Radiation Graft Modification of N-Vinyl-2-Pyrrolidone onto Ethylene-Propylene Rubber

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ABSTRACT
Radiation grafting of N-vinyl-2-pyrrolidone (NVP) onto ethylene-propylene elastomers (EPM rubbers) by the simultaneous method is studied. The present work centers upon gamma radiation induced grafting of N-vinyl-2-pyrrolidone (NVP) onto four different EPM rubbers. Metal based homopolymerization inhibitors including Mohr's salt, Cu(NO₃)₂ and FeSO₄ are evaluated and found to prevent homopolymerization and significantly increase graft yield. Lithium nitrate is also evaluated as a graft promoter. The role of the type of EPM rubber on grafting efficiency for a variety of monomers is investigated, to optimize grafting conditions for each EPM rubber and monomer. The effect of multifunctional acrylic additives including TMPTA, PEGDA and PGTA is also studied. The structures of the resulting grafted EPM rubber are studied by SEM.

Key Words
additives, radiation, grafting, N-vinyl-2-pyrrolidone, ethylene-propylene

INTRODUCTION
Rubbers based on ethylene-propylene are widely used due to their good mechanical properties, highly saturated structure and associated resistance to aging and ozone deterioration. While they strongly resist acids and alkalis, they suffer from low wettability and low biocompatibility. This limitation can be reduced by introducing suitable monomers to polyolefins using either chemical or radiation graft copolymerization, initiated by high energy radiation and UV. Graft modification of EPM or EPDM rubber has been improved by a variety of techniques in free radical polymerization [1], gamma irradiation [2], peroxidation [3], anionic polymerization [4] and mechanoradical or co-mastication methods [5]. However, because of fast homopolymer formation and/or substrate degradation, most of the previous methods have limited application. Attempts to graft vinyl monomers onto EPDM using ionizing radiation failed due to extensive...
homopolymerization. Alternative methods where inhibitors were used to reduce excessive homopolymerization led to improved results [6]. Metallic ions such as Fe$^{3+}$, Fe$^{2+}$ and Cu$^{2+}$ are known to have an inhibitory effect on free radical polymerization [7,8].

Additives have been shown to increase the grafting yields for a variety of monomers onto backbone polymers using UV radiation [9,10]. The use of di- and polyfunctional monomers, such as TMPTA and DVB, as additives for gamma and UV grafting have been investigated [11,12]. The addition of mineral acid has been claimed to enhance grafting yield under certain conditions. Addition of a small amount of mineral or organic acid into monomer solution as an additive enhances the grafting yield of styrene onto PE [13].

In the present work attempts to graft a biomonomer (NVP) onto the surface of different EPM rubbers have been made using Co$^{60}$ gamma radiation. The effects of monomer concentration and different salts on the graft behaviour of these monomers have been studied. The effect of changing EPM rubber structure, in particular the ratio of the constituent monomers, has also been investigated. The depth and homogeneity of the grafted polymer were measured by selective staining methods, with cross-sections and new surfaces being subsequently studied by scanning electron microscopy (SEM).

**EXPERIMENTAL**

**Materials**
The properties of the raw EPM rubber (Exxon Chemical Company) used are shown in Table 1. NVP (GAF Chemical Corp., N.J., U.S.A.) was used as received. The monomer was stored below 5 °C to prevent homopolymerization. Cupric nitrate, lithium nitrate and ferrous sulphate (Ajax Chemical, Australia) were general purpose reagent grades and used as received. Water was twice distilled. Mohr's salt (ammonium ferrous sulphate) (May & Baker Ltd, England) and dicumyl peroxide-40% powder/ granules with chalk- (Proxid-Chemic GmbH-Interox) were used as received. The MFAs used were trimethylol propane-triacrylate (TMPTA), polyethylene glycol-diacrylate (PEGDA) and propylene glycol-triacrylate (PGTA) (Anchor Chemical, Australia) were used as received.

**Vulcanized Elastomer Preparation**
Each grade ethylene-propylene rubber was pre-masticated in a "Haake 600" internal mixer at 100 °C for 5 minutes using "Banbury" rotors at 60 rpm, prior to mixing with 3.0 phr dicumyl peroxide on a two-roll mill at 70 °C. The compounded rubber was then moulded into 2.0 mm thick sheets, using a "Stacey" compression press at 150 °C for 10 minutes, in general accordance with ASTM D 3182-89. Vulcanized sheets were cut into strips (15X60 mm) then Soxhlet extracted with a mixture of toluene-methanol (50:51) for 36 hours. Samples were then dried to remove residual organic solvent, washed with distilled water and again dried prior to the grafting experiments.

**Grafting Procedure**
Graft polymerization was carried out by the simultaneous method. Dried, tared EPM samples

<table>
<thead>
<tr>
<th>Table 1. Types of EPM rubber used.</th>
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<tbody>
<tr>
<td>EPM Type</td>
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<tr>
<td>-----------</td>
</tr>
<tr>
<td>Vistalon 404</td>
</tr>
<tr>
<td>Vistalon 504</td>
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<tr>
<td>Vistalon 805</td>
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<tr>
<td>Vistalon 808</td>
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(in duplicate) were placed in the monomer-solvent mixtures in glass tube containers and nickel-chrome springs were 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 the Australian Nuclear Science and Technology Organization (ANSTO). Samples were irradiated at 0.4 kGy/hr to a 7.5 kGy total dose in all experiments.

After irradiation, samples were removed from the grafting solution and soaked for three days in a (50:50 v/v) acetone-water mixture to remove homopolymer. During that time, the solvent was changed several times. Adhering bulk polymer (if any) was removed by vigorous rubbing with a sponge soaked in acetone-water. The graft yield was calculated as the increase in weight per initial film area since available evidence indicated that predominantly surface grafting was being achieved. SEM analysis of modified substrates shows that grafting is predominantly at the surface.

**Scanning Electron Microscopy**

Small pieces (typically 4 mm$^2$ cross-sections), were immersed in 2.5% eosin in a 3:1 (v/v) water-methanol solution for 24 hours a 2% aqueous phosphotungstic acid (PTA) solution for 36 hours or 2.5% aqueous mercurochrome solution for 48 hours. After staining, samples were washed in distilled water for 4 hours to remove excess stain, and then dried in an oven. Prior to examination the coloured samples were immersed in liquid nitrogen for several minutes and broken with tweezers. Specimens were then sputter-coated with gold. Surface topography, depth and homogeneity of the grafted polymer were studied using a "SCAN-360" (Cambridge) scanning electron microscope.

**RESULTS AND DISCUSSION**

**Effect of Structural Parameters of EPM Rubber on Grafting Yield**

The results of grafting yield obtained for different EPM rubber grades are shown in Figure 1. As shown in Table 1, the ethylene content of these rubbers increases in the order Vistalon 808 > Vistalon 504 > Vistalon 404, while their molecular weights are similar. The grafting efficiency of these rubbers are in the order as: Vistalon 808 > Vistalon 504 > Vistalon 404, indicating that increasing the ethylene content increases the grafting yield.

The results also show that Vistalon 808 seems to graft more readily than Vistalon 805 (with the same ethylene content, but higher molecular weight (Table 1)). This indicates that the ability of the EPM rubber to produce active sites for grafting increases with increasing molecular weight.

The highest graft yields could be achieved when Vistalon 808 (highest ethylene content and highest molecular weight) was used. In contrast, the graft yields of all monomers onto Vistalon 404 (with the lowest ethylene content and the lowest molecular weight) were very low. The same trend has been reported by Kathab and co-workers [6] in grafting onto EPDM rubbers. These authors have attributed this to the steric hindrance effect of side groups of pure polypropylene.

For EPM rubber it has been shown [14] that
the rate of radiation crosslinking of the rubber is also enhanced when it has a higher molecular weight and higher ethylene content. Gaylord and co-workers [15], suggested that under the effect of high energy radiation, propylene crosslinks less and undergoes chain scission more than polyethylene.

It has also been shown [16] that the yield of gamma grafting of vinyl monomers onto polyethylene (PE) is slightly greater than polypropylene (PP), and under the same experimental conditions the grafting degree of the different polymers follows [17,18] the order:

\[ \text{PE} = \text{EPM} \gg \text{PP} \]

The simplest explanation of this behaviour is that both secondary and tertiary macroradicals are expected from hydrogen abstraction on the polymeric substrate promoted by gamma rays. Their relative concentration depends on their stability (tertiary > secondary) and population (secondary > tertiary) [19]. Therefore, for radiation grafting of EPM rubber, although the radicals produced in polypropylene are more stable than those of polyethylene, the higher G-value of radicals produced by polyethylene will result in a higher grafting yield of EPM rubber with higher ethylene content. The G-values of radicals produced by PP are reported to be 0.26 while for PE it is 1.9 [20].

Effect of Reaction Variables on the Grafting Yield
The extent of graft copolymerization of the monomer was examined as a function of monomer concentration. As shown in Figure 1, grafting yield increases with increasing monomer content up to maximum. This optimal monomer concentration occurs at about 80 wt\%, regardless of which EPM rubber is used and corresponds to a Trommsdorff peak in grafting. A further increase in monomer concentration, however, results in a decrease in graft yield.

Solution polymerization of NVP at high concentrations leads to gel separation [21], not because of crosslinking or high molecular weight homopolymer formation, but because poly(NVP) is not soluble in certain NVP-water mixtures. Thus, gel produced in the polymerization can subsequently be readily dispersed in excess water [21]. Also, the gradual addition of water to a solution of poly (NVP) in NVP causes gel separation only at a monomer concentration ranging from 60-90\%, attributed to complex formation between water and NVP, resulting in a species which is more readily attacked by free radicals. Here, addition of water to the reaction will increase the rate of homopolymerization until all the NVP is converted into complex, where a maximum rate of homopolymerization will be observed. Further addition of water simply dilutes the complex and so the homopolymerization rate is reduced (Fig. 2).

Comparing the results discussed above (Fig. 2) with those obtained for the graft copolymerization (Fig. 1) indicates that the extent of both homopolymerization and grafting reactions of NVP are governed by parameters involving the solvation of the monomer forming complex species as shown:

\[ R_{\text{homopolymer}} \propto [\text{complex}] \]

Role of Inhibitors
Homopolymerization can cause serious problems in solution grafting using the mutual method. As shown previously, in the absence of inhibitors and with water as solvent, the graft yield was strongly

![Graph showing initial polymerization rate against NVP concentration in water, T=50 °C, AIBN: mol dm⁻³](image-url)
limited by homopolymerization. This is due to the high $G$-value of these monomers compared with the low $G$-value of EPM rubber.

Metallic ions such as $\text{Cu}^{2+}$, $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ are known to inhibit free radical polymerization [8,22]. Table 2 shows the results obtained from the radiation grafting of NVP onto vulcanized Vistalon 808 in aqueous solutions of either cupric nitrate, ferrous sulphate or Mohr's salt inhibitors. Without the presence of inhibitor, the grafting solution becomes either gelled or extremely viscous under the experimental conditions used, thus rendering recovery of grafted samples difficult at the completion of the reaction.

For cupric nitrate, only 0.005M and 0.1M concentration were selected, since these amounts have previously been reported to be the most effective for NVP [22].

Although both Mohr's salt (0.05 M) and $\text{Cu}^{2+}$ (0.005 M) increased the graft yield of NVP, it was found that $\text{Cu}^{2+}$ is more effective than Mohr's salt in depressing the homopolymerization of this monomer. $\text{Fe}^{2+}$ was found to have a similar inhibiting effect on both homopolymerization and grafting copolymerization reactions (Table 2).

The inhibitory effect in radiation grafting of vinyl monomers has been attributed to the transfer of an electron from the propagating chain into the incomplete d-shell of the metal ions [8]. In this regard, Garnett [17] has proposed that the inhibiting salt is partitioned predominantly in the more polar bulk solution rather than the grafting solution absorbed within the polymer when the backbone polymer is nonpolar, therefore, homopolymerization is reduced and more monomer will be available for absorption in the graft reaction. It was explained that low salt concentrations in the nonpolar backbone polymer lead to increased graft yields, since absorbed monomer radicals are not scavenged by salt, while with polar backbone polymer high concentrations of salt would be present in both solution and backbone polymer leading to lower grafting yields.

From the above, the nature of the salt can play an important role in the enhancement of the grafting reaction. It must not only be soluble in the reaction media but also be capable of chain radical complex formation. For instance, the difference in the effectiveness of $\text{Cu}^{2+}$ to that of $\text{Fe}^{2+}$ and Mohr's salt in NVP has been attributed to the higher electron affinity of $\text{Cu}^{2+}$ [6].

However, the results presented in Table 2 suggest that the electron affinity of the salts is not the only parameter which controls their inhibiting effect. The nature of the monomer can also influence salt effectiveness, with the rate of NVP homopolymerization being strongly affected by the complex formed between water and NVP monomer. This means that although Mohr's salt can affect chain radical complex formation, it may also co-ordinate with NVP to reduce the complex species formed between monomer and water which will, in turn, decrease the monomer reactivity. This may be the reason why grafting yields cannot be increased by $\text{Fe}^{2+}$ salts.

**Lithium Salt**

Specific inorganic salts such as lithium nitrate have been used as well as mineral acids to increase the ionic strength of the grafting solution and enhance graft yields of vinyl monomers onto polyolefins [10]. To study the effect of lithium salts, an

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Additives</th>
<th>Graft Yield (mg/cm²)</th>
<th>Liquid Formed Around Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVP</td>
<td>No additive</td>
<td>0.24</td>
<td>Highly viscous liquid</td>
</tr>
<tr>
<td></td>
<td>$\text{Cu(NO}_3\text{)}_2$, 0.005M</td>
<td>3.70</td>
<td>Solution</td>
</tr>
<tr>
<td></td>
<td>$\text{Cu(NO}_3\text{)}_2$, 1.0M</td>
<td>0.0</td>
<td>Solution</td>
</tr>
<tr>
<td></td>
<td>$\text{FeSO}_4$, 0.01M</td>
<td>0.1</td>
<td>Low viscous liquid</td>
</tr>
<tr>
<td></td>
<td>Mohr's Salt, 0.05M</td>
<td>0.59</td>
<td>Highly viscous liquid</td>
</tr>
</tbody>
</table>

| 20 wt% | | | |

| 20 wt% | | | |

Table 2. Effect of various salts on the radiation grafting of (NVP) onto EPM rubber.

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Fig. 3. Comparison of EPM types, monomer concentrations and additives, by the effects on radiation grafting of (NVP) onto EPM rubber. (Additive = 0.2M LiNO₃). Dose rate = 0.4 kGy/hr and total dose = 7.5 kGy.

aqueous (0.2M) solution of lithium nitrate was used for the graft copolymerization of NVP.

The results shown in Figure 3 show that in the absence of inhibitors, Li⁺ can significantly suppress homopolymerization and increase grafting for the monomer. This can be seen when these data are compared with the corresponding controls (no Li⁺) in Figure 1 and Table 3. The increase in grafting yield has been reported to be due to monomer partitioning [10]. The effect is complicated and other processes, such as radiolytically produced hydrogen atoms, will make some contribution; on the basis of current evidence [23] this will be small. When homopolymer inhibitors are present, however, the lithium salt does not affect the reaction, presumably due to the fact that the inhibiting salt which is polar itself does not markedly increase the polarity of the system which is further complicated by the polarity of the monomers [9,23].

Multifunctional Acrylates

The effectiveness of three MFAs' additive amounts (1% v/v) were examined in both the absence and presence of inhibitors (Table 4). The MFAs used were trimethylol propane-triacrylate (TMPTA), polyethylene glycol-diacylate (PEGDA) and propylene glycol-triacrylate (PGTA), none of which is water soluble.

In both the absence and presence of the inhibitors, addition of MFAs was found to have a significant effect on increasing the graft yields of the monomers onto the substrate (Figures 3-6).

The mechanism of each MFA's effect on enhancement of graft yield has previously been explained as the occurrence of branching of the growing grafted substrate chains when one end of the MFA, (e.g., TMPTA) immobilized during grafting, is bonded to the growing chain. The other end is unsaturated and free to initiate new chain growth via scavenging radicals. The new branched substrate chain may eventually terminate or crosslink by reacting with a free radical or an immobilized MFA radical. Grafting is thus

Table 3. The effects of monomer structure concentration on the radiation grafting of (NVP) onto EPM rubber (Vistalon 808).

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Monomer Concentration</th>
<th>20% 40% 80% 100%</th>
<th>20% 40% 80% 100%</th>
<th>20% 40% 80% 100%</th>
<th>20% 40% 80% 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVP</td>
<td>without inhibitors</td>
<td>0.2 0.5 2.8 0.9</td>
<td>without inhibitors, with lithium nitrate</td>
<td>0.9 1.1 3.3 1.5</td>
<td>with inhibitors*</td>
</tr>
<tr>
<td></td>
<td>with inhibitors and lithium nitrate</td>
<td>1.2 2.8 24.5 17.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solvent = water

* 0.005M Cu(NO₃)₂ for NVP

Table 4. The effects of various additives upon homopolymerization during radiation grafting of (NVP) onto EPM rubber (without inhibitor).

<table>
<thead>
<tr>
<th>Additives</th>
<th>NVP (wt%)</th>
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<th></th>
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<tbody>
<tr>
<td></td>
<td>20%</td>
<td>40%</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid Formed Around Sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Soft gel</td>
<td>Clear gel</td>
<td>Hard gel</td>
<td></td>
</tr>
<tr>
<td>LiNO₃</td>
<td>Highly viscous liquid</td>
<td>Clear gel</td>
<td>Hard gel</td>
<td></td>
</tr>
<tr>
<td>Water + TMPTA</td>
<td>White gel</td>
<td>Hazy gel</td>
<td>Hard gel</td>
<td></td>
</tr>
<tr>
<td>LiNO₃ + TMPTA</td>
<td>Viscous liquid</td>
<td>Hazy gel</td>
<td>Hard gel</td>
<td></td>
</tr>
<tr>
<td>Water + PEGDA</td>
<td>Soft hazy gel</td>
<td>White hard gel</td>
<td>Hard gel</td>
<td></td>
</tr>
<tr>
<td>LiNO₃ + PEGDA</td>
<td>Viscous liquid</td>
<td>Hard hazy gel</td>
<td>Hard gel</td>
<td></td>
</tr>
<tr>
<td>Water + PGTA</td>
<td>Soft clear gel</td>
<td>Clear gel</td>
<td>Hard clear gel</td>
<td></td>
</tr>
<tr>
<td>LiNO₃ + PGTA</td>
<td>Soft clear gel</td>
<td>Clear gel</td>
<td>Hard clear gel</td>
<td></td>
</tr>
</tbody>
</table>

reflect the higher hydrocarbon functionality of the TMPTA and PGTA, leading to higher absorption of monomer into the backbone polymer (i.e., increased partitioning) resulting in enhanced reactivity [24].

**Morphology**

A cross-section of grafted EPM rubber was studied by use of SEM; in the example, Figures 5a and 5b, the darker region of the heavy metal treated sample represents the unstained substrate. At low magnification (50X) the original untreated samples have a smooth surface, but that of grafted substrates, however, become rougher, increasing progressively with increase in graft yields. It can be seen from Figure 6 that particles of poly(NVP) are embedded into the matrix of each substrate, lumps developing in the surface as grafting proceeds. It is apparent that for the period where the graft level increases with monomer concentrations, lumps gradually enlarge. Thus, SEM provides evidence for the grafting of NVP onto the surface of EPM rubber but there is no evidence of bulk grafting of these monomers into substrates.

**CONCLUSION**

The graft efficiency of EPM rubber increases with
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Fig. 5. SEM cross-section micrographs of EPM substrate grafted with NVP: (a) monomer concentration = 20%, graft yield = 3.70; (b) monomer concentration = 80%, graft yield = 27.5.

Increasing the ethylene content and molecular weight of the rubber while attempts to graft EPM rubber in aqueous solution of NVP lead to extensive homopolymerization.

Metal-based homopolymerization inhibitors including Mohr’s salt, Cu(NO$_3$)$_2$ and FeSO$_4$ can prevent homopolymerization and significantly increase graft yield.

Addition of polyfunctional additives such as multifunctional acrylates can significantly enhance the grafting yield of the polar monomer onto EPM rubber.
ACKNOWLEDGEMENTS

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