GRAFT COPOLYMERIZATION OF NATURAL RUBBER WITH FUNCTIONALIZED GLYCIDYL METHACRYLATE VIA THERMAL AND FREE RADICAL INITIATION: EFFECT OF PROCESSING TEMPERATURES AND TIMES

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Abstract: As an unsaturated elastomer, the natural rubber (NR) is difficult to maintain adhesivity with the other additive materials, limiting their use during the process of manufacturing. Therefore, it is necessary to modify the surface to improve thermal and oxidative resistance. This study aims to modify the natural rubber through a functionalization of glycidyl methacrylate (GMA) and its effect on temperatures and times during processing. Functionalization of NR was carried out via free radical initiation by varying the working times and temperatures. Characterizations via FTIR were performed to confirm the functional groups of NR and functionalized NR, while the analysis of grafting was carried out to describe the propose proposed reaction mechanisms. FTIR spectra confirmed the presence of functional groups contributing to NR including stretching O-H of peptide group (3285 cm^{-1}), stretching and absorption of CH_3 (respectively 2725 cm^{-1} and 1456 cm^{-1}), and functionalized GMA were observed after functionalization (1730 cm^{-1}). Working times and temperatures allowed the GMA to disperse evenly, resulting higher chance of homo-polymerisation via crosslinking of poly-GMA, optimum at 160-190ºC. In conclusion, the thermal initiation process at the optimum temperature allows the maximum grafting degree of GMA on NR, reaching up to 80% at 170°C, and results in a much more stable reaction through free radical initiation.

Keywords: Natural rubber; GMA; free radical initiation; thermal functionalization; temperatures; times

Abstrak: Sebagai salah satu elastomer tak jenuh, karet alam (NR) terbatas dalam menjaga kemampuan daya rekatnya dengan bahan aditif lain, sehingga membatasi penggunaan praktisnya dalam proses manufaktur. Oleh karena itu, diperlukan modifikasi khususnya di permukaan untuk meningkatkan ketahanan terhadap panas dan oksidasi. Penelitian ini bertujuan untuk memodifikasi NR melalui fungsionalisasi clycidyl metacrylate (GMA) dan mengkaji pengaruh suhu dan waktu selama proses fungsionalisasi berlangsung. Fungsionalisasi NR diinisiasi melalui radikal bebas dengan variasi waktu dan suhu reaksi. Karakterisasi menggunakan FTIR dilakukan untuk mengkonfirmasi keberadaan gugus fungsi pada NR dan NR-terfungsionalisasi, sedangkan analisis grafting dilakukan untuk menjelaskan mekanisme reaksi yang diusulkan. Spektra FTIR menunjukkan adanya gugus fungsi pada NR berupa regangan O–H (3285 cm^{-1}), regangan dan serapan CH_3 (masing-masing pada 2725 cm^{-1} dan 1456 cm^{-1}), serta munculnya puncak khas GMA-terfungsionalisasi pada 1730 cm^{-1}. Variasi waktu dan suhu reaksi memungkinkan terjadinya dispersi GMA yang lebih merata, meningkatkan peluang terjadinya homopolimerisasi melalui ikatan silang poli-GMA, pada suhu 160–190°C. Secara keseluruhan, proses inisiasi termal pada suhu optimum menghasilkan derajat grafting maksimum GMA pada NR hingga 80% pada 170°C, serta menghasilkan reaksi yang lebih stabil melalui mekanisme inisiasi radikal bebas.

Kata kunci: Karet alam; GMA; inisiator radikal bebas; fungsionalisasi termal; suhu; waktu

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Introduction

Natural rubber (NR), an unsaturated elastomer containing 93–95% cis-1,4-polyisoprene, has many desirable properties such as high elongation, and outstanding resilience. However, it also comes also with some shortcomings such as high sensitivity to heat and oxidation due to the presence of double bonds in its chains (Ngolemasango et al., 2003; Roberts, 1988). As the main materials for tire manufacturing, one of the major problems encountered during the production, for example, is the poor adhesion between the tyre cord (mostly nylon, rayon, polyester, and aramid fibers). This leads the rubber materials with poor bonding affinity between the polar cord material and the hydrophobic rubber molecules (Whba et al., 2024). To overcome this drawback, adhesion- ms, such as recorcinol-formaldehyd latex and polyisocyanates, have been utilized to provide a coating on the cord surface during tire manufacture to improve adhesion at the interface between the cord or metal and rubber (Enganati et al., 2022; Fakley et al., 2005; Sasidharan Achary et al., 2001). Graft copolymerization of glycidyl methacrylate onto natural rubber could be an attractive technique to enhance adhesion without drastically altering the original properties of the rubber (Mekpothi et al., 2021). Different chemical modifications have been performed in NR, and to increase its useful properties; this includes preparation of graft copolymers of NR with various types of vinyl monomers such as styrene (St) (Rimdusit et al., 2021; Zhu et al., 2024), maleic anhydride (MA) (Nakason et al., 2004; Wongthong et al., 2013), glycidyl methacrylate (GMA) (Song et al., 2022), methyl and alkyl methacrylate (George et al., 2003; Suriyachi et al., 2004; Zainal et al., 2020). There are somecopolymer products that have been used extensively in the area of polymer reactive blending as compatibilizers for certain incompatible polymer pairs

(Chanda, 2024; Suriyachi et al., 2004). However, there is a limited amount of work in the literature on the grafting of GMA (I) onto natural rubber.

Research Methodology

Materials

In this study, natural rubber was purchased from the local company with grade 10, SIR-10. All chemical reagents including acetone, benzoyl peroxide, BPO (II), dicumyl peroxide, DCP (III), 2,4-dimethyl-2,5-bis-(tert-butyl peroxy)hexane, Trigonox-101, T-101 (IV), and 1,1-di(tert-butylperoxy)-3,3,5-trimethyl cyclohexane (Trigonox-29B90, T-29B90) (V), were in analytical grades, purchased from Sigma-Aldrich.

Functionalization Procedures

Preparation and Initial Processing of NR

The initial step involved extracting some natural rubber (NR) sheets (SMR-L) in acetone condition for 24 hours to purify the NR from natural substances. The purified NR sheets were then dried in a vacuum oven at 80°C for 24 hours. The raw NR (SMR-L) was cut into chips, masticated into sheets using a two-roll mill at room temperature for 2 minutes, and subsequently cut into small pieces.

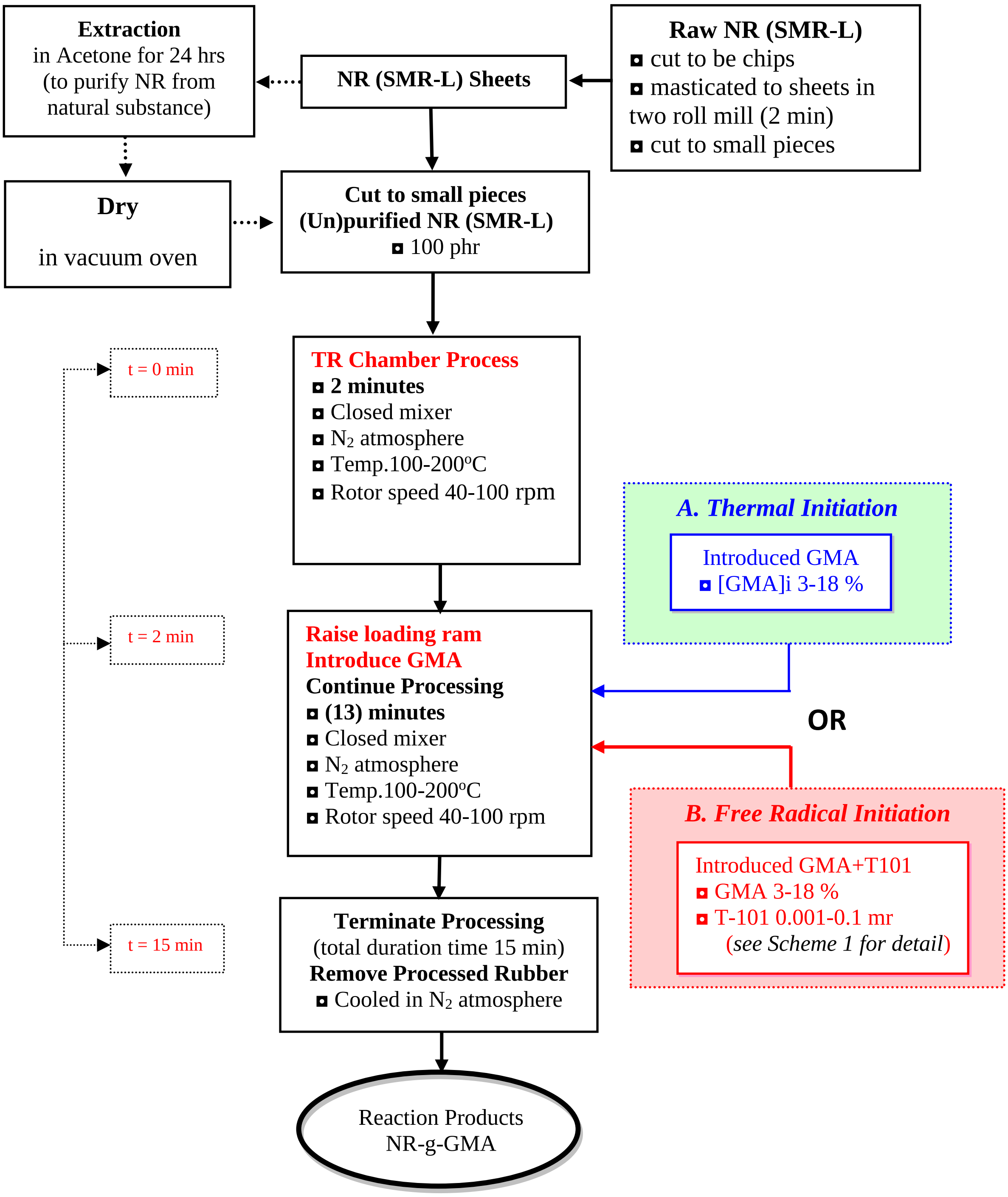
Masticating and Processing in Torque Rheometer

The masticated NR was loaded into the torque rheometer (TR) chamber and processed for 2 minutes in a closed mixer under a nitrogen (N_2) atmosphere at temperatures ranging from 100°C to 200°C, with rotor speeds between 40 rpm and 100 rpm. After 2 minutes, the loading ram was raised to introduce glycidyl methacrylate (GMA) and the processing continued.

Incorporation of GMA

The introduction of GMA and the continuation of processing were performed under two different initiation steps: (1) Thermal Initiation: GMA was introduced at concentrations of 3-18%, and (2) Free Radical Initiation: A premixed solution of GMA (3-18%) and peroxide (T-101 at concentrations of 0.001-0.1 phr) was introduced. The premixing was done using an ultrasonic bath for 5 minutes before introducing it into the masticated NR using a long needle syringe, ensuring the addition time was kept below 15 seconds.

In both steps, the processing was continued for an additional 13 minutes, maintaining a closed mixer environment under a nitrogen (N_2) atmosphere at temperatures between 100°C and 200°C and rotor speeds from 40 rpm to 100 rpm. Scheme. 1 below illustrates the steps of functionalizations.



Scheme 1. Schematic illustration of Functionalization

Results and Discussion

When natural rubber is processed with GMA in the presence or absence of peroxides, the processed rubber samples may contain grafted GMA (NR-g-GMA), homopolymerized GMA (poly-GMA), unreacted GMA (free-GMA), and branched or cross-linked natural rubber. To eliminate any unreacted GMA and poly-GMA from the reaction products and to ensure the correct measurement of the grafting degree of GMA-grafted NR, the processed rubber was purified using an extraction method with acetone. The content of GMA-grafted NR in the purified samples was then determined and characterized by titration and/or FTIR methods.

Natural rubber is known to contain natural substances, mainly proteins and lipids (phospholipids, esters of higher fatty acids, and sterols) (Q. Chen et al., 2022a; Chuayjuljit et al., 2004; Inphonlek et al., 2022; Shi et al., 2023). When extracted with acetone using a Soxhlet apparatus, these substances are removed. The FTIR spectrum of acetone-extracted natural rubber shows similar absorption peaks to those of raw natural rubber, except for the absorption peak at 3285 cm^{-1} (due to stretching O-H from protein) and a shift in the peak at 1742 cm^{-1} to 1718 cm^{-1}, likely due to the stretching of the >C=O group of natural protein, which becomes much smaller (Fig.1).

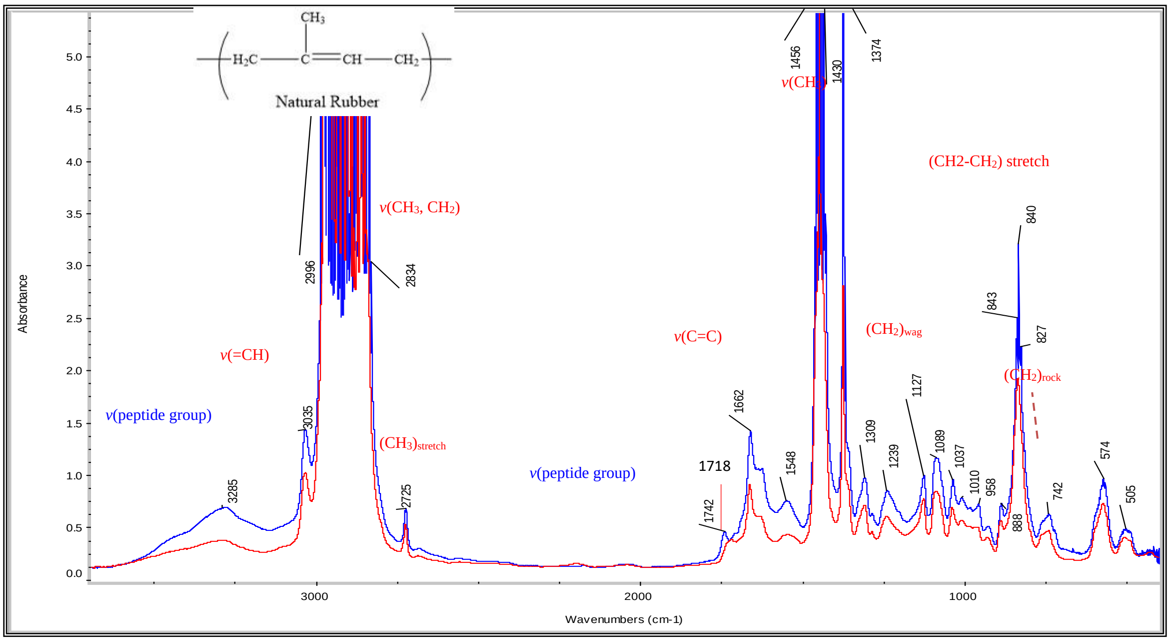


Figure 1. FTIR spectra of cured pressed raw NR before (blue) and after (red) extraction with acetone for 24h, pressed at 150°C for 2 min

Processing natural rubber with GMA, with or withoutperoxide, results in a significantly different physical appearance compared to raw natural rubber. Products processed at temperatures above 180°C and in the absence of peroxide showed a brown color and became tacky, whereas no obvious color change was observed when the reaction was carried out below 160°C, regardless of the presence of peroxide. The higher the processing temperature and GMA concentration, the deeper the brown color of the reaction product.

The acetone Soxhlet extraction removes the carbonyl absorption of GMA (free and poly-GMA) at 1730 cm^{-1}. This extraction method was used throughout to purify the natural rubber and the functionalized NR-g-GMA products. Therefore, the same Soxhlet extraction procedure was adopted for natural rubber processed with GMA at 180°C in the presence of the peroxide T-101 (free radical initiation for grafting). Figure 2 shows that the carbonyl band at 1730 cm^{-1}, corresponding to grafted GMA, remains even after exhaustive Soxhlet extraction with acetone, providing evidence of GMA grafting onto NR.

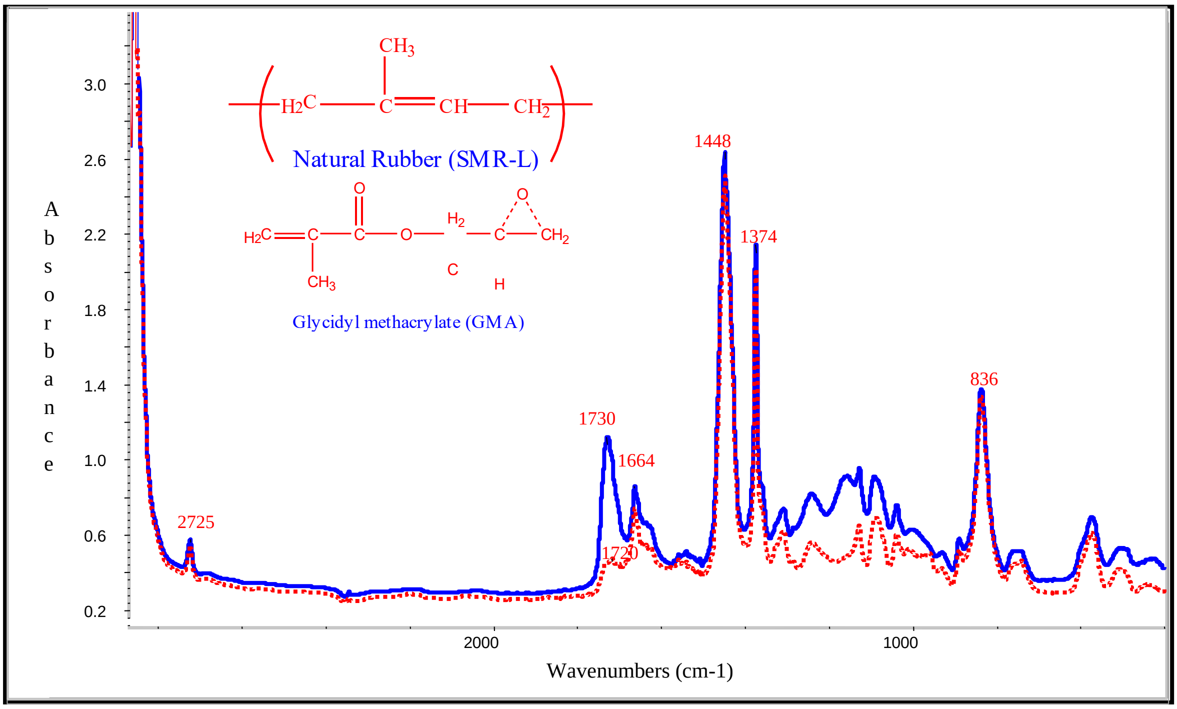


Figure 2. FTIR spectra before (blue) and after (red) acetone Soxhlet extraction cured pressed films (pressed at 150°C, 2 min) of processed NR-GMA, thermal initiation at low temperature

In the case of thermal initiation, NR was processed with GMA in the absence of peroxide at temperatures ranging from 100°C to 200°C. As shown in Fig. 3, there was a slight difference in the changes in torque values at the different processing temperatures used for thermal initiation. Initially, as expected, the torque values increased to a maximum value (loading torque maximum), with this value being lower at higher processing temperatures. After further processing, upon the addition of GMA into the molten NR and lowering the ram (closed ram), the torque values increased to reach a torque maximum (highest value at 160°C). There was a noticeable change in the final torque values, which decreased at higher processing temperatures. Additionally, the natural rubber became brown and tackier at temperatures above 200°C.

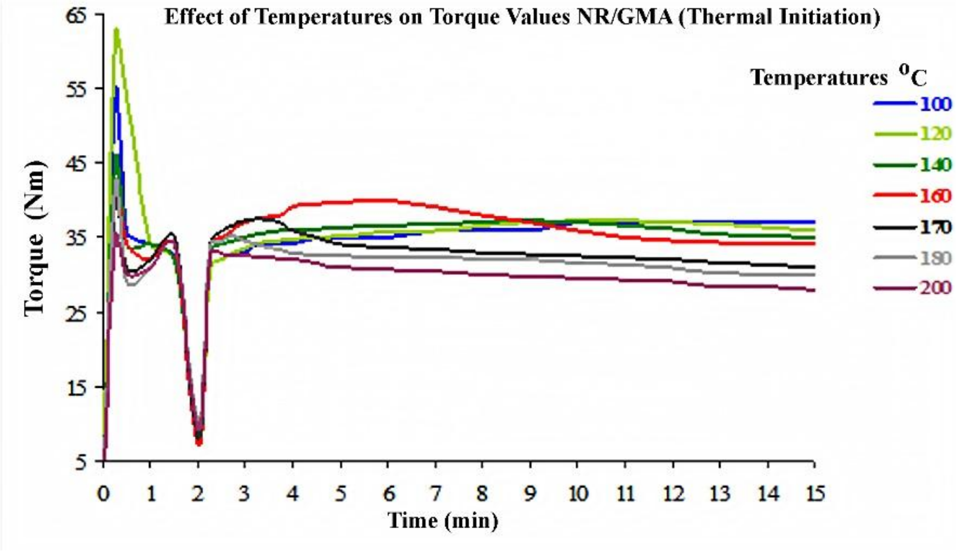


Figure 3. The effect of temperature on torque-time curves and torque characteristics of processed NR/GMA system

For thermal initiation, the grafting reaction of GMA was shown to require a temperature higher than 160°C, preferably between 160°C and 200°C. Increasing the processing temperature significantly improved the dispersion of GMA in the rubber and affected the balance between various competing reactions (conversion of GMA to homopolymerization (poly-GMA), cross-linking, and chain scission of NR chains) relative to the target GMA grafting reaction(Jiang et al., 2022; Yan et al., 2024). The degree of grafting of GMA onto natural rubber depends on the processing temperatures and the initial concentration of GMA. Fig. 4 shows that grafting is highest at processing temperatures of 160°C for GMA at 6% and at 190°C for GMA at 15%. It appears that there is a correlation between the degree of grafting of GMA and the torque maximum, with optimum grafting and the highest torque value occurring at the same processing temperature.

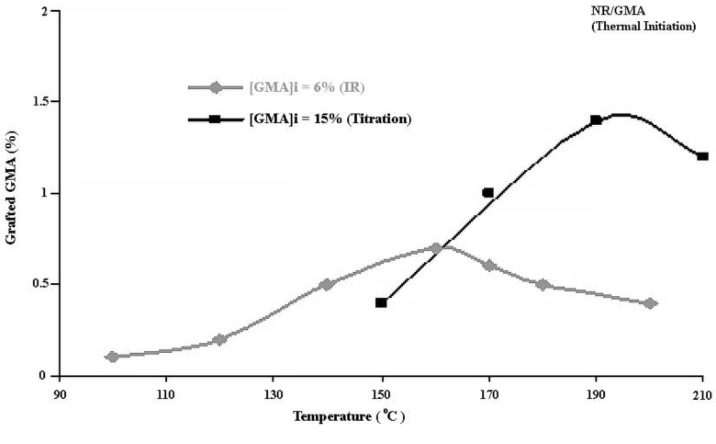


Figure 4. The effect of temperatures on the grafting degree of processed NR/GMA [GMA]i = 6% and [GMA]i = 15%

In the case of free radical initiation, processing NR with GMA in the presence of peroxide (T-101) demonstrated that the peroxide T-101 could affect the extent of the GMA grafting reaction and the level of cross-linking or chain scission of the polyisoprene, as reflected in changes in the torque characteristics and the degree of grafting. The changes in torque-time curves, torque characteristics, and the grafting degree of GMA on NR at different processing temperatures are shown in Fig. 5 and Fig. 6, respectively.

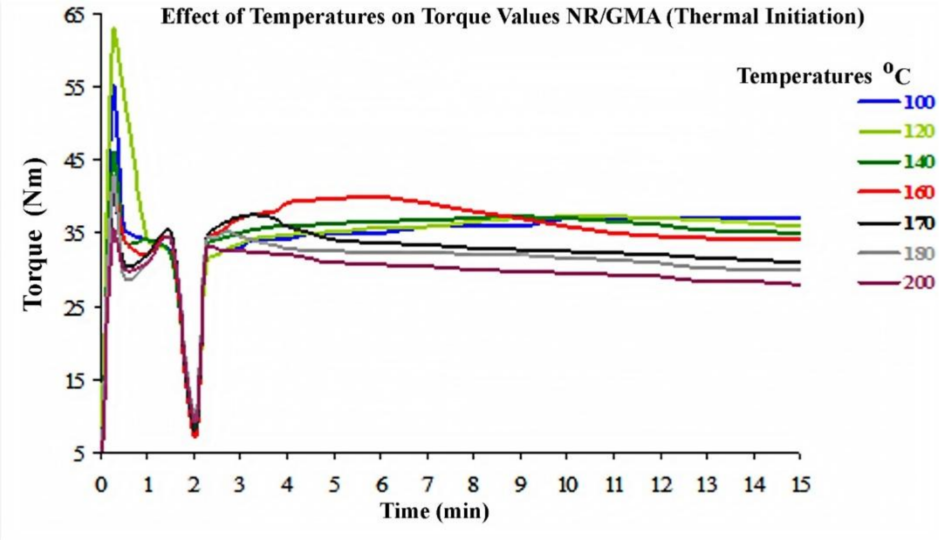


Figure 5. The effect of temperature on torque-time curves and torque characteristics of processed NR/GMA/T-101 and its comparison to thermal initiation system

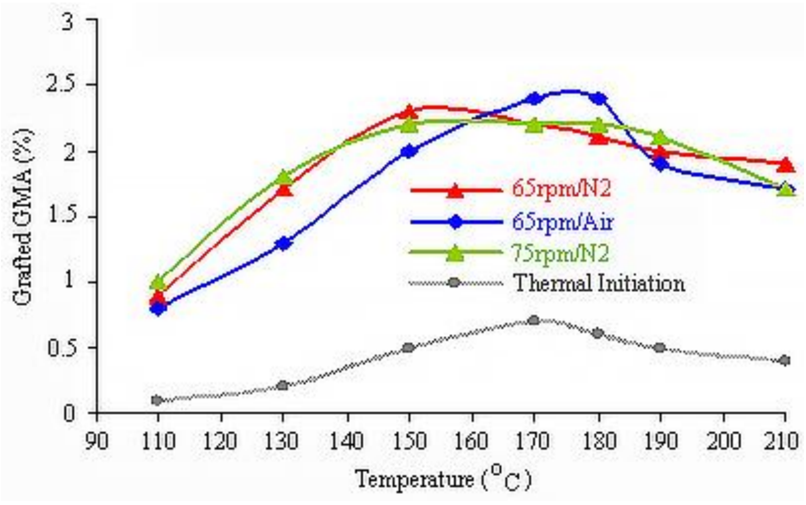


Figure 6. The effect of temperature on GMA grafting level of processed NR/GMA/T-101 compared with different rotor speeds and thermal initiation

As shown in Fig. 5, the final torque and the torque maximum of the NR/GMA/T-101 system, processed under different conditions, exhibit a significant difference compared to thermal initiation (at the same temperatures). This difference is due to the competition between the grafting reaction (GMA conversion to GMA-grafted NR) and side reactions, including homopolymerization, cross-linking, and chain scission of the rubber. The peroxide T-101 effectively initiates the grafting reaction of GMA onto natural rubber. By raising the processing temperature, the grafting degree of GMA increased between 140°C and 180°C but started to decline at higher temperatures. (Fig. 6).

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 a GMA concentration of 15%, a T-101 to GMA molar ratio of 0.02, and temperatures of 150°C and 170°C. It was found that the grafting reaction occurred rapidly under both thermal and peroxide initiation conditions. However, the reaction in the presence of peroxide (T-101) proceeded faster than the thermal-initiated reaction, nearly completing within 10 minutes (see Fig. 7). The percentage of conversion of GMA monomers increased rapidly in the first 2.5 minutes, after which the rate of increase slowed. The grafting efficiency initially increased gradually up to 80% conversion and then increased slowly.

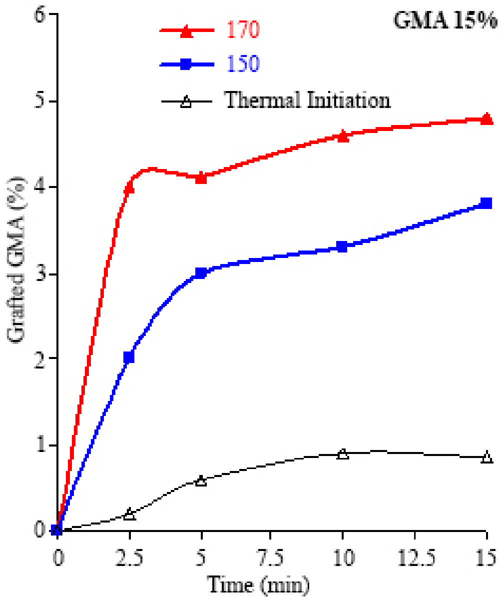
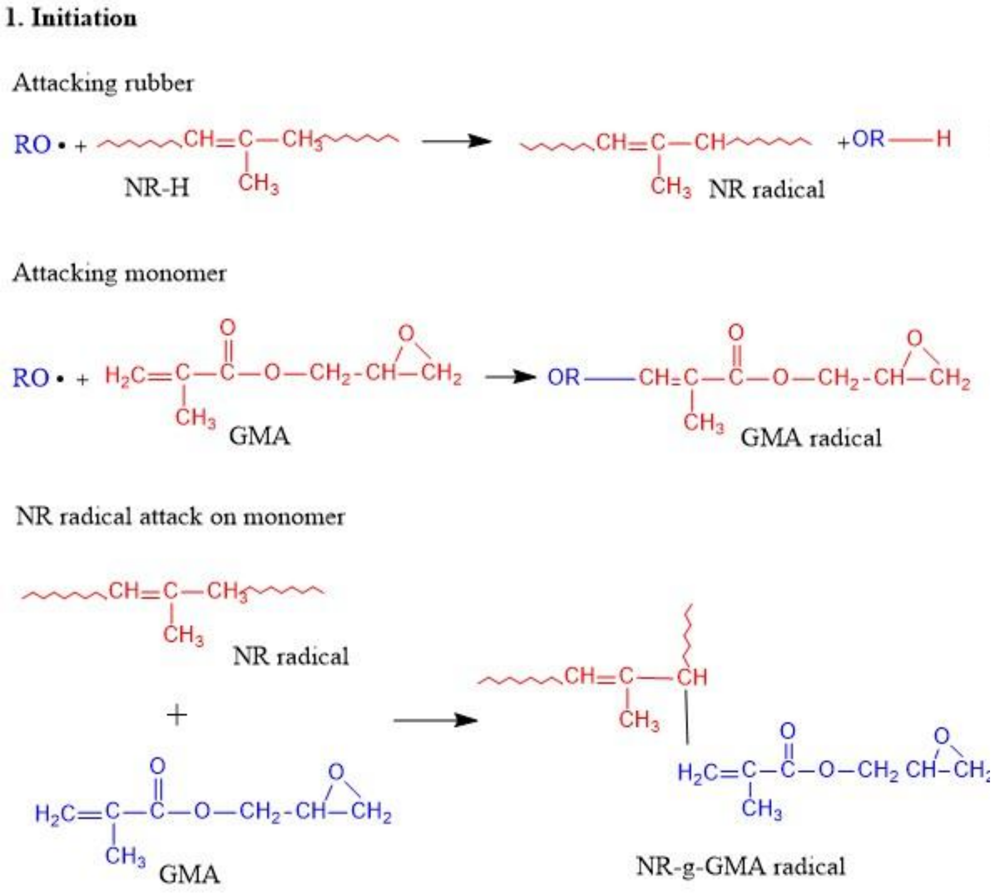


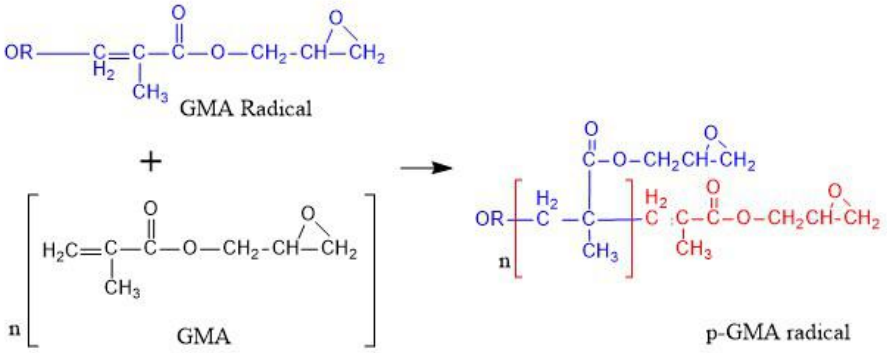
Figure 7. Effect of processing time on GMA grafting degrees of processed NR with GMA in the absence (thermal initiation) and presence of peroxide T-101 (0.02 mr) in different temperatures.

sIn the preparation of GMA-grafted NR, the grafting reaction is initiated by 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 alkoxyl, butoxyl, and alkyl radicals (RO·) in the ‘molten’ NR system. These radicals might interact with the monomer GMA or the rubber molecule, producing a macroradical that initiates grafting. Scheme 2 provides a proposed mechanism for the graft copolymerization of GMA onto NR via free-radical initiation.

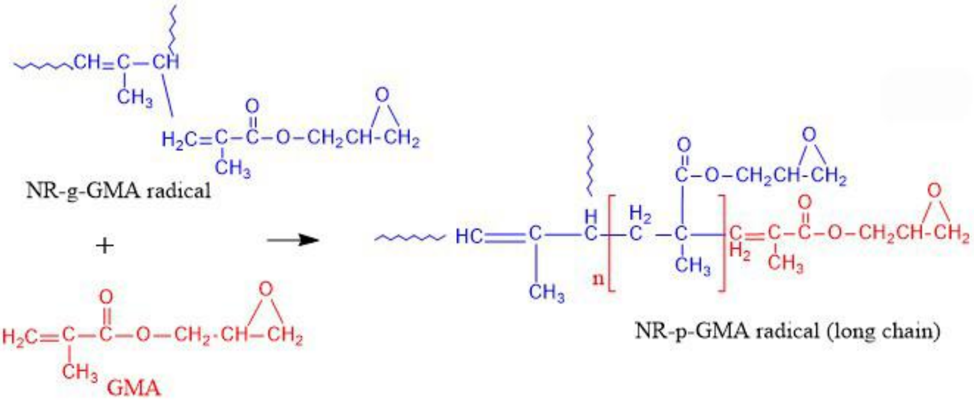


2. Propagation

Free polymerization (homopolymerization) of monomer

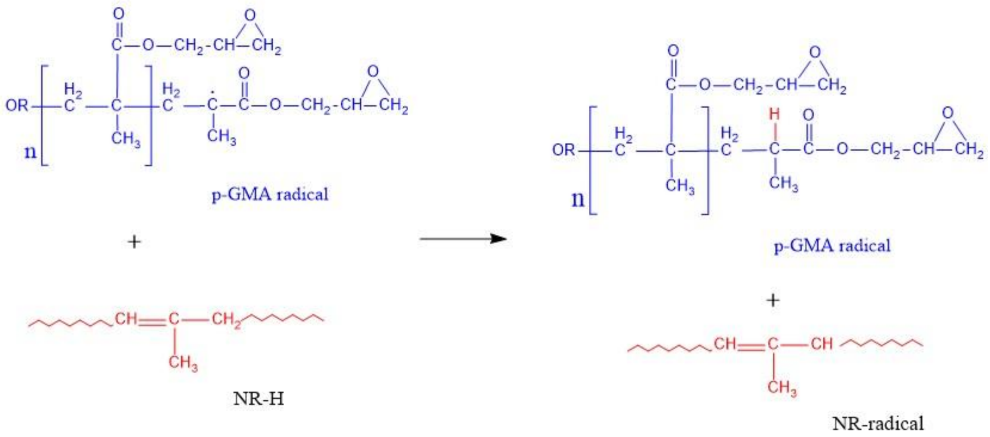


Graft polymerization

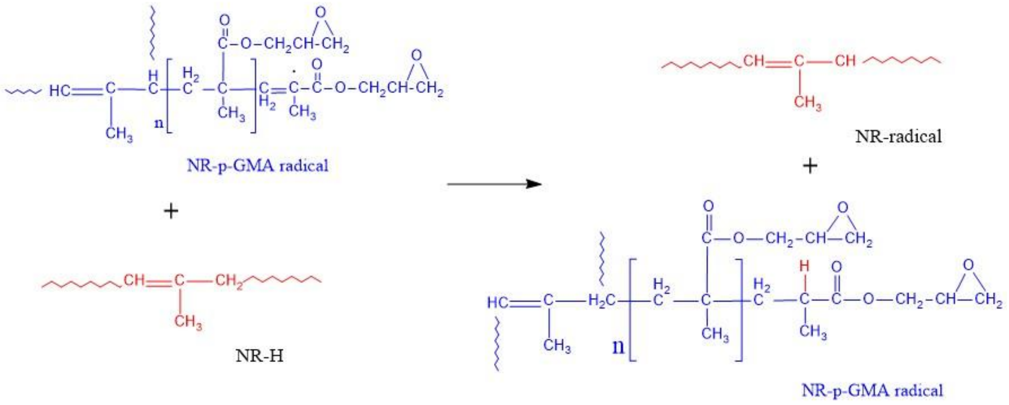


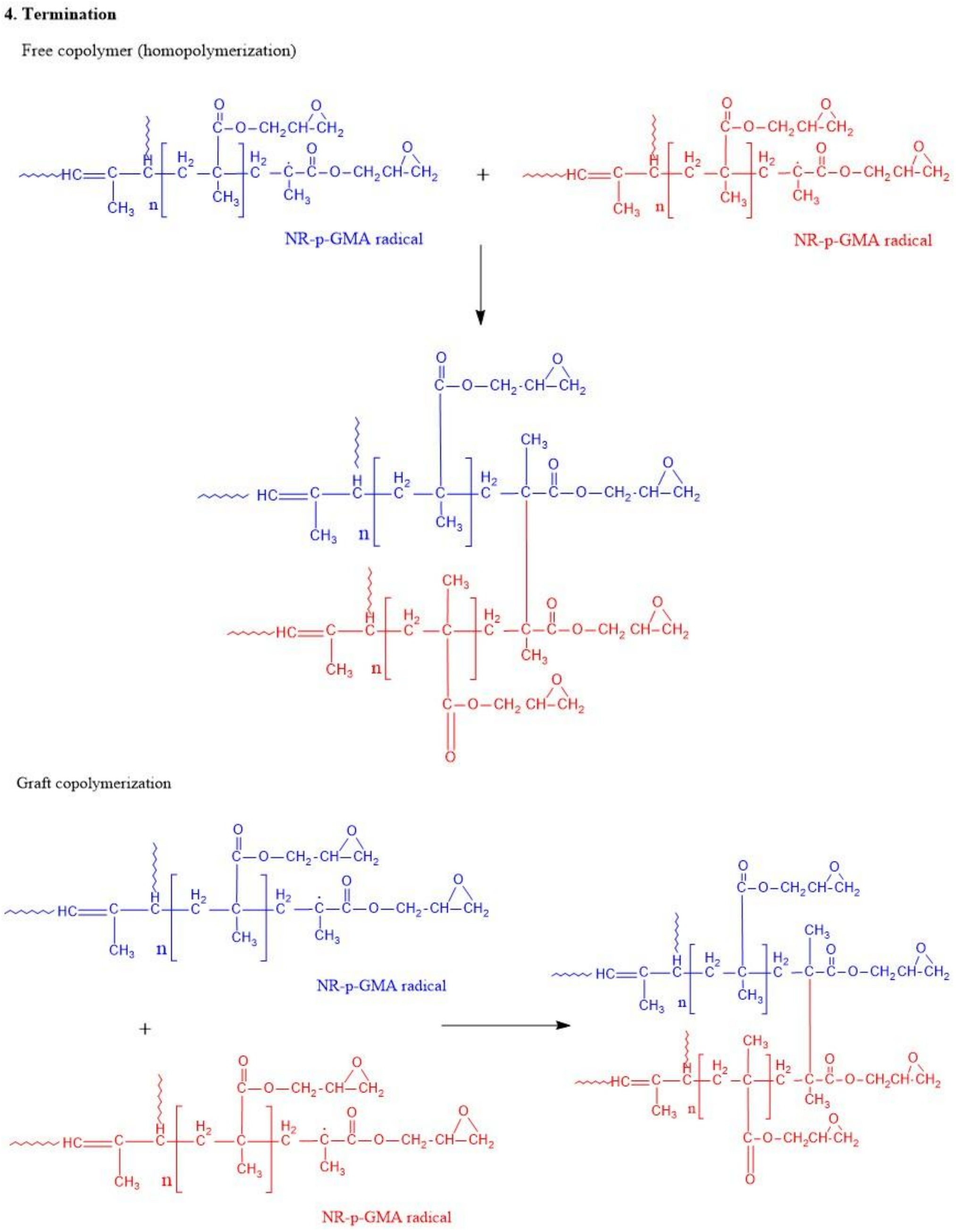
3. Chain Transfer to Macroradical

Transfer to rubber (NR-H)



Transfer to rubber





Scheme 1. Reaction mechanism of GMA grafting onto NR (cont.)

The alkoxyl, butoxyl, and alkyl radicals can add to double bonds or abstract hydrogen atoms to produce polyisoprenyl radicals (Scheme 1 in the initiation), which initiate monomers to form graft copolymers. Additionally, they can initiate monomers (Scheme 1 initiation) to form polymeric radicals (Scheme 2 propagation), which can combine with polyisoprenyl radicals to terminate (Scheme 1 termination) or transfer to NR to form graft copolymers (Scheme 1 propagation, transfer to macroradical). Some of the free homopolymer-GMA radicals can also terminate to form free copolymers (Scheme 1 graft polymerization). It is reasonable to assume that grafting occurs through an initiator radical attack on natural rubber; however, chain-transfer processes cannot be neglected. Lehrle and team (G. Chen et al., 2022) studied the mechanism of graft copolymerization of methyl methacrylate (MMA) onto natural rubber in the presence of vinyl acetate (VA) and suggested that graft copolymer formation involved chain transfer reactions when azo-isobutyronitrile (AIBN) was used as the initiator. A similar observation was made by Merkel et al. in the grafting of methyl methacrylate onto polybutadiene (Merkel et al., 1987). In the case of grafting methyl methacrylate onto natural rubber, the excessive free PMMA radicals react more with each other to form free copolymers rather than grafting onto natural rubber, reducing the chain length of the grafts. Therefore, PMMA production is promoted more at high initiator content. On the other hand, the probability of the polymerization process involving free polymer radicals and the natural rubber backbone is lower than the rate of termination of free polymer radicals, favoring the termination process of copolymers over polymerization..

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 the fraction that either remains unchanged or is consumed in side reactions such as homopolymerization. In the experiments examined here, the results clearly showed that grafting glycidyl methacrylate (GMA) onto 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. 6). However when compared to typical reactions of grafted GMA on polyolefins (e.g., PP and EPR), the observed grafting degree of GMA on NR by thermal initiation becomes quite meaningful (Hayeemasae et al., 2022; Ngudsuntear et al., 2022; Song et al., 2022). Similar results have been reported for the grafting of maleic anhydride onto NR (Grasland et al., 2019; Wongthong et al., 2013). This is almost certainly due to the reactivity of the double bond on the NR backbone, which generates a sufficient amount of macroradicals via mechano-scission that react with the GMA monomer. The grafting reaction of GMA onto NR in the solid state is complicated due to the extremely high viscosity of natural rubber (Q. Chen et al., 2022b). Even at high temperatures, natural rubber does not behave like a normal plastic melt, and hence high shearing forces are exerted onto the rubber during mixing (pseudo plasticity)(Salaeh et al., 2022; Trinh et al., 2023).

The macroradicals from polyisoprene not only initiate the grafting reaction of GMA onto the polymer chains but also contribute to branching and cross-linking within the polymer. The processing temperature plays a crucial role in the overall free radical grafting process, affecting both the kinetic and thermodynamic aspects of all the elementary reactions. Allyl radicals recombine or combine with other (primarily formed) radicals approximately 100 times faster than they undergo disproportionation, leading to an increase in the molecular weight of NR.(Seidel et al., 2013; Wang et al., 2015).

Conclusion

The graft copolymerization of natural rubber with the monomer glycidyl methacrylate (GMA) was successfully achieved through both thermal and free radical initiation using the peroxide Trigonox-101 (T-101) via a melting process in an internal mixer. In the thermal initiation process, the highest grafting degree of GMA was obtained at a processing temperature of 160-190°C, while in the presence of peroxide T-101, the maximum grafting degree was achieved at a lower processing temperature of 140-160°C. The presence of peroxide Trigonox-101 accelerated the graft copolymerization reaction of GMA on natural rubber and significantly enhanced the grafting degree of NR-g-GMA. The grafting degree of GMA on natural rubber is influenced by the ease of macro radical formation in natural rubber chains through the mechano-scission process during thermal initiation via H-abstraction and the formation of more stable allyl radicals.

Conflict of Interest

The authors declare that there is no conflict of interest.

Acknowledgments

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