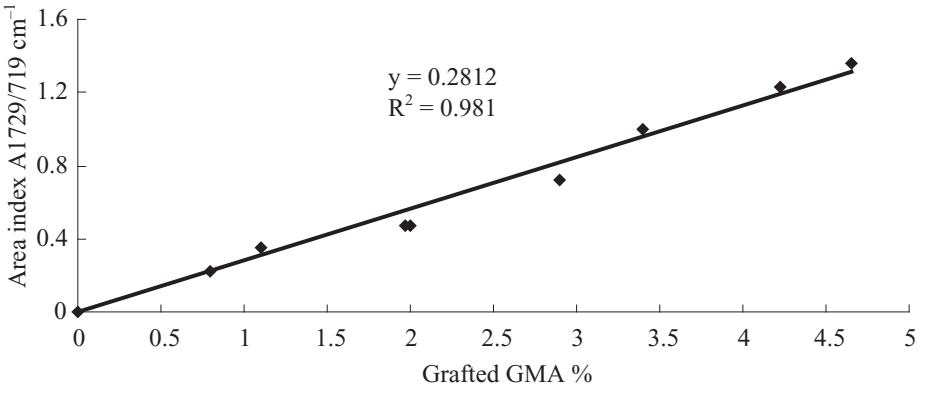


Figure 7. Calibration curve established from titration against FTIR area ratio.

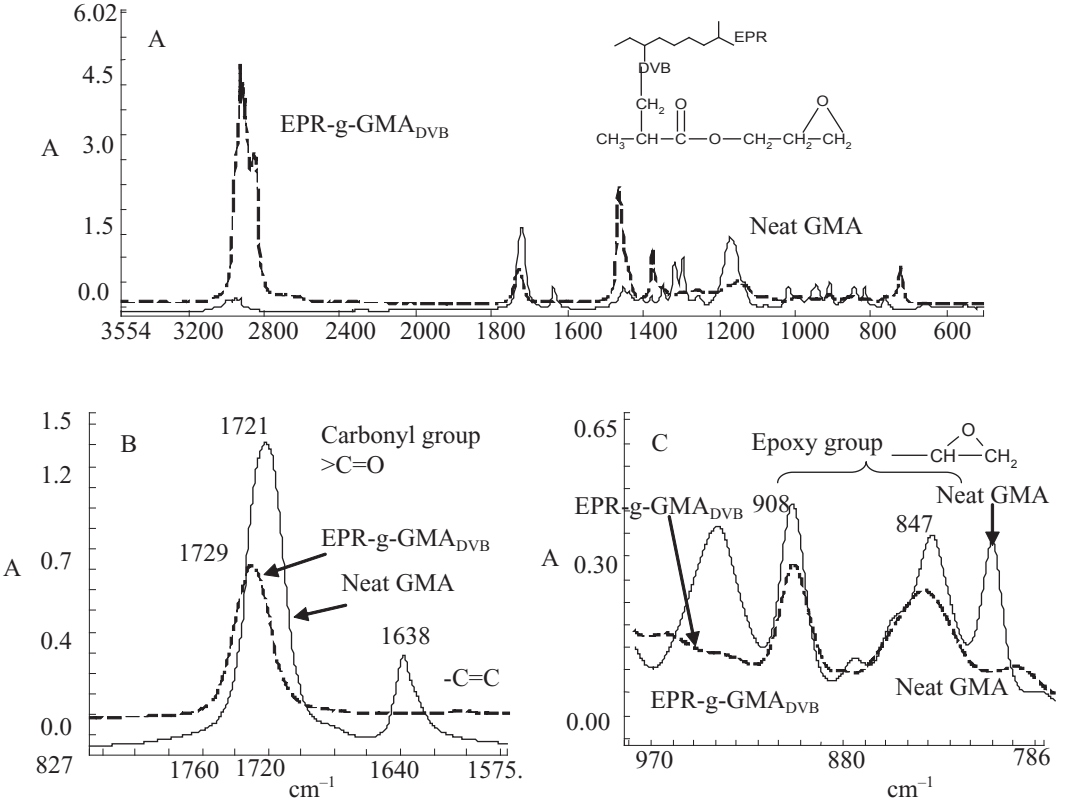


Figure 8. Comparison of spectra of neat GMA between KBr windows and EPR-g-GMA$_{DVB}$.

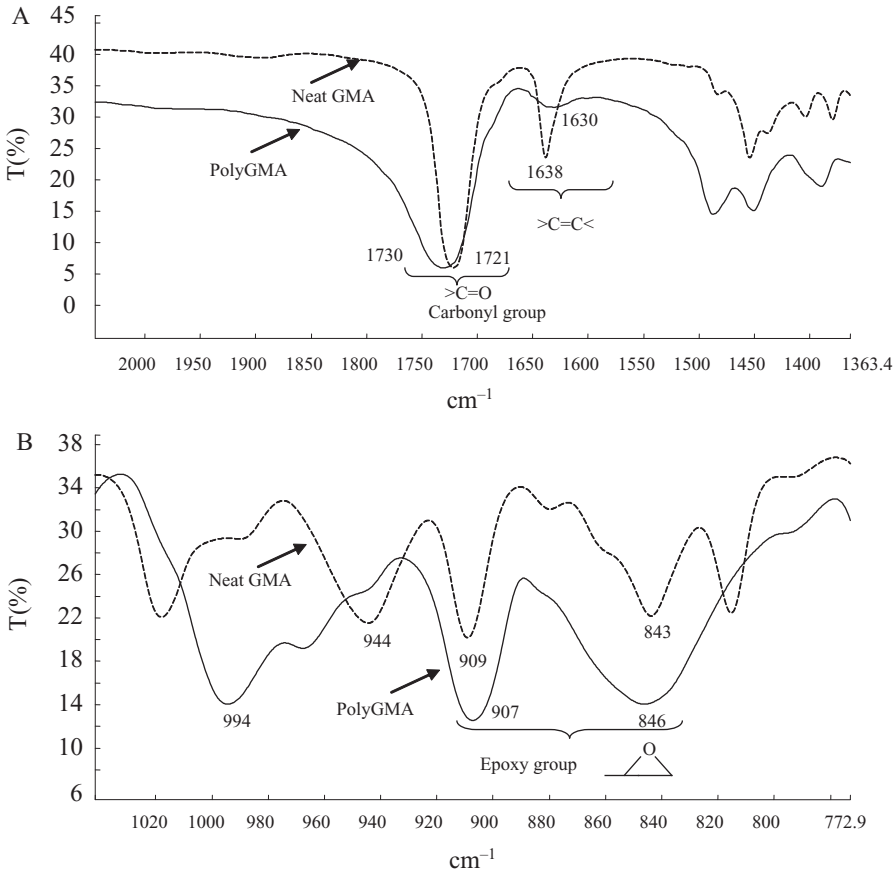


Figure 9. FTIR spectra of synthesised polyGMA in KBr disc and neat GMA between KBr windows.

cm^{-1} to saturated and broad carbonyl peak at 1730 cm^{-1} and from the substantial reduction of the acrylic double bond absorption at 1638 cm^{-1}, whereas the epoxy group absorptions at 909 cm^{-1} and 843 cm^{-1} were still clearly present.

Effect of Initiator Concentration on the Grafting Reaction

The effect of peroxide concentration on the extent of grafting is shown in *Figure 10*. It is clear that higher peroxide concentration results in higher grafting level of both systems. In the GMA/DVB grafting system, the concentration of peroxide that was required to achieve grafting was much lower than that used in the conventional grafting system (in the absence of DVB) and was therefore varied between 0.017 p.h.r. to 0.13 p.h.r. (using GMA concentration of 10 p.h.r.).

It was reported[9,15,29] that the presence of reactive comonomers such as trimethylolpropane triacrylate (TRIS) or

styrene in grafting systems would significantly improve the grafting degree and reduce the extent of monomer homopolymerisation. High level of grafting was achieved at only a fraction of the peroxide concentration used in the conventional system with the consequence of undermining the GMA homopolymerisation reaction so that no measurable polyGMA was detectable when DVB was present at all peroxide concentrations examined, see *Figure 11*. It was observed that increase in the grafting level is also paralleled by an increase in the level of GMA homopolymerisation. In the conventional grafting system, two main side reactions always accompany the grafting reaction. The side reactions may produce at least two undesired products including polyGMA through reaction between GMA radicals with another GMA radical and crosslinking reaction in EPR structure to form crosslinked EPR. However, the amount of side reaction products formed depends on the concentration of GMA and peroxide used in the grafting process. Compared to a conventional EPR-g-GMA_{CONV} (in the absence of a comonomer), the presence of the comonomer DVB in the grafting system was shown to result in more branching and crosslinking (shown from an increase in melt flow index (MFI), see *Figure 12*.

The work reported here shows that increasing the initiator concentration in the conventional grafting system would increase the level of GMA grafting but at the same time the system gives rise to a substantial increase in the extent of polymer degradation by branching and crosslinking (EPR used here has an ethylene:propylene ratio of 8:2) as evidenced from the observed dramatic reduction in the Melt Flow Index (MFI) values reflecting an increase in polymer viscosity and molecular weight, see *Figures 12*.

Effect of GMA Concentration on the Grafting Reaction

The effect of GMA concentration on the GMA grafting level in the presence of DVB

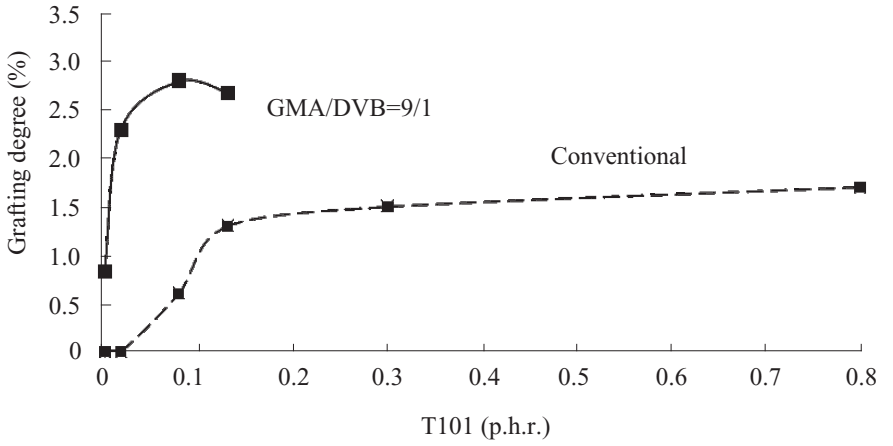


Figure 10. Effect of peroxide concentration on grafting level. $[GMA]_i$=10 p.h.r.

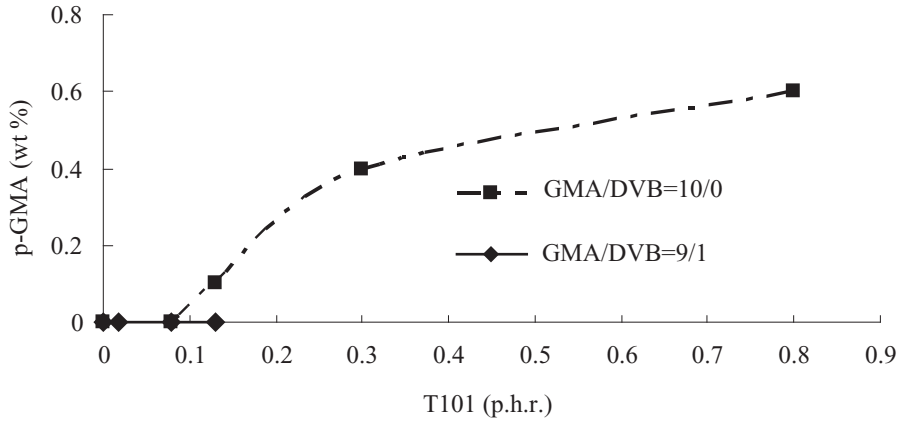


Figure 11. Effect of DVB on formation of polyGMA in GMA/DVB system. GMA/DVB= 9/1w/w, $[GMA]_i$=10 p.h.r.

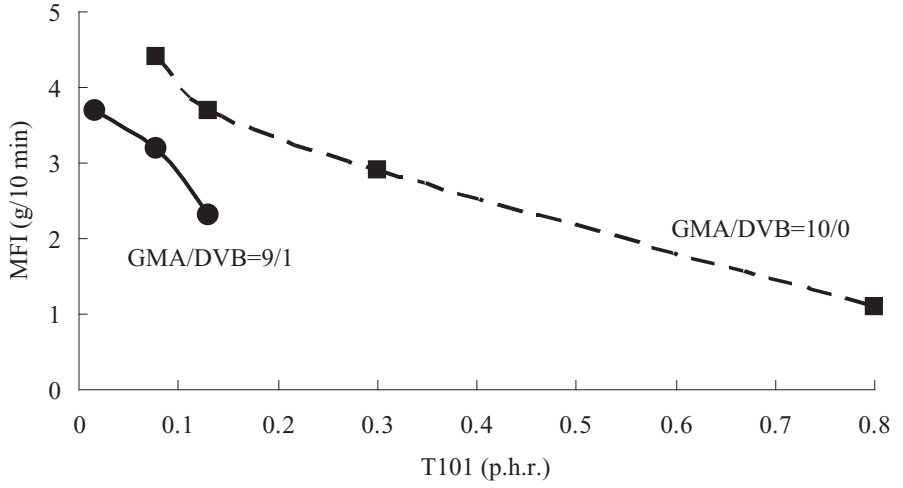


Figure 12. Effect of peroxide concentration on MFI of GMA/DVB system and conventional system. GMA/DVB=9/1w/w, $[GMA]_i$=10 p.h.r.

was also examined. The concentration of GMA was varied from 5 p.h.r. to 15 p.h.r. and used at a constant T101 concentration of 0.13 p.h.r. and the GMA/DVB ratio was fixed at 9/1 w/w. The level of GMA grafting, increased with increasing the initial amount of GMA up to 5% and more importantly, this occurred with no polyGMA formation, see *Figure 13*. Small increase in the grafting level was observed in the conventional system at higher GMA concentration, see *Figure 14*. The importance of the homopolymerisation reaction becomes even more evident when higher initial GMA concentrations are used, going from 10% to 15%, where it becomes evident that the GMA-homopolymerisation becomes the dominant reaction in the grafting system (higher concentration of polyGMA compared to that of g-GMA). This illustrates again the effectiveness of DVB in enhancing the melt grafting efficiency at the expense of the homopolymerisation reaction. Since DVB is very reactive towards GMA, the DVB radical can easily react with the GMA radical by trapping it. This causes the GMA radicals to be less available for coupling reactions to form polyGMA resulting in a decrease in the formation of polyGMA when DVB is present (in the GMA-DVB system).

It is clear therefore that the strategy for increasing the GMA-grafting level in the conventional system, by increasing concentration of either the peroxide or the initial GMA content, is not a successful one as this approach also results in favouring the competition from unwanted side reactions and in particular increase the importance of radical-initiated GMA-homopolymerisation (propagation) at the expense of graft-initiation reaction.

The mechanism of the melt free radical grafting of GMA on EPR in the conventional and the DVB systems is shown in *Scheme 1*. The thermal decomposition of the peroxide initiator gives rise to alkoxyl radicals (*Scheme 1, Rn 1*) with further decomposition

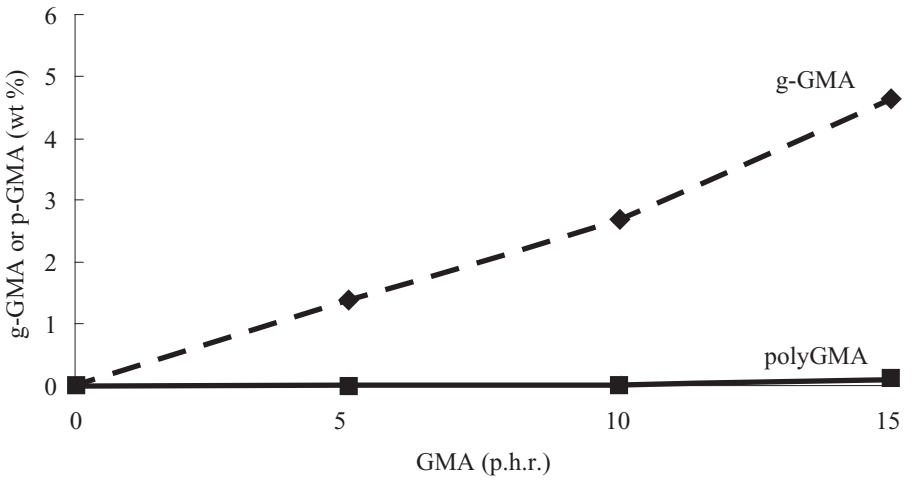


Figure 13. Effect of initial GMA concentration on grafting level in GMA/DVB system. T101=0.13 p.h.r., GMA/DVB=9/1w/w.

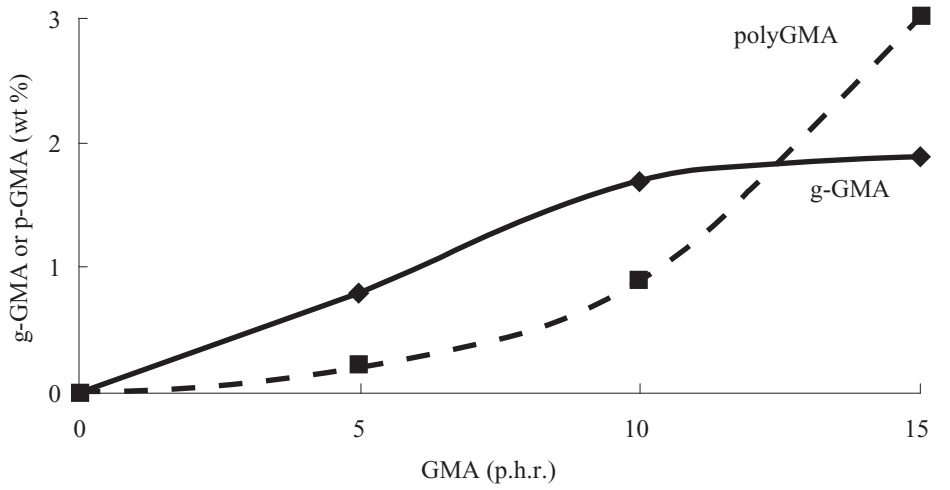


Figure 14. Effect of initial GMA concentration on grafting level in a conventional system. T101=0.8 p.h.r.

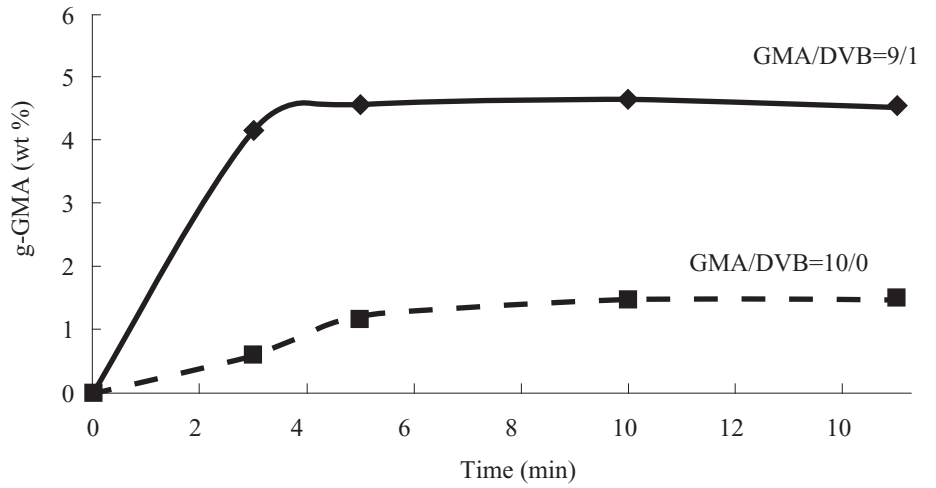
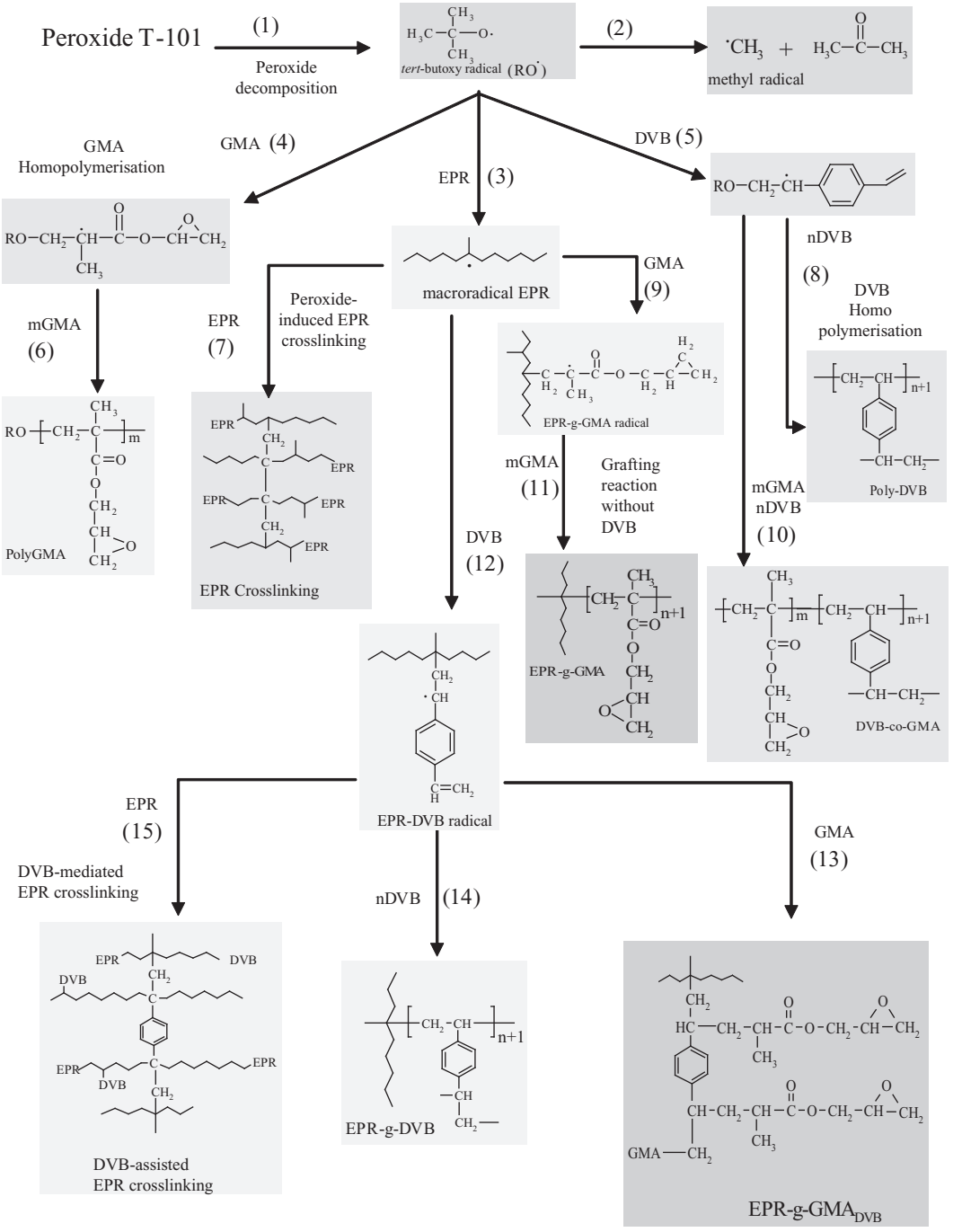


Figure 15. Comparison of kinetic reaction of grafting reaction between the GMA/DVB system and a conventional system. GMA/DVB=9/1 w/w, T101=0.13 p.h.r., $[GMA]_i$=15 p.h.r.



Scheme 1. Mechanism of grafting reactions.

through the β chain scission of the akoxyl radical to form methyl radicals, (*Scheme 1, Rn 2*). These radicals are very reactive towards H-abstraction giving EPR macroradicals (*Scheme 1, Rn. 3*). The grafting reaction in the conventional system takes place through the reaction of GMA with EPR macroradical to form GMA grafted EPR, *Scheme 1, Rn. 11*. The side reactions may produce polyGMA through the reaction between GMA radicals with another GMA radical, *Scheme 1, Rn. 6*. Since the EPR used in this study consists of high PE to PP ratio of 8:2, the polymer degradation through crosslinking becomes important, *Scheme 1, Rn. 7*. In the GMA-DVB grafting system, the side reaction is quite complicated where it involves reaction of comonomer and monomer and also comonomer with EPR. The comonomer DVB is highly reactive toward EPR macroradical and GMA radical. The grafting reaction is initiated by the addition of DVB on the EPR macroradical giving rise to a propagating EPR-DVB macroradical, (*Scheme 1, Rn. 12* and *Rn .14*). Copolymerisation of the EPR-DVB macroradicals with GMA results in the EPR-g-(DVB-co-GMA), (*Scheme 1, Rn. 13*). In the conventional grafting system, two main side reactions always accompany the grafting reaction. The side reactions in the GMA-DVB grafting system may produce DVB mediated EPR crosslinking through the copolymerisation reaction among the EPR-DVB macroradicals radicals, *Scheme 1, Rn. 15*.

Effect of Kinetics on the Grafting Reaction

The kinetics of the GMA grafting in the presence of DVB at various initial GMA concentrations is presented in *Figure 15*. The grafting rate increased rapidly to a maximum level after 2 minutes at GMA concentrations of 10 p.h.r. with the reaction rate being much faster in the presence of DVB. Indeed, examination of the kinetics of these reactions, show clearly that the rate of the GMA grafting reaction is faster than the rate of the graft-reaction of a conventional system, giving rise to the formation of a higher (compared to g-GMA) amounts of grafted GMA that are formed throughout the melt reaction.

The extent of grafting and homopoly-merisation reactions were determined (in purified samples) from the kinetics of the EPR-g-GMA_{DVB} grafting system. *Figure 16* shows clearly that in the GMA/DVB system of 9/1 w/w, the rate of GMA grafting is very fast (reaction is complete in the first 2-3 minutes) and the amount grafted is high with less than 0.1% of homopolymer formed at the end of the reaction. This contrasts with the corresponding conventional system (in the absence of DVB), which gives a much higher extent of GMA-homopolymer formation (at 15 p.h.r. initial GMA concentration, 3% polyGMA was found) and a consequent lower rate and amount of graft-GMA yield. (*Figure 17)*.

Effect of DVB Concentration on the Grafting Reaction

A major advantage in using the comonomer DVB is the fact that no (or very low) GMA homopolymer is formed in the grafting system, *Figure 18*. These results confirm the high reactivity of DVB towards both the polymer macroradical and GMA thus undermining the chance for the GMA radicals to propagate and produce polyGMA, and in turn increasing the extent of g-GMA formation. The higher reactivity of DVB towards EPR macroradical, compared to that of GMA/macroradical, is further illustrated from the observation that even in the complete absence of a peroxide, *i.e* in a shear-initiated reaction, GMA-grafting can still be achieved (up to 1%), whereas no grafting was obtained in the conventional system processed in the absence of peroxide.

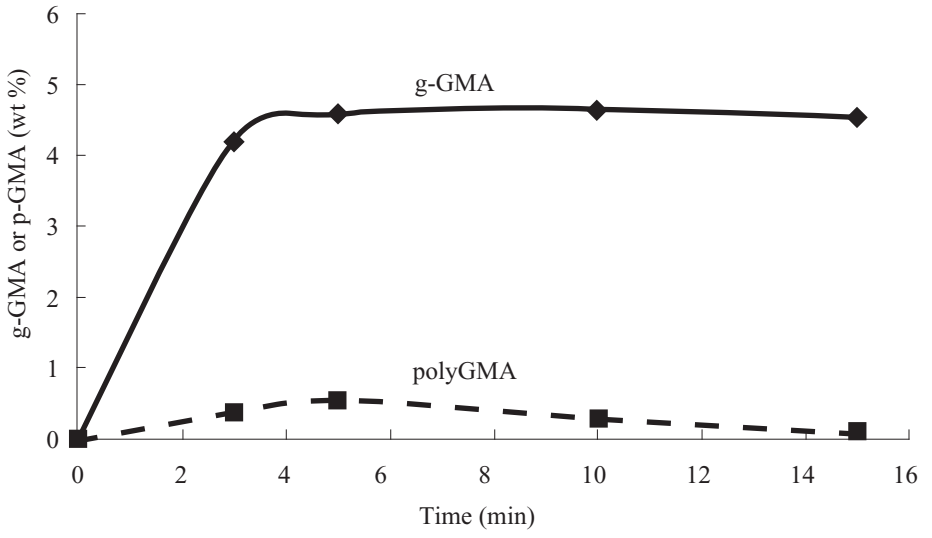


Figure 16. Effect of processing time on GMA grafting and polyGMA level in conventional EPR-g-GMA$_{CONV}$ system. [GMA]$_i$=15 p.h.r.

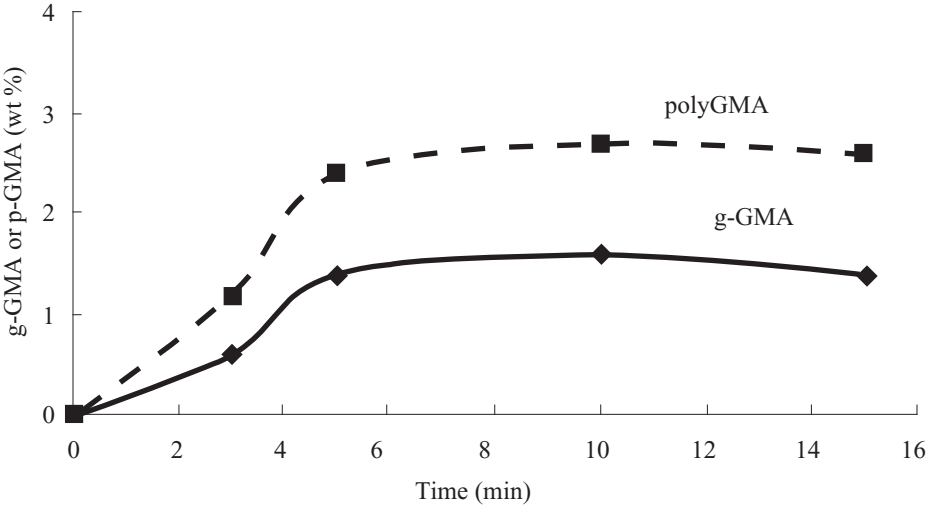


Figure 17. Effect of processing time on GMA grafting and polyGMA level in conventional EPR-g-GMA$_{CONV}$ system. [GMA]$_i$=15 p.h.r.

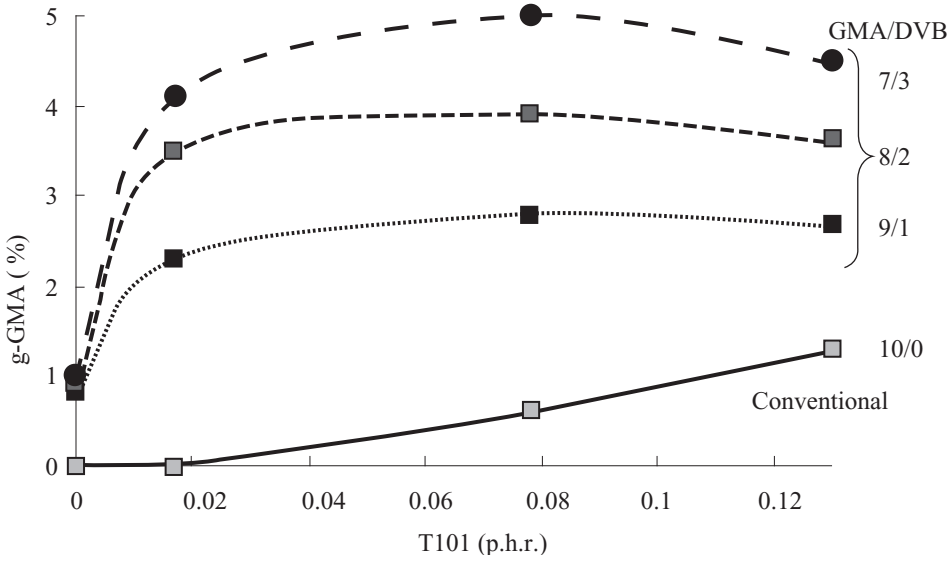


Figure 18. Effect of DVB concentrations on grafting levels.

Analysis of the xylene-insoluble fractions of the EPR-g-GMA_{DVB} (GMA/DVB ratio of 7/3 w/w) sample at time intervals during processing has shown that at the point of torque maximum (after 3 min processing) the sample contained 32% insoluble gel, whereas at the end of the reaction (15 min) the gel content had decreased substantially to 1.0%, see *Figure 19B*. The IR absorption spectrum of the insoluble fraction at 3 min processing showed a clear and large benzene absorption corresponding to DVB, see *Figure 19D*. The very high amount of gel (32%) present at the early stages of the reaction and particularly at the point of torque maximum (at 3 min) and the presence of IR absorption peak characteristic of DVB supports the suggestion of a higher extent of DVB-assisted crosslinking reactions in the earlier stages of the melt grafting process due to the high reactivity of DVB towards EPR macroradicals. From these results, it can be concluded that the high reactivity of the formed DVB-EPR radicals results in DVB-assisted crosslinking EPR and/or the formation of EPR-g-DVB, giving rise to the observed increase in the melt viscosity (the torque peak) and extensive reduction in MFI almost down to zero at 3 min (*Figure 19C*) supported by the very high extent of insoluble gel measured at this point of maximum torque of the melt processing.

CONCLUSIONS

The highly reactive comonomer, divinyl benzene (DVB), used in the melt free radical grafting of glycidyl methacrylate (GMA) on EPR (with E:P of 8:2) was shown to give a much higher level of grafting (up to 5 wt%) compared to a similar but conventional system (in the absence of DVB). Another advantage in using the comonomer is that the high GMA grafting level can be achieved

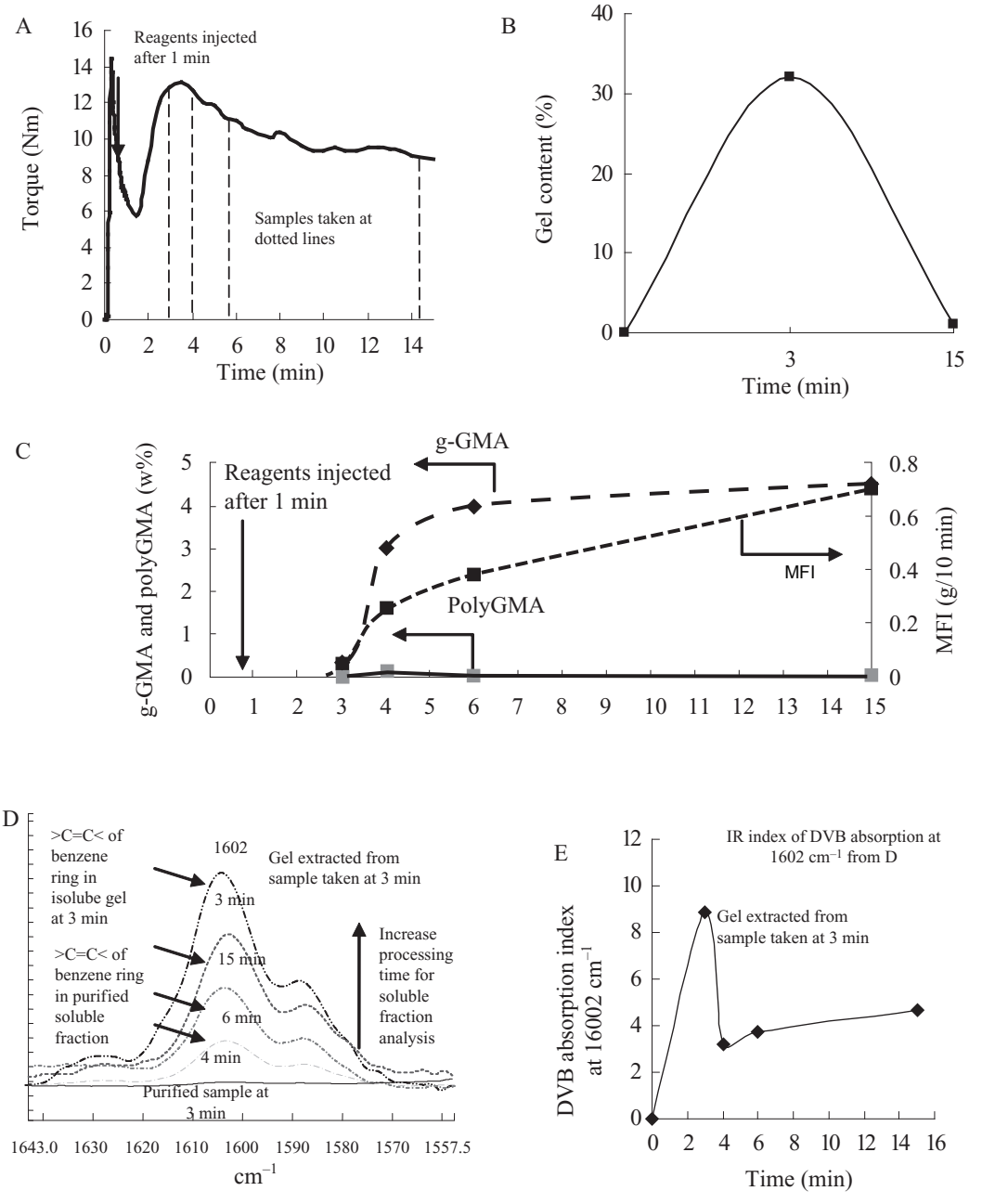


Figure 19. Analysis of EPR-g-GMA$_{DVB}$ processed and purified samples, taken out at different processing times. GMA=10 p.h.r., T101=0.13 p.h.r., GMA/DVB=7/3 w/w, 190ºC. Sampling was taken at the times shown in dotted lines in A.

at a much lower peroxide concentration compared to the conventional system, thus not contributing to polymer degradation reactions. Further, the amount of polyGMA formed in the EPR-g-GMA_{DVB} polymer was found to be negligible and this contrasts with the conventional grafting system that gave rise to polyGMA as a consequence of the need to use a much higher peroxide concentration to achieve an increased level of grafting and even under these conditions, the overall GMA grafting efficiency remained at a low level, accompanied by higher levels of polyGMA formation. The use of low GMA/DVB ratio resulted in a significant increase in the extent of grafting. The effect of GMA concentration in the presence of DVB gave rise to an increase in the extent of grafting level with only a very small amount of polyGMA formed in the system. In contrast, an increase in the GMA concentration in the conventional system was unfavourable in terms of grafting. However, in the conventional system, higher GMA concentrations resulted in the formation of a remarkable amount of polyGMA with only a small increase in the extent of the grafting level. Examining the kinetics of the grafting reactions of DVB and the conventional systems has revealed that the grafting reaction rate in the DVB system was higher compared to the conventional system with the grafting reaction being almost complete in the very early stages of processing, with maximum grafting level achieved in the first 5 minutes.

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