Surface Modification of SBR and NR by Hydrophilic Monomers (I): Effect of Structural Parameters and Inhibitors

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ABSTRACT

Radiation grafting of two hydrophilic monomers (i.e., acrylamide and acrylic acid) onto styrene-butadiene rubber (SBR) and natural rubber (NR) by the simultaneous method was studied. Attempts to graft SBR and NR in aqueous solution of acrylic acid and acrylamide lead to extensive homopolymerization. Metal-based homopolymerization inhibitors including Mohr’s salt and cupric nitrate were evaluated and found to prevent homopolymerization and significantly increase graft yield. The role of substrate structure on grafting efficiency for two hydrophilic monomers was investigated. The properties of the resulting copolymers have been studied by SEM techniques.

Key Words: SBR, NR, surface modification, grafting, γ-radiation

INTRODUCTION

Rubbers based on styrene-butadiene rubber (SBR) and natural rubber (NR), are widely used due to their good mechanical properties such as flexibility, tensile and abrasion resistance. They, however, suffer from low wettability and therefore low biocompatibility. This limitation can be removed by introducing suitable monomers using either chemical or radiation graft copolymerization initiated by high-energy radiation or UV (to introduce active sites, etc.). Because, ultraviolet radiation is of low energy, photoinitiators are generally needed to make the reaction more efficient (by reducing the activation energy) but gamma rays can be used without photosensitization.

Attempts to graft vinyl monomers onto ethylene-propylene-diene terpolymer (EPDM) using ionizing radiation failed due to extensive homopolymerization [1]. Alternative methods where inhibitors were used to reduce excessive homopolymerization lead to improved results [1]. Metallic ions such as Fe$^{3+}$, Fe$^{2+}$ and Cu$^{2+}$ are known to have an inhibitory effect on free radical polymerization [2,3].

In other reports, graft copolymerization of acrylic acid (AA) onto polytetrafluoroethylene showed that ferrous ammonium sulphate (Mohr’s salt) suppressed homopolymerization [4]. This was confirmed when homopolymerization was reduced during
grafting of acrylic acid and methacrylic acid [5]. Mohr's salt has also been found to suppress acrylic acid homopolymerization, without a marked change in the grafting rate onto polyethylene [6]. Despite some recent patents addressed on hydrophilic coating of surfaces of polymeric substrates [7,8], there are not enough information about radiation surface grafting of SBR and BR polymers.

In the present work two different biomonomers, acrylamide and acrylic acid (AAm and AA) have been grafted onto the surface of SBR and NR rubbers, using Co-60 gamma radiation to increase wettability and biocompatibility properties of these materials.

The effect of monomer concentration with two different salts on the grafting behaviour of these monomers has been studied.

**EXPERIMENTAL**

**Materials**

Styrene-butadiene rubber (SBR: 1502) was received from Bayer Co. (Germany) and natural rubber (NR-crepe) was received from Mal. Co. (Malaysia). Acrylamide, acrylic acid, cupric nitrate and Mohr’s salt were purchased from Merck, Germany and dicumyl peroxide (99% powder) was purchased from Nippon, Japan. All the chemicals were used as received.

**Vulcanized Elastomers Preparation**

The rubbers were pre-masticated using a two-roll mill (Farrel, England) at 40 rpm and 50 °C for 5 min following its mixing with 1.0 phr dicumyl peroxide at the same condition. The compounded rubbers were then moulded into 3 mm sheets, using a Collin compression press at 165 °C for 14 min. Vulcanized sheets were cut by using a handy punch (CEAST) on base of ASTM D638 T.4. Then samples were washed with distilled water and were dried prior to the grafting experiments.

**Grafting Procedure**

Graft copolymerization was carried out by the simultaneous method. Dried, tarred rubber samples were placed in the monomer-solvent mixtures in the glass tube containers and stainless steel thin rod was used to maintain submersion.

Dissolved oxygen was replaced by nitrogen; the tubes were sealed and irradiated at room temperature in the Co-60 source facility at Atomic Energy Organization of Iran (AEOI). Samples were irradiated at 4.5–6 kGy of total dose in all experiments.

After irradiation, samples were removed from the grafting solution and soaked for three days in a suitable solvent (acetone-water mixture for AAm, and DMF for AA) to remove homopolymer. The final solution was checked by IR spectroscopy examination to ensure having a solution free from homopolymer.

During that time, the solvent was changed several times. Samples were washed with distilled water and then dried in an oven over night. The graft yield was calculated as the weight of graft per initial film area using the following relation:

\[
\text{Graft yield} = \frac{W_d - W_s}{S}
\]

Where:

- \( W_d \): weight of the grafted, vacuum oven dried sample;
- \( W_s \): weight of unmodified sample; \( S \): initial sample surface area.

**Scanning Electron Microscopy**

For SEM analysis, samples were immersed in liquid nitrogen for several minutes and they were broken with tweezers. Specimens were then sputter-coated with gold. Surface topography, depth and homogeneity of the grafted polymer were studied using a Hitachi, HHS-2R (Japan) SEM.

**RESULTS AND DISCUSSION**

**Effect of Structural Parameters of SBR and NR Rubbers on Grafting Yield**

The results of grafting yield obtained for SBR and NR rubbers are shown in Tables 1-3. The results indicated that NR grafted more than SBR in all experiments, except when grafting yield is not considerable. This can be attributed to steric hindrance effect of side groups of
Table 1. The effect of monomer concentration on radiation grafting of monomer AA onto NR and SBR (with two different additives).

<table>
<thead>
<tr>
<th>Monomer concentration (wt %)</th>
<th>Additives</th>
<th>Grafting yield (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NR</td>
</tr>
<tr>
<td>20</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>negligible</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td>negligible</td>
</tr>
<tr>
<td>40</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>negligible</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td>4.91</td>
</tr>
<tr>
<td>60</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>negligible</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td>8.02</td>
</tr>
<tr>
<td>70</td>
<td>--</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>8.02</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td></td>
</tr>
</tbody>
</table>

SBR rather than NR. Therefore, produced radicals are able to attack easier to NR rather than to SBR.

Although, due to shielding effect of aryl groups in SBR backbone, separation of hydrogen atoms in benzylic situation was hardly accomplished [9], because of high level of consumed energy, production of these radicals and aryl groups of SBR can make resonance with generated radicals in benzylic rings of polymeric backbone.

Therefore, for radiation grafting of SBR, produced radicals in benzylic situation are more stable than produced radicals in NR. Consequently, the producing radicals in solution were attracted more slowly by SBR. This resulted in a higher grafting yield of NR to SBR.

Effect of Reaction Variable on the Grafting Yield

Role of Inhibitors

Homopolymerization can cause serious problems in solution grafting using the mutual method. As shown in Tables 1 and 2, in the absence of inhibitors and with water as solvent, the graft yield decreases to zero level by homopolymerization. This is due to the high G-value of these monomers (compared with the

Table 2. The effect of monomer concentration on radiation grafting of monomer AA onto NR and SBR (with two different additives).

<table>
<thead>
<tr>
<th>AA monomer concentration (wt %)</th>
<th>Additives</th>
<th>Grafting yield (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NR</td>
</tr>
<tr>
<td>20</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td>1.55</td>
</tr>
<tr>
<td>40</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td>20.7</td>
</tr>
<tr>
<td>60</td>
<td>--</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>cupric nitrate</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>Mohr's salt</td>
<td>36.2</td>
</tr>
</tbody>
</table>
Table 3. The effect of various additives on homopolymerization, during radiation grafting of monomers AA and AAm onto SBR and NR.

<table>
<thead>
<tr>
<th>Monomer concentration (wt %)</th>
<th>Characteristics</th>
<th>No additives</th>
<th>Mohr's salt (0.01 M)</th>
<th>Cupric nitrate (0.01 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>Liquid formed around sample</td>
<td>form</td>
<td>soft gel</td>
<td>viscous liquid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>colour</td>
<td>clear</td>
<td>red</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>form</td>
<td>gel</td>
<td>viscous liquid</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>clear</td>
<td>clear</td>
<td>viscous liquid</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>form</td>
<td>hard solid</td>
<td>viscous liquid</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>colour</td>
<td>clear</td>
<td>viscous liquid</td>
</tr>
<tr>
<td>AAm</td>
<td>Liquid formed around sample</td>
<td>form</td>
<td>soft gel</td>
<td>viscous liquid</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>colour</td>
<td>clear</td>
<td>red</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>form</td>
<td>gel</td>
<td>viscous liquid</td>
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<td></td>
<td>clear</td>
<td>clear</td>
<td>viscous liquid</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>form</td>
<td>hard solid</td>
<td>viscous liquid</td>
</tr>
</tbody>
</table>

G-value of SBR and NR rubbers). This is also related to high dose rate used in the experiments, as it is known that increasing the dose rate would increase the homopolymerization strongly [10].

Metallic ions such as Fe$^{3+}$, Fe$^{2+}$ and Cu$^{2+}$ are known to inhibit free radical polymerization [2,3]. Tables 1 and 2 show the results obtained from the radiation grafting of AAm and AA onto vulcanized SBR and NR in aqueous solutions of either cupric nitrate or Mohr's salt inhibitors. Molal concentration (0.01 m) of these materials was selected, since these amounts have previously been reported to be the most effective on decreasing the homopolymerization of acrylic monomers [11].

Cupric nitrate not only strongly reduces homopolymerization, but also affects the grafting yield of monomer AA onto SBR and NR. The grafting yield increases with increasing monomer concentration. The results are shown in Figure 1 and Figure 2.

Figure 1. Comparison of grafting yield of monomer AA (additive: 0.01 M Cu(NO$_3$)$_2$) onto SBR and NR.

Figure 2. Comparison of grafting yield of monomer AA (additive: 0.01 M Mohr's salt) onto SBR and NR.
polymerization and prevents high gel formation of AA but also has a strongly increasing effect on the graft copolymerization for AA monomer. On the other hand, in the case of AAm, cupric nitrate not only decreases the homopolymerization, but also prevents the formation of graft copolymerization. In other words, even at high AAm concentration (70%) using the cupric nitrate results in a small amount of graft copolymerization (Figures 1–4).

In comparison to cupric nitrate, although in the presence of Mohr's salt homopolymerization yield of both AAm and AA is higher, the higher graft yield was however, achieved for both monomers.

Role of Monomer Structure
Although graft yields for both monomers follow the same trends, the order of reactivity is AA>AAm. The factors influencing graft yield may vary from one monomer to another. Thus, in order to clarify the mechanism, it is necessary to study homopolymerization of each individual monomer. In the case of AAm, the homopolymerization in aqueous solution proceeds in a homogeneous media and the system frequently leads to unusually high molecular weight polymer.

The rate of conversion of AAm homopolymer in aqueous solution has been found to be one of the fastest polymerization. This is attributed to the ratio of $k_p/k_t^{1/2}$ (where $k_p$ is the propagation rate constant and $k_t$ is the termination rate constant) being exceptionally high for AAm free radical polymerization [12]. With the low rate of termination, the build-up of high molecular weight polymers is exceptional. The termination reaction is considered limited by the restricted movement of radicals in crystal lattice [12]. Furthermore, AAm homopolymer has a "pop-corn" structure, resulting from cross-linking via imide linkage [12].

Homopolymers that are partially imidized exhibit lower solubility in water [12]. The intermolecular imide represents a thoroughly cross-linked polymer which is quite insoluble, while the intramolecular imide may show only partial insolubility [12]. Thus it can now be understood why grafting yields are low at low monomer concentration, as cross-linked AAm homopolymer formation is favoured rather than the grafted chains. Although homopolymerization is relatively slow, it can still dominate the grafting reaction by consuming the monomer. A higher monomer concentration, however, increases the rate of homopolymerization, it also strongly enhances grafting yield due to higher diffusion into the active centers in the substrate.

![Figure 3. Comparison of grafting yield of monomer AAm (additive: 0.01 M Mohr's salt) onto SBR and NR.](image1)

![Figure 4. Comparison of grafting yield of monomer AAm (additive: 0.01 M Cu(NO₃)₂) onto SBR and NR.](image2)
El-assy et al. [13] have given similar explanation for radiation grafting of AAm onto fluoropolymers. As shown in Figures 1–4, the grafting yield is higher for AA than for AAm, because AA has a lower rate of homopolymerization.

The difference in the reactivity of AAm and AA towards homopolymerization can be attributed to differences in side groups, viscosities and the states of aggregation of the monomer (AAm monomer is
crystalline while AA is not), so that each of these parameters has its own contribution in determining the kinetics of homopolymerization.

**Morphology**

The surface topography of the grafted NR and SBR were studied by use of scanning electron microscopy. As shown in Figures 5–8, at low magnification, the original untreated samples have a smooth surface. The surface of grafted substrate, however, become rougher, increasing progressively with increase in the graft yields for both monomers. Thus SEM provides evidence for the grafting of AA and AAm onto the surface of SBR and NR, but there is no evidence of bulk grafting of these monomers into substrates.

**CONCLUSION**

Attempts to graft SBR and NR in aqueous solution of AA and AAm lead to extensive homopolymerization. Although metal based homopolymerization inhibitors including Mohr’s salt and cupric nitrate can prevent homopolymerization and significantly increase graft yield. In the case of AAm, cupric nitrate prevented not only the homopolymerization but also the graft copolymerization. It was also found that the graft efficiency of NR and SBR increases with decreasing the steric hindrance.

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