

Modified Rubber via Grafting of Polymer on Olefinic Site

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ABSTRACT: Natural rubber (NR) is a very reactive rubber because of its structure. The modification of NR with other functional groups can be achieved by incorporation of monomer carrying the desired functional group in the polymerization process using ene reaction. Grafting of a second polymer on to the natural rubber backbone leading to the chemical modification of the polyisoprene occurs at allylic double bond system. This route following grafting gave good control over the extent of reaction as the reaction limits itself on individual olefinic sites present on rubber and does not employ a catalyst that gets poisoned by non rubbers. With the help of ene reaction not only the molecular wt of the polymer that underwent grafting can be accurately determined but the no of grafting sites can also be controlled. Azo compounds have been used as effective modifiers of NR as they have long-term stability and have fewer tendencies to decompose to free radicals.

INTRODUCTION

The cis structure of Natural rubber (NR) with two olefinic sites makes it one of the most reactive diene rubber; firstly because of the presence of three electron donating alkyl group that increases the electron availability at the double bond thus making it more reactive towards electrophilic reagents. Secondly, the three-alkyl group increases the stability of positive ions and free radicals that gets formed from the olefin through double bond opening.

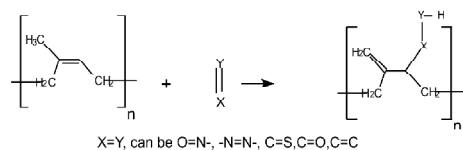
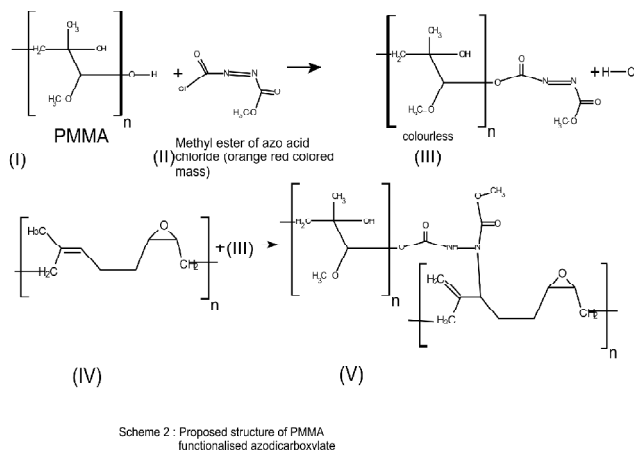
Apart from its high reactivity the need for modified rubber was felt because of many major drawbacks shown by NR like storage hardening, less water, less oil resistance, less strength but high tackiness, etc. The phenomenon like storage hardening [1] occurs because of cross linking of rubber chains through foreign groups like aldehydes which undergo cross linking via aldol condensation under the action of non rubbers like amino acids.[2,3] Even model epoxide compounds have been found to react with amino compounds to form adducts which causes cross links[4-6] in the rubber system when mixed with it. Hence researchers have been long working on various methods of modifying rubber so as to make best use of cross linking property of rubber in order to

get better desired properties comparable to synthetic rubber. There are broadly three types of modification of natural rubber:

1. Changes occurring without the inclusion of new atoms but resulting from bond rearrangements like C-C cross-linking, cyclisation, cis–trans isomerization.
2. Introduction of new chemical groups entering from olefinic double bond via addition or substitution reactions.
3. Grafting of a second polymer on to the natural rubber backbone leading to the chemical modification of the polyisoprene allylic double bond system.

Lot of work has been done on first type of modification [7, 8].The present work deals with third type of modification leading to a change in not only chemical properties of rubber but physical properties as well, like increased hardness, strength with decreased tackiness. In rubber modification, it has been found that, if the introduced group is polar with respect to NR, the properties like oil resistance and air permeability of NR gets improved along with chemical resistance [9]. The modification of NR with other functional groups can be achieved by incorporation of monomer carrying the desired functional group in the polymerization process using ene reaction as shown in scheme (Figure 1).

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Scheme 1: The general ene reaction

Figure 1: Scheme of the General “ene” Reaction

The ene reactions have various advantages over other routes i.e.:

1. They do not employ catalysts, which get poisoned by non-rubbers in NR.
2. These reactions have high efficiency and do not show any side reaction.
3. Works best with NR as electron rich alkyl substituted double bond is available on NR.
4. Can carry variable functional groups.

Studies have revealed that of the several ENE reagents the C-nitro and azo compounds [10-12] are the most effective modifiers of NR. The azo compounds have acceptable long term stability at ambient temperature in excess of 100 °C and also less tendency to decompose to free radicals. During grafting of polymers to NR the polymer of desired molecular weight needs to be synthesized with a terminal hydroxyl group. Anionic polymerization is carried out in which the polymeric carbanion reacts with ethylene oxide using butyllithium or fluorenyllithium as an initiator. After introducing a hydroxyl group in the polymer, the former was mixed with an azo compound to obtain azodicarboxylated functionalized polymer. Simple melt mixing of the azo polymer with ENR led to grafting. This type of grafting has various advantages like:

1. The molecular wt of the polymer that underwent grafting can be accurately determined.
2. The no of grafting sites can be controlled.

The ENR that was used was 50% epoxidised i.e. only half of the olefinic sites were available for the ENE reaction, whereas the other half was occupied by epoxy ring. The objective behind this research was two fold, firstly to improve the behavior of NR not only during manufacture of various products from them, but also the performance during use.

EXPERIMENTAL

Materials

All the solvents were distilled before use and stored. Malaysian Rubber Association donated NR. Hi Media Lab supplied PMMA. Azoacid chloride and ethylene oxide were purchased from B.D.H. chemicals. 9 – Fluorenyllithium, heptanone – 4 and 1, 2 dimethoxy ethane were purchased from Aldrich.

Methyl methacrylate was washed four to five times with aqueous NaOH (25% by wt) in order to remove the inhibitor and then washed with deionised water upto a constant pH value. The monomer thus obtained was made to polymerize. Anionic polymerization of methyl methacrylate (0.5 mole) [13,14] was carried out in highly solvating media i.e, 750 ml of 1,2 dimethoxy ethane at -20°C, initiated by 9 – fluorenyllithium as an initiator in three necked flask equipped with a mechanical stirrer, thermometer along with inlet and outlet tubes for nitrogen gas. The temperature of the reaction mixture was maintained at -20±1°C for 1 hour and during that time the solution became very viscous. To this viscous solution, ethylene oxide [15] was passed with stirring followed by addition of 20 ml of dil HCl. The reaction mixture was warmed to room temperature and the solution was poured into five liters of ethanol, which was being vigorously stirred, precipitated the polymer. A solid mass got separated out which was dried and dissolved in 800/ml of acetone and the solution was filtered. To the filtered portion a small amount of heptanone – 4 was added and the mixture was cooled to -10°C and held at that temperature for 48 hrs. After 48 hours a deep orange red colored mass got separated and was dried for spectral

analysis. A small amount of dried mass was dissolved in azo acid chloride (5×10^{-3} mol/lit). The addition was carried out till the deep orange red colour was completely lost indicating the presence of azodicarboxylate functionalized PMMA [16-19]. This was further confirmed from spectral analysis using Perkin Elmer Infra Red Spectrophotometer (M-783). In order to modify rubber, the rubber particles in latex were epoxidised to 50% following method of D.R. Burfield [20] and the epoxide content was determined by Differential Scanning Calorimeter [21] and Infra Red spectroscopy technique [22]. Direct mixing of azodicarboxylate functional Polymethyl methacrylate (5% by wt of ENR) with ENR at 120°C maintaining the motor speed at 60 rpm for 5 minutes was carried out in a Haake Torque Rheocord (90), in order to get PMMA grafted ENR.

RESULTS AND DISCUSSION

IR spectra of the dried deep orange red mass showed a broad peak at 3450cm^{-1} thus showing the presence of terminal hydroxyl group attached to the polymer PMMA. The spectral analysis of the mass obtained after adding azo acid chloride, showed characteristic peaks which were absent in the IR spectra of pure ENR. On mixing the obtained azodicarboxylate functional Polymethyl methacrylate with 50% ENR, various characteristic bands were obtained at 3400cm^{-1} (-NH) and 1740cm^{-1} (-NH-CO-OR) besides some of the already existing bands of pure ENR, like $870\text{--}880\text{cm}^{-1}$ (assym. epoxy ring stretching), $1240\text{--}1260\text{cm}^{-1}$ (sym epoxy ring stretching) and 3040cm^{-1} being characteristic of epoxy group. The reduced intensity of the peak at 1060cm^{-1} (Cis-alkenes stretching of $>\text{C}=\text{C}<$), $1312\text{--}1315\text{cm}^{-1}$ (deformation of $=\text{CH}$ from cis alkene group $\text{CH}_3-\text{C}=\text{CH}-$) and 1130cm^{-1} (deformation of CH_3 from $>\text{C}=\text{C}<$) were used as a qualitative evidence of grafting taken place at olefin site. These results show that since the epoxidation level was kept at 50%, the grafting of azodicarboxylate functional Polymethyl methacrylate must have taken place via scheme (Figure 2), as there was no change seen in the epoxidation level after grafting.

The Figure 2 is based on the same principle which was seen in ene or electro cyclic reaction. This was confirmed by matching the I.R. spectra of ENR which showed the same intensity of epoxy peak i.e. $870\text{--}880\text{cm}^{-1}$ (assym. epoxy ring stretching) and $1240\text{--}1260\text{cm}^{-1}$ (sym epoxy ring

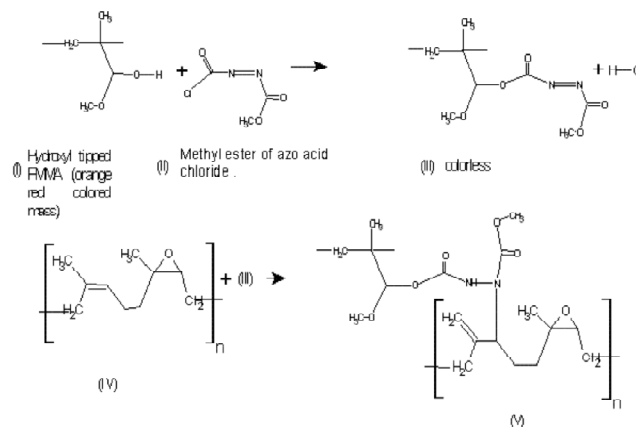


Figure 2: Scheme of Grafting of Azodicarboxylate Functionalized PMMA via "ene" Reaction

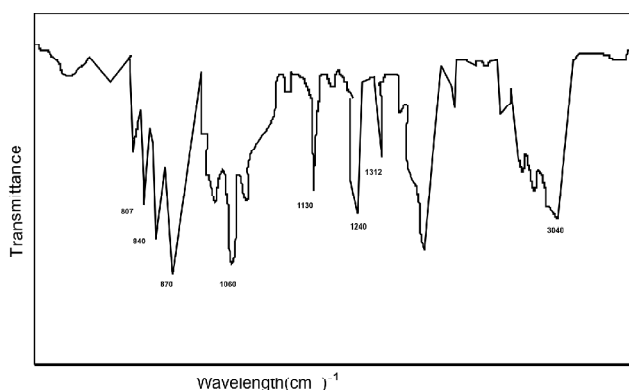


Figure 3: IR spectrum of ENR before Grafting

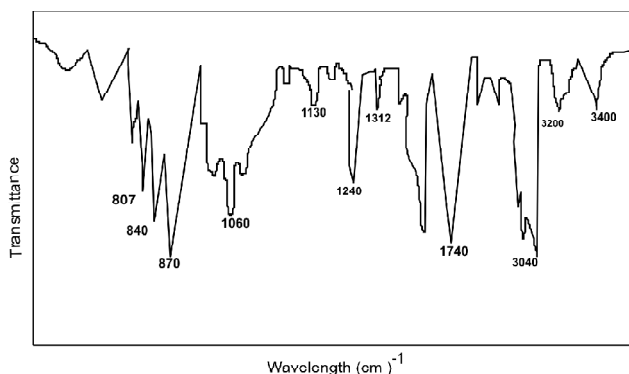


Figure 4: IR Spectrum of ENR after Grafting

stretching), before Figure 3 and after mixing Figure 4 with azodicarboxylated functionalized polymer.

CONCLUSION

The electro cyclic reaction is the most efficient route as compared to addition and substitution reactions as it does not depend on a catalyst that gets poisoned by the presence of non-rubbery content in NR. The polymer of desired molecular

weight was synthesized with a terminal hydroxyl group which was later transformed to an azo polymer, which on melt mixing with ENR gave a highly efficient grafted thermoplastic rubber without any tackiness and was harder than the NR.

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