Adhesion Studies of Tyre Cords with Rubber. I. Synthesis and Characterization of Natural Rubber Graft Copolymers

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SYNOPSIS

Glycidyl methacrylate and N-vinyl pyrrolidone have been grafted onto natural rubber at 32°C using the simultaneous cobalt-60 irradiation technique. The natural rubber samples were swollen in the monomers for 24 h and thereafter subjected to gamma irradiation. The homopolymers formed in the graft copolymerization reactions and unreacted monomer were removed by solvent extraction using acetone and methanol for glycidyl methacrylate and N-vinyl pyrrolidone monomer, respectively. The influence of total dose and monomer concentration on the graft parameters was investigated. The dependence of the rate of grafting on the monomer concentration was found to be 0.93 and 0.80 for glycidyl methacrylate and N-vinyl pyrrolidone, respectively. DSC and TGA studies of the polymers were undertaken. Grafted copolymers based on glycidyl methacrylate were relatively less thermally stable compared with ungrafted natural rubber.

INTRODUCTION

Rubber and plastic industries have experienced rapid growth recently as these polymeric materials replace many conventional materials, such as aluminium, steel, glass, and paper, in various applications. Natural and synthetic rubbers have been utilized for tyre production for several years.[1-5] Cords from polymer fibers are widely used in tyres and hence the cord/rubber adhesion is important for tyre performance and durability.

One of the major problems encountered during tyre manufacture is the poor adhesion between the tyre cords (mostly nylon, rayon, polyester, and aramid fibers) and the rubber materials that results from low chemical affinity between polar cords, such as nylon and hydrophobic rubber. To overcome this drawback, adhesion-promoting systems, such as resorcinol-formaldehyde latex and polyisocyanates, have been utilized to provide a coating on the cord surface during tyre manufacture to improve adhesion at the interface between the cord and rubber.[6-10] In general, a layer of adhesive forms an intermediate between the cord and rubber and thus two interfaces, rubber/adhesive and adhesive/cord, are introduced in place of one.[3,8]

Radiation-curable acrylates have been utilized to modify the surface of polyester cords to improve adhesion to standard rubber adhesives and thereby to rubber-based materials.[11] Several authors and establishments[12-15] have also reported improved adhesion between fibrous cords and rubber through first coating the cord with either isocyanates, diisocyanates, blocked isocyanates, or polyepoxides or ethylene ureas and then with resorcinol-formaldehyde resin. Graft copolymerization of suitable vinyl monomers onto either the tyre cords or rubber materials/substrates could be an attractive technique to enhance adhesion without drastically altering most of the original properties of these polymeric systems.

Natural rubber has been modified through grafting methods using free radical initiation, photochemical, mechanical, and irradiation processes[16-19] to impart desired properties onto these polymeric materials. Glycidyl methacrylate is a very reactive monomer since it contains both vinyl and epoxide groups. Thus, the unsaturated group could be utilized to graft copolymerize onto natural rubber while

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the epoxide ring may be opened during vulcanisation. In addition, since diamines and other chemicals are used in the formulation of rubber compound, these compounds would further crosslink the epoxide rings. The glycidyl methacrylate and N-vinyl pyrrolidone possess polar groups and these monomers when grafted onto natural rubber could improve adhesion to tyre cords. For example, glycidyl methacrylate contains epoxide rings that when opened then introduce surface $-OH$ groups that may act as reactive sites for an adhesive.

As part of the adhesion studies of tyre cords with rubber materials, we report herewith the graft copolymerization of glycidyl methacrylate and N-vinyl pyrrolidone onto natural rubber by simultaneous irradiation technique using cobalt-60 as the source of gamma rays.

EXPERIMENTAL

Natural rubber, grade RMA IV, was supplied by S.K. Industry, New Delhi. Purification was made by precipitation into methanol from benzene. Another method of purification of the rubber samples was through soxhlet extraction using methanol and later acetone for 5 d and dried in a vacuum oven for 3 d. However, since the graft copolymers were intended for tyre manufacture and preliminary investigation did not show significant differences in grafting yields between natural rubber purified by precipitation or by solvent extraction, the latter samples were utilized for the grafting investigations.

Glycidyl methacrylate (Fluka Chemicals) and N-vinyl pyrrolidone (Fluka Chemicals) were used as received.

Graft Copolymerization Procedure

Weighed samples of natural rubber were swollen in known amounts of monomer in conical flasks at room temperature for 24 h to attain equilibrium swelling of the natural rubber. Irradiation was performed at 32°C using cobalt-60 gamma chamber 900 unit supplied by Bhabha Atomic Centre, Bombay, India, with a dose rate of 40 rad/s. After a specified time of dosage, the graft copolymerisation reactions were terminated by adding a large quantity of acetone and methanol for the glycidyl methacrylate and N-vinyl pyrrolidone, respectively, to the conical flasks. The graft copolymers were then isolated by selective solvent extraction of the polymer mixture using acetone to remove poly (glycidyl methacrylate) and methanol for poly (N, vinyl pyrrolidone) ho-

mopolymers in a soxhlet apparatus for 3 d. The graft copolymers were dried in a vacuum oven at 50°C. The effects of total dose and monomer concentration on the graft parameters were investigated.
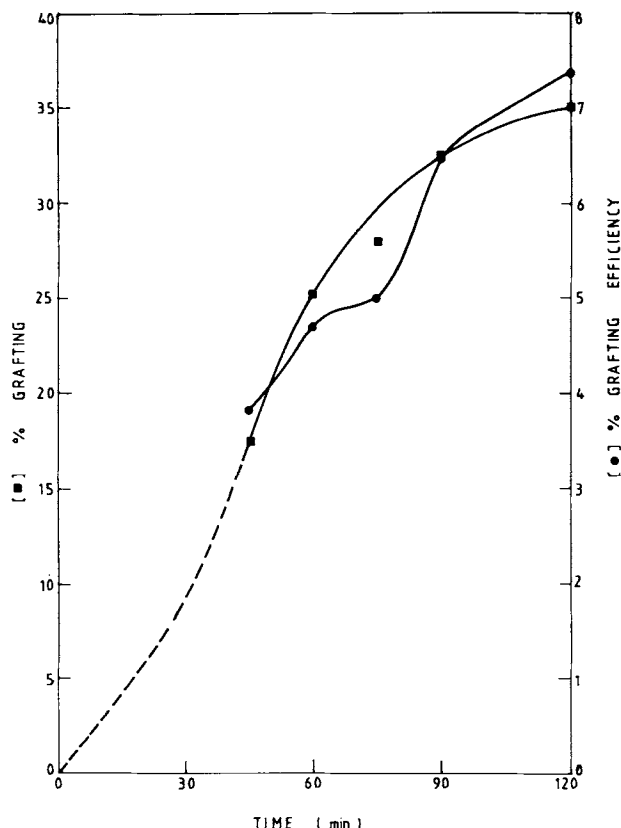
The percent grafting was defined as the ratio of the increase in mass due to grafting to the original mass of natural rubber. However, the percent grafting efficiency was the ratio of the increase in mass due to grafting to the mass of monomer used.[16]

Characterization

Thermogravimetric analysis (TGA) studies were carried out on Stanton Redcroft TG-750 thermobalance under nitrogen atmosphere at a heating rate of 10°C/min starting from room temperature to 600°C. The primary thermograms were obtained by plotting percent residual mass against temperature. Relative thermal stability of the samples were evaluated by comparing the initial decomposition temperature and temperatures at which the samples undergo different percent decomposition. Differential scanning calorimetry (DSC) was performed using a Du Pont 990 thermal analyser at a heating rate of 10°C/min under nitrogen in the temperature range of 30–160°C. The instrument was calibrated using indium as a reference material. The heat of fusion was calculated from the area under the thermogram curve of the polymeric materials.

RESULTS AND DISCUSSION

Investigations of monomer uptake by natural rubber showed that equilibrium swelling is attained within a period of 12 h. However, for the grafting experiments the rubber samples were immersed in the monomers for 24 h. The swollen natural rubber was irradiated with gamma rays from cobalt-60 source. Gamma radiation has been known to generate free radicals on polymeric backbones. In general, in simultaneous irradiation technique when polymer and monomer are subjected to radiation radicals are produced both on the polymer and monomer.[20-25] The free radicals initially produced may add to the double bonds on the unsaturated natural rubber and to the monomer and may also participate in the hydrogen abstraction reactions from the polymer backbone. The various resulting polymer macroradicals initiate chain growth reactions leading to the production of graft copolymers and homopolymers. Figures 1 and 2 show the effect of total dose on the graft parameters. Since a constant dosage rate of 40 rad/s was utilized, the total dose is proportional to
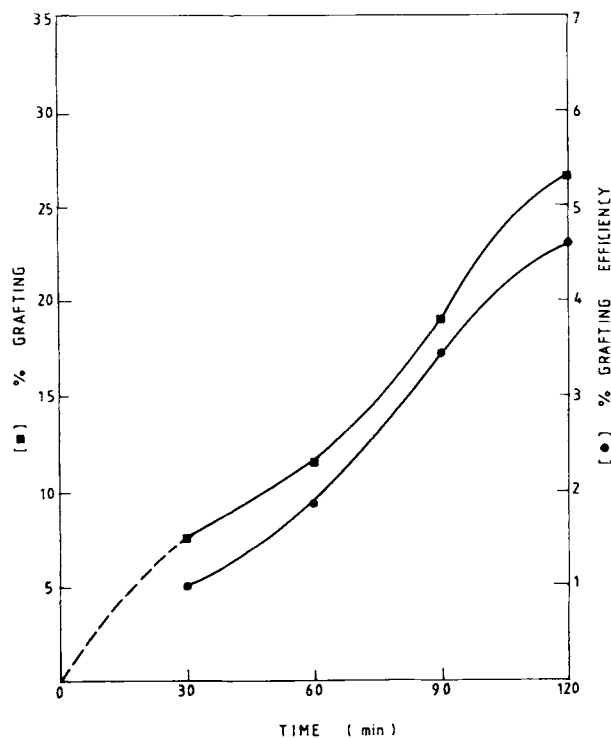
ing divided by the total mass of homopolymer formed and increase in mass dose to grafting. Since optimal grafting is required, efficiency should be defined in terms of the ability of monomer to add to the natural rubber. Homopolymerisation is undesired. Observed percent grafting efficiency increased at higher dosage time.

In simultaneous-irradiation technique, grafting reaction competes with homopolymerisation. At higher dosage time, more grafting sites are created and more monomer could diffuse easily to the grafting sites leading to increased percent grafting efficiency. The percent grafting and efficiency results show that glycidyl methacrylate produced more graft copolymers than N-vinyl pyrrolidone at a given total dose. The differences in their relative reactivity ratios and diffusibility (swellability) of the monomers into natural rubber may be responsible for these observations. The relation of percent grafting and efficiency with monomer concentration are shown in Figures 3 and 4. Grafting was performed at a temperature of 32°C using a fivefold variation in monomer concentration and total dose of 0.144 Mrad and 0.288 Mrad for glycidyl methacrylate and N-vinyl

Figure 1 Variation of ■ % grafting and ● % grafting efficiency in natural rubber—GMA system with total dose at a dose rate of 40 rad/s at 32°C using total no. of moles of GMA = 3.79 × 10⁻² mol.

the dosage time. Due to the multifunctionality and high reactivity of glycidyl methacrylate, the tendency of polymers to degrade and crosslink, and high reactivity of N-vinyl pyrrolidone leading to gel formation of the monomers at relatively high total dose, the grafting experiments were conducted at total dose below 0.3 Mrad. Our investigation showed that glycidyl methacrylate and N-vinyl pyrrollidone when grafted onto natural rubber could produce higher percent grafting but extraction of the gelled homopolymers becomes difficult. Similar observations have been reported earlier[22,24] on the grafting of vinyl monomers onto segmented polyurethanes. As expected, percent grafting increases with increased total dose (dosage time). The rate of grafting was higher initially but tends to level off at higher dosage time. This may be due to the depletion in the monomer concentration and available reactive grafting sites. Our definition of percent grafting efficiency differs from methods used by several authors[23] where efficiency was defined as mass increase due to graft-

Figure 2 Variation of ■ % grafting and ● % grafting efficiency in natural rubber.—NVP system with total dose at a dose rate of 40 rad/s at 32°C using total no. of moles of NVP = 4.71 × 10⁻² mol.
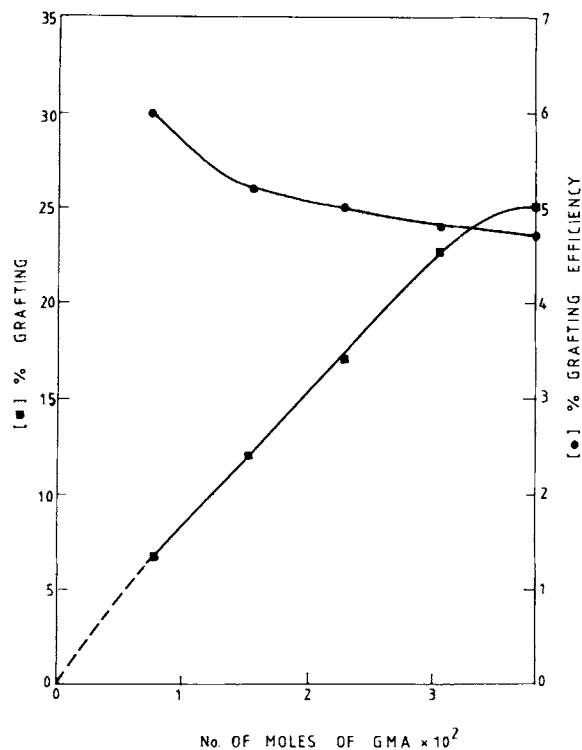
Figure 3 Variation of ■ % grafting and ● % grafting efficiency in natural rubber.—GMA system with total no. of moles using total dose = 0.144 Mrad at 32°C.
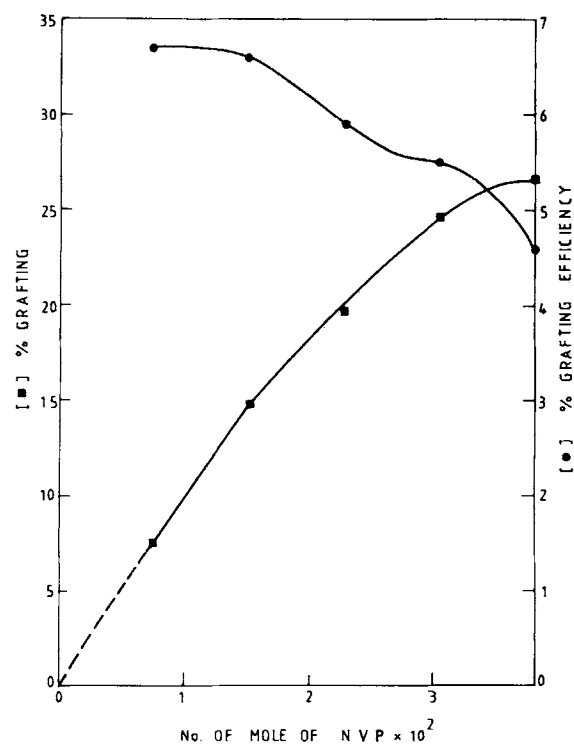
Figure 4 Variation of ■ % grafting and ● % grafting efficiency in natural rubber—NVP system with total no. of moles using total dose = 0.288 Mrad at 32°C.

pyrrolidone, respectively. There is a marked increase in percent grafting with increase in average molecular mass of the grafts at higher concentration. In addition, during grafting the monomer continuously diffuses into the polymer matrix and the ability of natural rubber macroradical to initiate grafting reaction would depend upon the availability of the monomer molecules in their vicinity. Several authors have reported similar trends for the graft copoly-

merisation of different polymeric materials.[22,23,26] The percent grafting efficiency slightly decreases with increase in monomer concentration.

The order dependence of the rate of grafting with respect to monomer concentration was obtained from the log–log plot of rate of grafting against monomer concentration. The rate of grafting has been determined by a technique utilized earlier.[26–30] Thus, the order dependence obtained was 0.93 and

Table I   Thermal Stability of the Grafted Polymers

		Temperature at Different Percent Weight Loss							
Sample	% Grafting	IDT[a]	12.5	25	37.5	50	62.5	75	87.5
A	0	298	373	381	394	402	410	420	437
B	7.5	247	353	367	384	391	399	410	436
C	19.3	220	314	346	366	378	391	406	420
D	25	238	339	365	375	388	398	414	450
E	50	215	300	334	354	370	390	409	441
PGMA	—	253	280	305	316	327	343	367	405

A; natural rubber; A–E are graft copolymers with different % grafting.
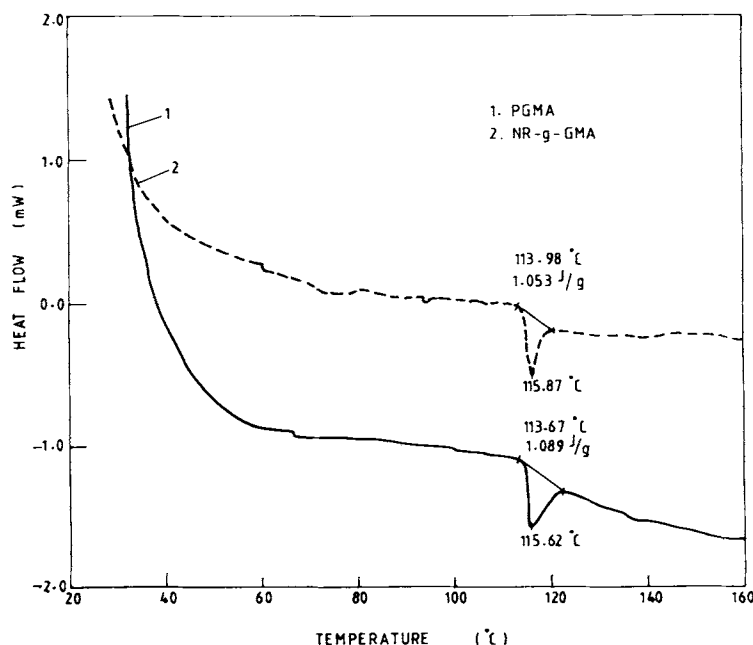[a] Initial decomposition temperature.
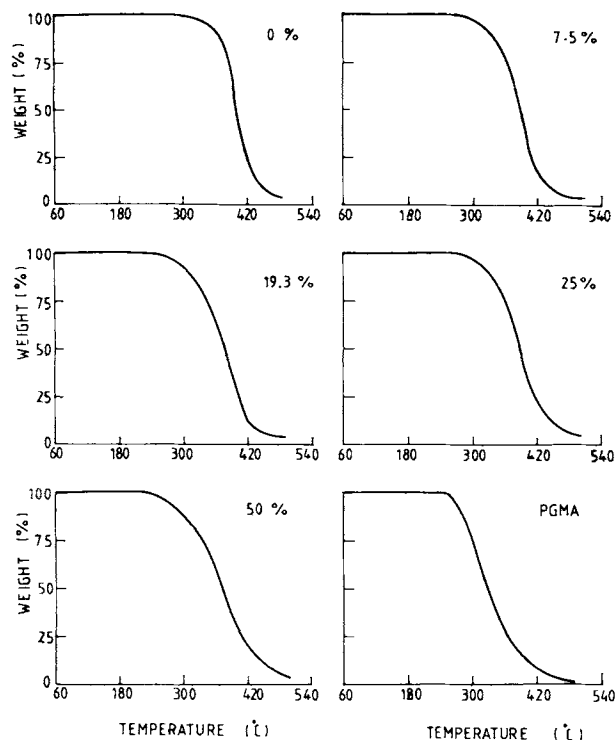
Figure 5 TGA thermograms of natural rubber, PGMA; and natural rubber grafted with GMA with various % grafting.

0.80 for glycidyl methacrylate and *N*-vinyl pyrrolidone, respectively. This rate expression is consistent with similar order dependence of grafting rate on

monomer concentration reported in the literature for some grafting copolymerization reactions.[16,31-33] This first-order dependence indicated that this grafting system proceeds with bimolecular termination reaction.[33]

In tyre manufacture, resorcinol–formaldehyde latex system (RFL) is the standard adhesive for rayon and nylon yarns. The optimal drying temperature of tyre cord dipped in RFL system varies between 155–230°C depending on time of drying (usually between 0.5–3 min). Besides, the rubber and other components of tyre are vulcanised at various temperatures (140–180°C) depending on the technology used for tyre manufacture. Therefore, thermal stability of the grafted copolymers were investigated to find their suitability for tyre manufacture. Also in the actual running of the tyre, temperature as high as 200°C may be developed due to frictional forces and hysteresis losses. Table I and Figure 5 show the thermal properties of grafted natural rubber and the original rubber. The graft copolymers were relatively less stable compared to natural rubber. Furthermore, thermal stability decreases with increase in percent grafting. This may be due to the lower thermal stability of poly(glycidyl methacrylate) (PGMA) compared to natural rubber. The thermal stability of PGMA is also shown in Table I for comparison. Sundardi et al.[34] and others[35] have shown that thermal stability of polymeric materials largely depends on the nature of monomer

Figure 6 DSC thermograms of natural rubber and natural rubber grafted with GMA (19%).

used for grafting. Though the graft copolymers were less thermally stable than natural rubber, the initial decomposition temperatures of the graft copolymers were high (above 200°C).

DSC studies (Fig. 6) were also carried out between room temperature and 160°C due to some limitations of our DSC system. Natural rubber has a glass transition temperature (T_g) of about −72°C. DSC thermograms of the graft copolymers showed no observable T_g for the PGMA branches. However, graft copolymers with 19% grafting have a melting temperature of about 115.87°C and heat of fusion of 1.053 J/g, compared to homopolymers, where PGMA melts at 115.62°C and heat of fusion of 1.089 J/g.

Adhesion tests between the graft copolymers and tyre cords are under investigation and will be the subject of further communication.

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