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# EFFECT OF ON MELT GRAFTING OF GLYCIDYL METHACRYLATE ONTO NATURAL RUBBER IN THE PRESENCE OF ORGANIC PEROXIDES

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## ABSTRACT

The main aim of this work was to study of melt grafting glycidyl methacrylate (GMA) on natural rubber (NR) using reactive processing methods. Four different peroxides benzoyl peroxide (BPO), dicumyl peroxide (DCP), 2,5-dimethyl-2,5-bis-(tert-butyl peroxy) hexane (T-101), and 1,1-di(tert-butylperoxy)-3,3,5-trimethyl cyclohexane (T-29B90) were examined as free radical initiators. An appropriate methodology was established and chemical composition and reactive processing parameters were examined and optimised. Procedures for purification of the reaction products were developed so that the extent of monomer grafting on the rubber can be characterised accurately, using mainly FTIR technique. The reaction mechanism of the functionalisation was also examined. It was found that the grafting degree of GMA increased with increasing of GMA's concentration. It was also found that T-101 was a suitable peroxide to initiate the grafting reaction of these monomers on NR.

*Keywords: functionalisation, melt grafting, natural rubber, radical initiator, reactive processing.*

## 1. Introduction

Natural rubber (NR) which is an unsaturated elastomer containing 93–95% cis-1,4-polyisoprene has many desirable properties such as high elongation, and outstanding resilience but also with some shortcomings such as its high sensitivity to heat and oxidation due to the presence of double bonds in its chains. NR has also low tensile strength, tensile modulus, and poor creep characteristics unless it is highly vulcanised (Coran and Patel, 1997). One of the major problems encountered during tyre manufacture, for example, is the poor adhesion between the tyre cord (mostly nylon, rayon, polyester, and aramid fibres) and the rubber materials as a result of poor bonding affinity between the polar cord material and the hydrophobic rubber molecules. To overcome this drawback, adhesion-promoting systems, such as recorcinol-formaldehyd latex and polyisocyanates, have been utilised to provide a coating on the cord surface during tyre manufacture to improve adhesion at the interface between the cord or metal and rubber (Lake, 1992). Graft copolymerisation of glycidyl methacrylate onto natural rubber could be an attractive technique to enhance adhesion without drastically altering the original properties of the rubber (Suriyachi, 2004). Different chemical modifications have been performed in NR in order to

increase its useful properties; this includes preparation of graft copolymers of NR with various types of vinyl monomers such as styrene (St) (Xavier, J. Samuel, T. Kurian, 2001), maleic anhydride (MA) (Ismail, Rusli and Rashid, 2005), methyl and alkyl methacrylate Thiraphattaraphun et.al, 2001). However, there is a limited amount of work in the literature on the grafting of GMA onto natural rubber.

## 2. Experimental

### 2.1 Material

Natural rubber was a commercial grade (SMR-L) supplied by the Malaysian Rubber Producer's Research Association (MRPRA), UK. Glycidyl methacrylate (GMA) was obtained from Aldrich Chemicals Co. and used without further purification. different peroxides were used for free radical grafting reactions: 2,5-di(tert-butylperoxy)-1,5-dimethyl hexane (TRIGONOX-101®) (T-101), 1,1-di(tert-butyl peroxy)-3,3,5-trimethyl cyclohexane (TRIGONOX 29-B90®) (T-29B90) were kindly donated by AKZO Chem. Netherlands, dicumyl peroxide (DCP) ex. Aldrich Chemical Co., and benzoyl peroxide (BPO) ex. Fluka Chemika. All other chemicals were of reagent grade and were used without further purification. Solvents employed for normal purpose were laboratory reagent grade, for

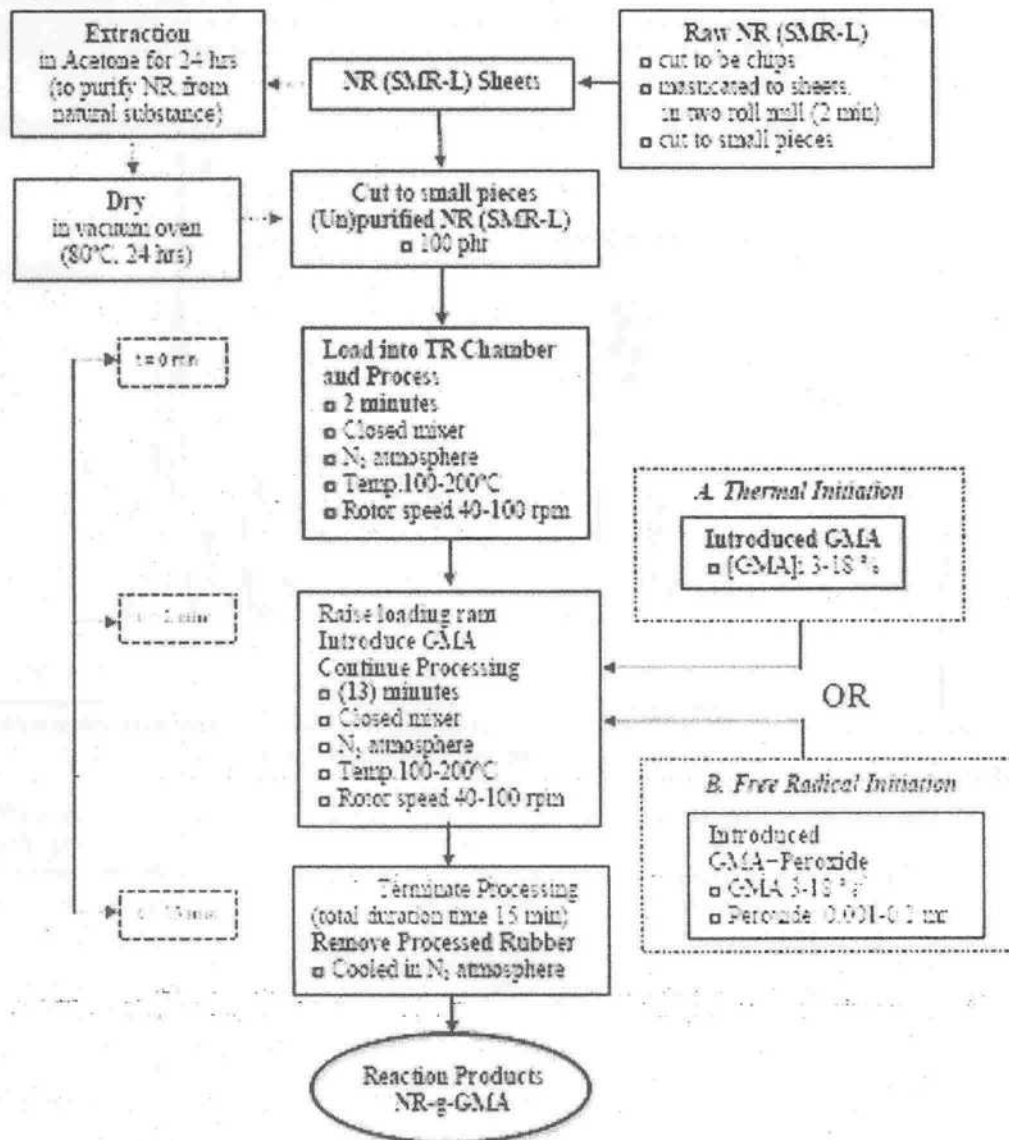
titration were HPLC grade, used as supplied from Fisons.

No	Name	Structure	Grade, Form & Properties	Supplier
1	Natural rubber (NR)		SMR-L (Bale)	MRPRA
2	Glycidyl methacrylate (GMA)		Colourless liquid Purity 95 %	Aldrich Chemical Co
3	2,5-di( <i>tert</i> -butylperoxy)-1,5-dimethyl hexane TRIGONOX 101 (T-101)		Colorless (liquid) Purity 97 %	AKZO
4	1,1-di( <i>tert</i> -butylperoxy)-3,3,5-trimethyl cyclohexane, TRIGONOX 29-D90 (T-29D90)		Colorless (liquid) Purity 90 % (in dibutyl orthalate)	AKZO
5	Dicumyl peroxide (DCP)		Colorless (liquid) Purity 97 %	Aldrich
6	Benzoyl peroxide (BPO)		White (powder) purity 98 %	Fluka

## 2.2. Preparation of Functionalised NR with GMA

Functionalisation of NR with GMA was conducted in the torque rheometer. Unless otherwise stated, compounds for reactive processing were prepared by pre-weighing exact amount of the rubber and monomers by total weight 35 g. The rubber was charged in the preheated mixing chamber, which was initially flushed with oxygen-free nitrogen for more than 15 seconds. After melting and torque stabilisation at the selected processing temperature (about 2-4 minutes after charging of the polymer), the ram was raised for the addition of any other chemicals (GMA and peroxide) by using a long metal-needle syringe to avoid losses. The ram was lowered down quickly to minimise the loss of GMA due to their high vapour pressure and volatility and this was taken as the zero time of reaction, see Scheme-1.

The reaction product was discharged and cooled under a stream of nitrogen or dry ice to avoid further oxidation and stored in a dry and cool place for further analysis. During mixing, the torque reading and mixing temperature were recorded throughout each run using PICOLOG Software. It was difficult to prepare thin films for FTIR measurement directly due to the tackiness and high viscosity of GMA-functionalised natural rubber (NR-f-GMA) samples, hence thin cured films had to be prepared. The rubber ingredients, zinc oxide, stearic acid, accelerator CBS (N-cyclohexyl-2-benzothiazole sulphamide), and sulfur were compounded on a two roll mill. In order to eliminate any unreacted GMA and poly GMA from the reaction products and to ensure the correct measurement of grafting degree of GMA-grafted NR, the processed rubber were purified by extraction method with acetone. The content of GMA-grafted NR of purified sample were then determined and characterised by titration and/or FTIR methods.



Scheme-1.

### 2.3. Determination of GMA Grafting Degree by Titration

An acid-base, non-aqueous back titration method was established to determine the grafting degree of GMA [119,125,127]. A modified procedure of the literature employing trichloro acetic acid (TCA)-xylene method was used in this work to determine the epoxy content in NR-g-GMA as follows: 1 g of the purified reaction product (PP-g-GMA) was dissolved in 100 ml of hot xylene (120-130°C) in a two-neck flask, connected to a condenser and maintained under nitrogen atmosphere. After the PP-g-GMA had completely dissolved (15-30 min) the condenser was

removed. The flask was stoppered and placed in an oil bath maintained at lower (stable) temperature of 105-110°C. The hot solution was then titrated with 0.1 N KOH (standard solution) in methanol. In the presence of indicator (five drops of 1 % w/v phenolphthalein in ethanol), endpoint was reached when the colour (pink) had formed and remains for at least 30 seconds.

### 3. RESULTS DAN DISCUSSION

It is well known that natural rubber contains some natural substances, mainly protein and lipids (phospholipids, ester of higher fatty acids, and

sterols) (Suchiva, 2000) and when it was Soxhlet extracted with acetone those substances were extracted and removed. The acetone extracted natural rubber (for 24 hours extraction) became light and more transparent. The FTIR spectrum of acetone extracted natural rubber shows similar absorption

peaks to those of raw natural rubber with the exception of the absorption peak at 3285 cm<sup>-1</sup> (due to  $\nu$ O-H of protein) and 1742 cm<sup>-1</sup> (shift to 1718 cm<sup>-1</sup>) most likely due to stretching of  $>$ C=O group of natural protein which becomes much smaller (Fig-1).

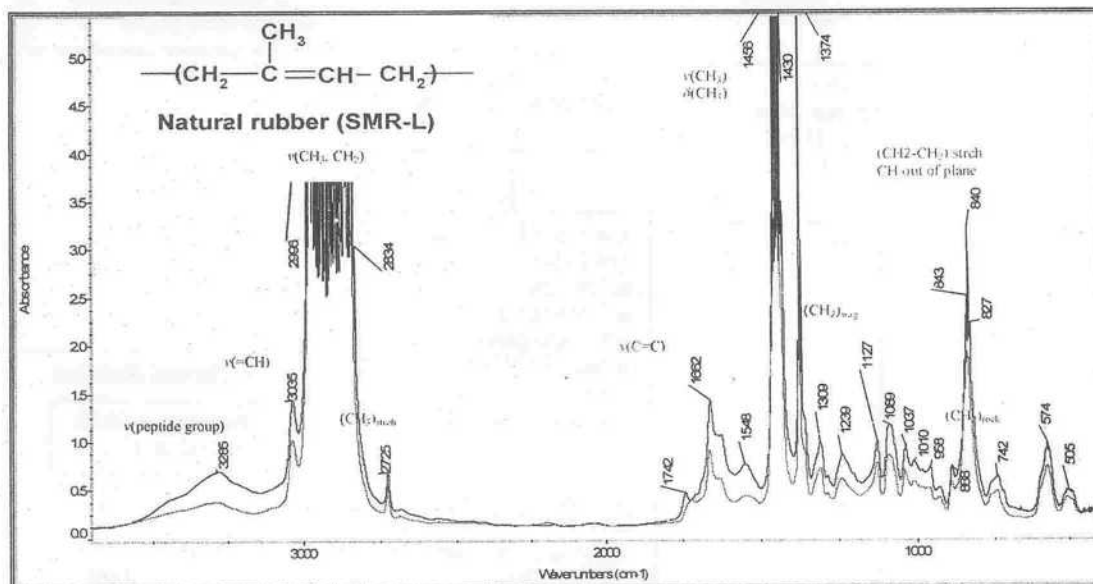


Fig-1 FTIR spectra of cured pressed raw NR before (blue) and after (red) extraction with acetone for 24h, pressed at 150oC for 2 min.

Processing natural rubber with GMA in the presence or absence of a peroxide gives rise to significantly different physical appearance from that of raw natural rubber. The products obtained at processing temperatures above 180oC and in the absence of peroxide showed a brown colour and became tacky, whereas no obvious colour change was observed when the reaction was carried out below 160oC in the presence or absence of peroxide. The higher the processing temperature and the higher the GMA concentration, the deeper was the brown colour of the reaction product.

In the study of grafting reaction by free radical initiation (in the presence of peroxide), four different peroxides were used to initiate the grafting reaction of GMA onto natural rubber; benzoyl peroxide (BPO), dicumyl peroxide (DCP), 2,5-dimethyl-2,5-bis (tert-butyl peroxy) hexane (T-101), and 1,1-di(tert-butylperoxy)-1,5-dimethyl hexane (T-29B90). The effect of peroxides different peroxides (BPO, DCP, T-101, and T-29B90) as initiators in terms of their concentration, the GMA concentration, processing temperature, and time, on GMA grafting degree on NR was investigated in detail.

The peroxide Trigonox-101 (T-101), as compared to BPO and DCP, has an even longer half times at higher temperatures ( $t_{1/2} = 11.4$  min at 160oC,  $t_{1/2} = 1.2$  min at 180oC, and  $t_{1/2} = 0.3$  min at 200oC). It was found that this peroxide could initiate the reaction of GMA and natural rubber at

temperatures above 140oC quite efficiently leading to much higher overall grafting degree compared to BPO and DCP. When the temperature was raised to 160oC, the grafting reaction was initiated quite efficiently by T-101 and the grafting degree of GMA increased at higher T-101 concentration. However, at higher T-101 concentration or processing temperature, the degree of NR cross linking became obvious and unacceptable.

### 3.1.Effect of Initial GMA Concentration

The effect of the initial GMA concentration on the level of grafted GMA in the presence of different peroxides (T101, DCP, BPO) is shown in Fig-2. These series of grafting processing experiments of GMA onto NR were prepared using different initial GMA concentrations of 3-18 % with a fixed peroxides concentration 0.02 mr (processing temperature 120oC for BPO, 160oC for DCP and 180oC for T-101). In the reactive processing step, GMA acts by trapping the macro alkyl radicals that would otherwise undergo chain scission or cross linking. Thus, use of a higher GMA concentration should give rise to higher grafting degree and less NR degradation. When the reaction was carried out at the optimum processing temperature for each of the three peroxides (BPO at 120 oC, DCP and T-101 at 160 oC), see Fig.2, the grafting level was shown to

increase continuously with increasing GMA concentration and the degree of GMA-grafted NR in the NR/GMA/BPO system (BPO as initiator) was very low compared to the other peroxides. The efficiency of the grafting reaction is most likely to be dependent on the rate of GMA diffusion into the natural rubber phase, especially at high peroxide

concentrations and GMA content with the rate likely to increase with increasing both the GMA content and the temperature. This suggests that the GMA content is one of the major parameters, which affects the grafting reaction at a given constant temperature and mixing speed.

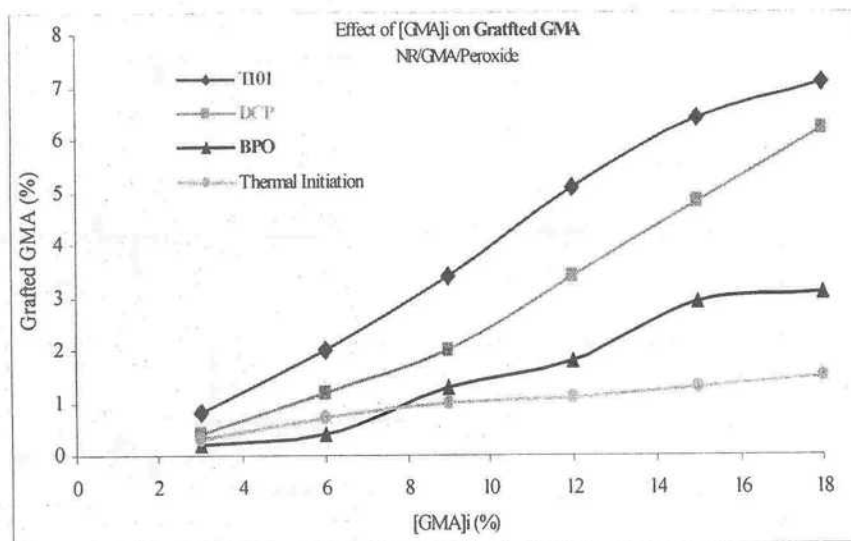


Fig.2 Effect of initial GMA concentration on grafting degree of GMA onto NR for thermal and peroxide initiation.

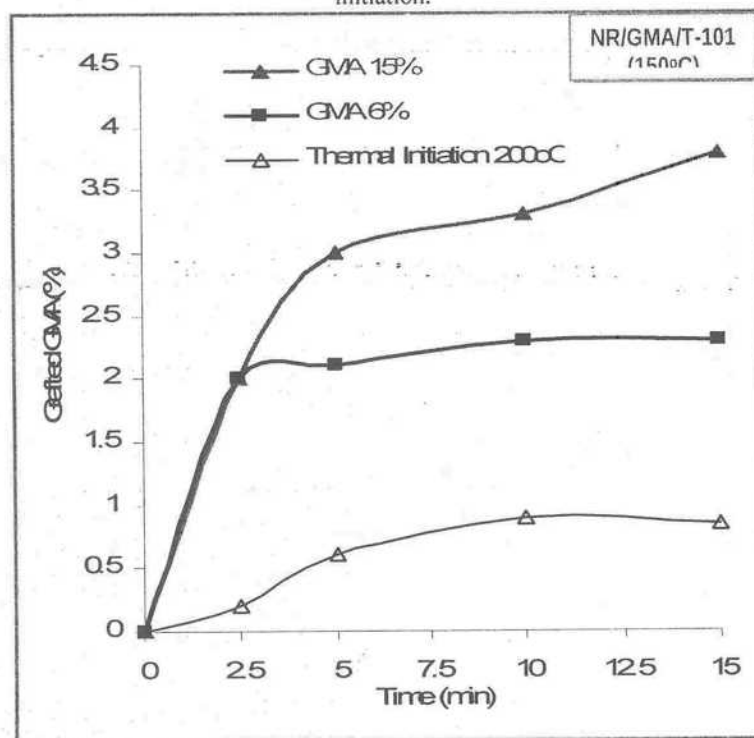


Fig.3 Effect of processing time on GMA grafting degrees of processed NR with GMA in the absence (thermal initiation) and presence of peroxide T-101 in different GMA initial concentration and different temperatures.

### 3.2. Effect of Processing Time

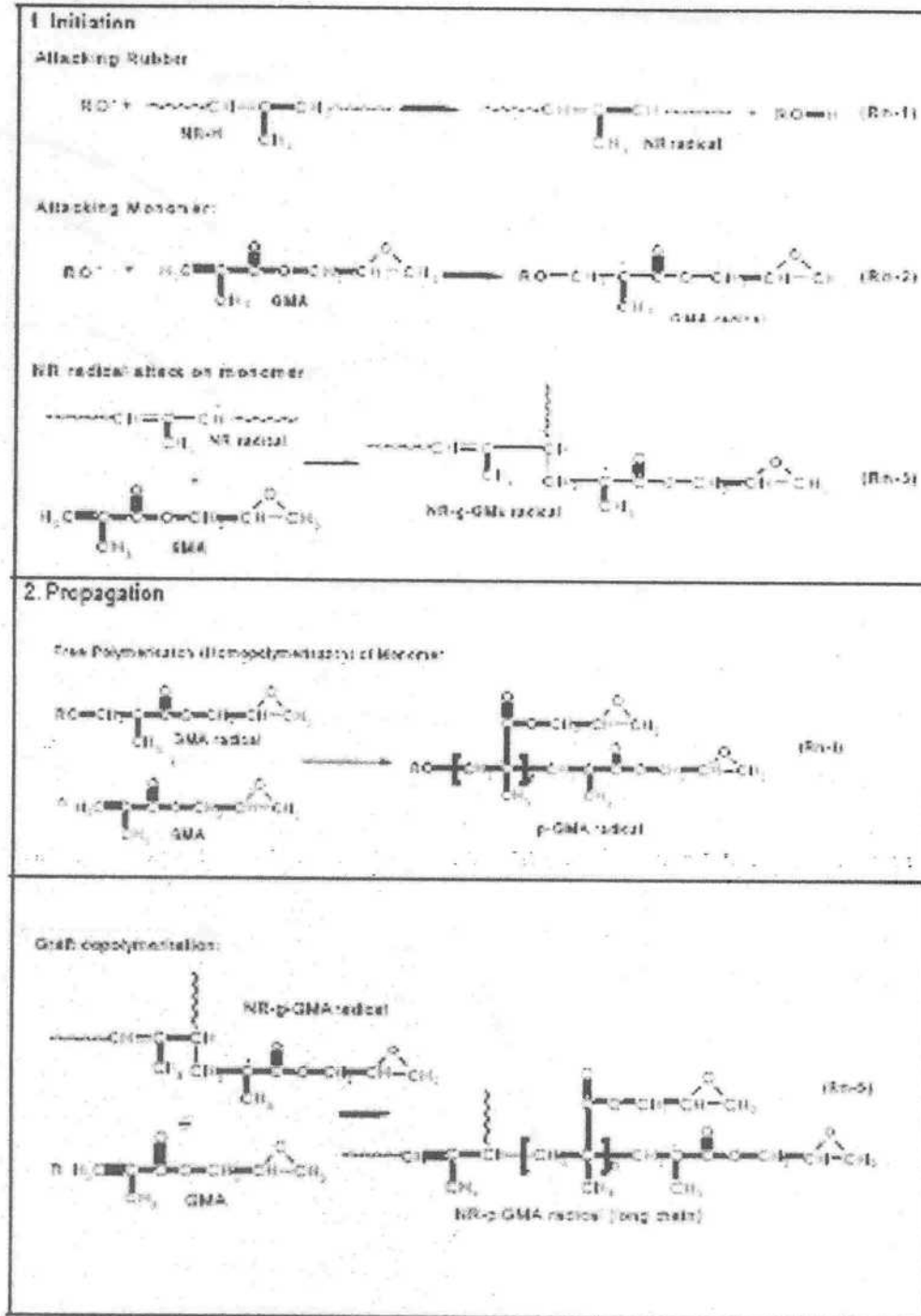
In order to investigate the kinetics of the grafting reaction of GMA onto NR a set of experiments was

prepared at a fixed composition, in the presence or absence of peroxide, with GMA concentration of 6 % and 15 %, T-101 0.02 molar ratio to GMA and temperature of 150°C and 200°C. It was found that



the grafting reaction took place rapidly in both thermal and peroxide initiation conditions. However, the reaction in the presence of peroxide (T-101) proceeded faster than that of the thermal initiated reaction and had nearly finished within 10 minutes

(see Fig.3). The percentage of conversion of GMA monomers increased rapidly in the first 2.5 minutes, after which the extent of increase slowed down. The grafting efficiency increased first gradually up to 80% conversion and then increased slowly.



Scheme-2 Reaction mechanism of GMA grafting onto NR.

## Grafting Mechanism

In the preparation of the GMA grafted-NR, initiation of grafting reaction is due to free radicals produced by the interaction of peroxide, GMA and NR. In the NR/GMA/T-101 system, for example, the peroxide T-101 decomposes to yield alkoxy, butoxy, and alkyl radicals (RO·) formed in the 'molten' NR system, which might interact with the monomer GMA or the rubber molecule producing a macroradical that initiates grafting. Scheme-2 gives a proposed mechanism for the graft copolymerization of GMA onto NR via the free-radical initiation.

The alkoxy, butoxy, and alkyl radicals not only can add to double bonds or abstract hydrogen atoms to produce polyisoprenyl radicals (Scheme-2, Rn-1), which initiate monomers to form the graft copolymers (Rn-3), but also to initiate monomers (Rn-2) to form polymeric radicals (Rn-4), which also can combine with polyisoprenyl radicals to terminate (Rn-9) or transfer to NR to form graft copolymers (Rn-5, Rn-6, and Rn-7). Moreover, some of the free homopolymer-GMA radicals can still terminate to form free copolymers (Rn-8). It is reasonable that grafting occurs by initiator radical attack on natural rubber; however, the chain-transfer processes can not be neglected (Lehrle and Willist, 1997) studied the mechanism of the graft copolymerization of methyl methacrylate (MMA) on natural rubber in the presence of vinyl acetate (VA) and suggested that the formation of graft copolymers involved the chain transfer reaction when peroxide azo-isobutyronitrile (AIBN) was used as initiator. A similar observation was made by Merkel et al. in the case of grafting of methyl methacrylate onto polybutadiene. In the case of grafting methyl methacrylate onto natural rubber, the excessive free PMMA radicals react with each other to form free copolymers more than to graft on the natural rubber and decrease the chain length of the grafts. Therefore, the production of PMMA is promoted more at high initiator content. On the other hand, the probability for the rate of chain transfer for the free polymer radicals to the natural rubber backbone is less than the rate of termination of free polymer radicals, favouring the termination process of copolymers over the chain-transfer process.

The success of a typical melt grafting experiment is usually measured in terms of the grafting yield dictated by the fraction of the monomer that becomes grafted onto the polymer backbone versus that which either remains unchanged or is consumed in side reactions such as homopolymerisation. In the experiments examined here, the results clearly showed that grafting glycidyl methacrylate (GMA) on natural rubber (NR) can be achieved by both thermal and peroxide initiation in the melt, though to varying degrees, the grafting efficiency of GMA by thermal initiation was quite low compared to that achieved by free radical initiation, see Fig-2. However, if one compares this with a typical reaction of grafted GMA on

polyolefins, e.g. PP (Galluci and Going, 1997), EPR (Zhang et al, 1996), then the observed grafting degree of GMA on NR by thermal initiation becomes quite meaningful. Similar results reported in grafting of maleic anhydride onto NR (Yao et al, 1998). This is almost certainly due to the reactivity of the double bond on the NR backbone, which would give rise to sufficient amount of macro radicals via mechano-scission that would react with the GMA monomer. The grafting reaction of GMA onto NR in the solid state however, is complicated due to the extremely high viscosity of the natural rubber. Even at high temperatures, the natural rubber does not behave like a normal plastic melt and hence high shearing forces would be exerted onto the rubber during the mixing (pseudo plasticity).

## 4. CONCLUSION

The success of a typical melt grafting experiment is usually measured in terms of the grafting yield dictated by the fraction of the monomer that becomes grafted onto the polymer backbone versus that which either remains unchanged or is consumed in side reactions such as homopolymerisation.

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