Chapter 3

Grafting of maleic anhydride onto natural rubber by gamma radiation

Grafting of polymeric materials under the influence of ionizing radiation has been known since the middle of the twentieth century as a versatile method for polymer modification [1-9]. Among other methods, radiation grafting has been considered for a longtime for the preparation of polymer electrolyte membranes for electrochemical applications [10].

Graft copolymers of maleic anhydride with synthetic and natural polymer have been widely studied in recent years. The copolymer products have been used extensively in the area of polymer reactive blending, as the main blend components [11-19], blend compatibilizers [12, 20-22, 23] or composite matrices [24]. Thermoplastic materials such as polypropylene [19,20,23,24,25,26] polyethylene [19,21,22,27,28,29] polystyrene [11,18] and polyester [30] are widely used as backbones of the graft copolymer. However, elastomeric backbones such as EPDM [14] EPR [11, 13, 15] and NR [12,16,17, 31-34] have also been studied. The graft copolymer of maleic anhydride onto the natural rubber molecules was generally carried out in the molten state [12,16,17]. The initiation system used in the graft copolymerization of MA onto NR was peroxide initiator [33] or the shearing action [12,16,17, 33,34] of the materials in an internal mixer at high temperature. Graft copolymer of MA onto the NR has also been prepared in the solution state [31,32]. However, there have been very limited data on preparation methods and material properties obtained from this technique. Natural rubber (STR 5L) was used as a polymer backbone for the grafting reaction with maleic anhydride in toluene solution.
Grafting with various functional monomers has been used as an effective tool for producing modified rubber with superior properties. Grafted rubber can be produced by chemical route or using gamma radiation (\(\gamma\)-ray). The chemical route is done in presence of peroxides. Irradiation of natural rubber swollen with methyl methacrylate was investigated by Angier and Turner [35]. A study on acrylonitrile graft NR prepared by \(\gamma\)-ray initiation was also reported [36]. Other functional monomers such as acrylic acid, methacrylic acid, glycidyl methacrylate sulfonic acid have also been successfully used for grafting modifications of natural rubber and olefins [37].

In this chapter the production of maleic anhydride grafted natural rubber (MA-g-NR) using gamma radiation and its characterization are proposed to be investigated.

### 3.1 Experimental

#### 3.1.1 Preparation of MA-g-NR

Maleic anhydride grafted natural rubber (MA-g-NR) was prepared by the following procedure. NR was initially mixed with MA in a Brabender Plasticorder at 50rpm for 10 minutes at 70\(^{\circ}\)C. The mix was then subjected to \(^{60}\)Co gamma irradiation for a period of 1½ hours in the gamma chamber. Trials were conducted by varying the radiation doses (0.5kGy, 2.5kGy, 5kGy, 7.5kGy and 10kGy) and maleic anhydride concentrations (1, 3, 5 and 10 percentage by weight). After irradiation, the unreacted MA was separated by dissolving the reaction products in toluene at reflux temperature and then precipitating the polymer by adding acetone. This was repeated until the recovered product was free from residual MA. The product was finally dried in a vacuum oven for 24hrs at 110\(^{\circ}\)C.
3.1.2 Maleic anhydride grafted natural rubber (MA-g-NR)

MA grafting reaction can be described as

\[
\begin{align*}
\text{CH}_2 & \quad + \quad \text{HC} & \quad \xrightarrow{\text{Radiation}} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} & \quad \text{HC} & \quad \text{H}_2 & \quad \text{CH} \\
\text{CH} & \quad \text{CH}_2
\end{align*}
\]

3.1.3 Characterization of MA-g-NR

3.1.3.1 Determination of grafting efficiency

The grafting efficiency was determined by titration method.

3.1.3.2 FTIR spectra

FTIR spectra are used for identifying the functional groups in maleated rubber.

3.1.3.3 Differential scanning calorimetry (DSC)

Grafting has been further confirmed from DSC data.

3.2 Results and discussion

3.2.1 Effect of radiation dosage on grafting efficiency

Figure 3.1 shows the variation of grafting efficiency (MA content) of MA-g-NR with different radiation dosages for 4.2% MA mixed NR. It can be seen that the MA grafting reaction is very much depended on the radiation dosage. The MA content increased sharply at radiation dose of 2.5kGy and then decreased on increasing the dose.
The variation in the MA content with irradiation dose was also confirmed from the FTIR spectra of the grafted samples. Figure 3.2 shows the IR spectra of the pristine and maleated NR at different radiation dosages. In maleated rubber, the additional peak at 1738 cm\(^{-1}\) which corresponds to the typical C=O stretching of anhydrides. The peaks at 1452 cm\(^{-1}\) and 1375 cm\(^{-1}\) correspond to the aliphatic CH\(_2\) bending vibrations in NR. The peak at 800 cm\(^{-1}\) corresponds to the CH\(_2\) rocking. A comparison of the relative intensity of the peak at 1738 cm\(^{-1}\) indicates that maximum grafting takes place at irradiation dose of 2.5 kGy.
The grafting of MA on NR takes place by ENE reaction [38, 39]. The joining of a double or triple bond to an alkene reactant having transferable allylic hydrogen is called ENE reaction. The reaction is reversible and the reverse is called retro-ENE reaction. In the present system, ENE reaction is promoted by irradiation dosage below 5kGy whereas the retro-ENE reaction becomes predominant at higher dosages.

3.2.2 Effect of MA concentration on grafting efficiency

Keeping 2.5kGy as the optimum radiation dosage for grafting, the grafting efficiency was also found to increase with MA concentration in the reaction mixture. Figure 3.3 shows the variation of MA content in MA-g-NR with MA concentration in the reaction mixture using the titration method according to the equation 2.1 in Chapter 2. The MA content proportionately increased from 0.7 % to 9.1 % on increasing the MA concentration from 1% to 10%.
Figure 3.3 Variation of MA concentrations in MA-g-NR with MA concentration in the reaction mixture.

3.2.3 Effect of MA grafting on NR tensile properties

MA grafting was found to improve the tensile properties of the vulcanizates without clay, possibly due to H-bond interactions. Figure 3.4 shows the variation of tensile strength of the vulcanizates with MA content. The tensile strength showed a sharp increase from 19.7MPa to 22.3MPa at an MA content of 0.7% and then showed gradual increase up to 23.4MPa with the increase of MA content to 4.2%. However, high MA content of 9.1% was found to retard the curing reactions of the rubber vulcanizates. So MA-g-NR with MA content of $\leq 4.2\%$ was used for further studies. A 19% increase in tensile strength is obtained for 5MA-g-NR vulcanizates compared to NR gum.
Radiation grafting of maleic anhydride onto natural rubber by gamma

Figure 3.4 MA content verses tensile strength of cured MA-g-NR with out clay.

3.2.4 Differential scanning calorimetry

The transition phenomena of the maleated natural rubber were studied by measuring the glass transition temperature ($T_g$) which is seen in figure 3.5. 10MA-g-NR shows the maximum $T_g$ value. As the grafting is increased the $T_g$ value increases to higher values. Pure NR shows the lowest $T_g$ value. The $T_g$ value of pure NR is $-63.36^\circ$C. As the MA concentration is increased to 10% the $T_g$ value is increased to $-44.82^\circ$C. Furthermore, the glass transition temperature increases with the increase of the MA concentration. This may be attributed to the restriction on chain mobility and flexibility because of the presence of the bulky grafted MA on the NR molecules. Increasing the grafted MA content also causes more inter chain interaction between polar groups of the graft copolymer. Hydrogen bonding is also more pronounced for the graft copolymer with the high grafted MA in the molecules. Higher the MA content the more stiffer will be the grafted rubber.
Figure 3.5 DSC thermograms of pure NR and MA-g-NR

3.3 Conclusions
This study shows that MA can be grafted to NR by the gamma radiation technique. MA concentration and radiation dose affect the grafting reaction significantly. Quantification of the grafted MA on the NR molecules can be determined using the titration method by determining the level of carboxylic acid which was determined by titration with standard KOH solution in methanol/benzyl alcohol. The estimation of the grafted MA level can also be performed using IR spectroscopy. It is found that MA grafting on NR molecules increases with MA concentration to a particular level with corresponding increase in the $T_g$ value.
References


Chapter 3