CHAPTER 5

MALEIC ANHYDRIDE GRAFTING OF POLYETHYLENES
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5.1. INTRODUCTION

Grafting in an extruder reactor involves reaction of a molten polymer with a monomer or mixture of monomers capable of forming grafts to the polymer backbone.\textsuperscript{1-5} Polyolefines have been modified with maleic anhydride (MA) for improving various properties such as compatibility. The modification is usually carried out in the melt and in the presence of free radical initiators like peroxides.\textsuperscript{6-10} Under such conditions the maleic groups are introduced to polymer macromolecules. Grafting is usually accompanied by the formation of crosslinks and hence improves the mechanical properties of the polyolefines and their blends.\textsuperscript{11-15}

The crosslinking of polyethylene molecules by main bonds into three dimensional networks leads to significant improvements of the material properties, which greatly enlarge the application fields of these low cost polymers. Compared with the untreated material, crosslinked polyethylene shows enhanced impact strength, better thermal performance and higher chemical resistance. Further, considerable improvements can be found in the resistance to wear, creep and ageing.\textsuperscript{16-20} Also, crosslinked products can incorporate large amounts of fillers without remarkable deterioration of the material properties.
The use of polymer blends to achieve property and price advantages has been a rapidly expanding field of research. Developing a blend with satisfactory overall physicomechanical behaviour will depend on the ability to control interfacial tension to generate a small phase size and strong interfacial adhesion to transmit applied force effectively between the component phases.\textsuperscript{21-35}

The process of reactive processing permits the preparation of functionalized polymers, including copolymers containing carboxyl groups which can not be made directly by the polymerisation process and opens up significant possibilities for the creation of new speciality and engineering plastics.\textsuperscript{36-50}

The reaction of a molten saturated polymer with maleic anhydride in the presence of a radical catalyst, under the appropriate conditions, yields a polymer containing appended individual succinic anhydride and maleic anhydride units, but accompanied by side reactions, including crosslinking and / or degradation. It has been proposed by Gaylord and Mehta that the additional crosslinking of the ethylene copolymer which occurs during reaction with MA, is due to the generation of additional radical sites on the polymer as a result of hydrogen abstraction by the excited MA. These additional sites can couple and / or add excited MA.

The proposed mechanism is shown in the following scheme.
Suggested mechanism for MA grafting of polyethylene
The extruder is an ideal reactor for polymer modification in that it serves as a pressure vessel equipped for intensive mixing, shear, control of temperature, control of residence time, venting of by-product and unreacted monomer as well as the transport of molten polymer through the various sections of the extruder, each serving as a mini-reactor and removal therefrom. Further, reactive extrusion is economically attractive since the extrusion and grafting are done in a single stage. However care should be taken to optimise the reaction conditions since reaction has to be completed along with the shaping. In this study the optimum parameters for maleic anhydride modification of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and their blend have been determined on a torque rheometer and these parameters have been utilised in actual reactive extrusion.

5.2. EXPERIMENTAL

Reactive Extrusion

Conditions for reactive extrusion were first determined on a Brabender torque rheometer model PL 3S equipped with roller type rotors, having a capacity of 40g. Different mixing conditions were generated by varying the temperature and rpm. The dosage of maleic anhydride (MA) was varied from 1-5% of the total weight of the polymer while that of dicumyl peroxide (DCP) at concentrations of 2-6% of the maleic anhydride content. Reactive extrusion was done on a laboratory general purpose plastic extruder attached to a Brabender
plasticorder model PL 2000 with an L/D ratio of 25 and a compression ratio of 2 and fitted with a ribbon die. The temperatures of the barrel and that of the die and the rpm of the screw were fixed as per the results obtained from the mixer.

5.3. RESULTS AND DISCUSSION

When the Polyethylenes are introduced in to the mixer the torque rises and stabilises at a value due to melting and homogenisation. The variation of stabilised torque with maleic anhydride content, of LDPE, LLDPE and their blend, at 160°C and 60 rpm in the torque rheometer mixer keeping the level of DCP content at 5% of the maleic anhydride, is shown in fig5.1. An increase in torque is observed with maleic anhydride content, probably due to the increase in the extent of maleic anhydride grafting/ crosslinking as expected. Highest value of stabilised torque is obtained for 5% maleic anhydride content showing that maximum amount of grafting/crosslinking occurs at this level of maleic anhydride and hence 5% maleic anhydride was chosen as the optimum. However, the efficiency of grafting reaction is dependent upon the structure, abstraction power, temperature and radical lifetime of the initiator employed. Hence the optimum percentage of maleic anhydride was also verified from the variation of tensile strength of the samples. Fig5.2. shows the variation of tensile strength of MA grafted LDPE, LLDPE and their blend, with percentage MA added at 160°C at 60 rpm. Maximum tensile strength is obtained for 5% MA, confirming that maximum grafting/crosslinking occurs at this MA content.
Fig 5.1 Variation of stabilised torque with MA content at 160°C

Fig 5.2 Variation of tensile strength with MA content at 160°C
Fig 5.3. shows the variation of stabilised torque with DCP content of MA grafted LDPE, LLDPE and their blend at 160°C and 60 rpm keeping maleic anhydride concentration constant at 5phr. The stabilised torque increases with DCP content, reaches a maximum and then decreases indicating there is an optimum DCP concentration. Maximum torque is obtained for 5% DCP (percent of MA) and hence 5% DCP was chosen as the optimum concentration. This result also suggests that there is an optimum radical concentration which depends on the [peroxide]/[monomer] ratio to promote grafting efficiency, beyond which the graft content levels off and termination reactions become prominent. The optimum DCP content was also verified from the variation of tensile strength of the samples. Fig 5.4. Shows the variation of tensile strength of MA grafted LDPE, LLDPE and their blend, with DCP content at 160°C and 60rpm. Maximum tensile strength is obtained for 5% DCP (percent of MA). Fig 5.5 shows the variation of stabilised torque with rpm at 160°C for maleic anhydride grafted LDPE, LLDPE and their 50/50 blend. In the case of maleic anhydride grafted polymers, maximum torque is obtained at 60rpm. This shows that the shear rate at this rpm is optimum for maleic anhydride grafting.

Generally, temperature is a critical factor of any chemical reaction, and this is especially true in the case of grafting reaction in the extruder. Furthermore, the grafting efficiency will depend upon the number of free radicals produced and its mobility and stability. Also, diffusion plays an important role as the reactions are carried out in the extruder. Fig 5.6 shows the variation of torque with temperature at 60rpm for LDPE, LLDPE and their blend with and without DCP& MA.
5.3 Variation of stabilised torque with DCP content at 160°C

5.4 Variation of tensile strength with DCP content at 160°C
Fig 5.5 Stabilised torque vs rpm

Fig 5.6 stabilised torque vs temperature
The torque rises when the temperature of the mixer increases from 130°C to 160°C indicating progressive improvement in grafting/crosslinking after which the torque decreases. This is probably because an increase in temperature causes a faster and complete decomposition of the initiator and hence produces more radicals and hence results in a higher graft content. 160°C registers the highest torque for all the combinations. This is probably due to better grafting/crosslinking efficiency at this temperature at the conditions employed.

The optimum conditions obtained from the torque rheometer have been adopted for reactive extrusion. Maleic anhydride grafting of polyethylenes was carried out in a laboratory extruder by using the optimum temperature (160°C), rpm (60) and optimum concentrations of maleic anhydride (5%) and DCP (5% of MA). To verify whether these conditions are the optimum, reactive extrusion was conducted at other temperatures and rpms also. Fig 5.7 shows the variation of tensile strength with temperature of extrusion for unmodified and modified LDPE, LLDPE and their 50/50 blend at 60rpm. Maximum tensile strength is obtained at 160°C as in the case of the mixer showing that the results obtained from the mixer can be employed in actual extrusion. Fig 5.8. shows the variation of tensile strength with rpm in the case of modified LDPE, LLDPE and their 50/50 blend at 160°C. A maximum value of tensile strength is obtained at 60rpm in all the cases. This shows that the shear rate/residence time under these conditions give the best choice for maleic anhydride grafting.
Fig 5.7 Tensile strength vs temperature

Fig 5.8 Tensile strength vs rpm
Fig 5.9 shows the variation of elongation at break (EB) with temperature, in the case of unmodified and MA grafted LDPE, LLDPE and their blend. It is found that the EB values decreased on MA grafting as expected. Fig 5.10 shows the variation of EB with MA content in the case of MA grafted LDPE, LLDPE and their blend at 160° C. EB values are decreased due to MA grafting.

Fig 5.11 shows the variation of EB with DCP content in the case of MA grafted LDPE, LLDPE and their blend at 160° C. EB values are decreased with DCP content. The maleic anhydride grafting on the polymer chains was confirmed by FTIR spectra. The FTIR spectra of MA grafted polymers are shown in figures 5.12-14. The IR spectra of maleic anhydride grafted polymers show the absorption at 1783 cm⁻¹ which is characteristic of the succinic anhydride groups.

Fig 5.15 shows the variation of viscosity at different shear rates at 170°C, in the case of LDPE, LLDPE, MA grafted LDPE and LLDPE. An increase in viscosity is obtained on MA grafting as expected. The increase in viscosity is due to the introduction of crosslinks between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. Fig 5.16 shows the variation of viscosity at different shear rates, at 170° C, in the case of blend and MA grafted blend. Here also MA grafting shows increase in viscosity.
Fig 5.9 Variation of EB with temperature

Fig 5.10 Variation of EB with MA content at 160° C
Fig 5.11 Variation of EB with DCP content at 160°C

Fig 5.12 FTIR spectrum of MA grafted LDPE
Fig 5.13 FTIR spectrum of MA grafted blend

Fig 5.14 FTIR spectrum of MA grafted LLDPE
Fig 5.15 Flow curves of unmodified and modified LDPE and LLDPE

Fig 5.16 Flow curves of unmodified and modified blend
Fig 5.17 shows the variation of gel content with mixing temperature for LLDPE. Maximum gel content is obtained at 160\(^{\circ}\)C confirming that maximum grafting/crosslinking occurs at this temperature. The increase in graft content is due to the increase in radical formation through the decomposition of initiator. The higher the radical concentration, the higher will be the chain transfer to the polymer backbone and hence higher the grafting. The gel content of LDPE is compared with that of LLDPE and 50/50 LDPE/LLDPE blend in table 5.1. LLDPE has a higher crosslink density than LDPE. Gel content, which relates to the three dimensional network structure, increases with LLDPE content, indicating that the LLDPE phase forms a relatively denser network structure.

![Graph showing variation of gel content with temperature of MA grafted LLDPE](image)

**Fig 5.17** Variation of gel content with temperature of MA grafted LLDPE
Table 5.1 Gel content values at 160° C

<table>
<thead>
<tr>
<th>Material</th>
<th>Gel Content(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE + DCP + MA</td>
<td>36.3</td>
</tr>
<tr>
<td>BLEND + DCP + MA</td>
<td>40.1</td>
</tr>
<tr>
<td>LLDPE + DCP + MA</td>
<td>42.2</td>
</tr>
</tbody>
</table>

Figs5.18-20 show the extrudate swell ratio vs shear rate of unmodified and MA grafted LDPE, LLDPE and their blend. It can be seen from the figures that the extrudate swell ratio (De/D) increases with the shear rate. This is expected because the recoverable elastic energy built up in the melt while flowing in the capillary increases as shear rate is increased. The figures also reveal that the extrudate swell ratio increases on MA grafting. The increase in swell ratio may be due to marginal reduction in crystallinity resulting from crosslinking.

Fig 5.18 Extrudate swell ratio vs shear rate of unmodified and modified LDPE
Fig 5.19 Extrudate swell ratio vs shear rate of unmodified and modified blend

Fig 5.20 Extrudate swell ratio vs shear rate of unmodified and modified LLDPE
Figs 5.21-23 show the variation of viscosity with shear rate at different temperatures of the MA grafted LDPE, LLDPE and their blend. The viscosity decreases with increase in temperature as expected.

The variation of log viscosity with reciprocal of absolute temperature at various shear rates of the MA grafted LDPE, LLDPE and their blend are shown in figures 5.24-26. The slope of these lines is proportional to the activation energy for viscous flow.
Fig 5.22 Variation of viscosity with shear rate at different temperatures of MA grafted blend

Fig 5.23 Variation of viscosity with shear rate at different temperatures of MA grafted LLDPE
Fig 5.24 Temperature dependence of viscosity of MA grafted LDPE

Fig 5.25 Temperature dependence of viscosity of MA grafted blend
The activation energy values are shown in table 5.2. The MA grafted polymers show marginally higher activation energy as expected. The difference in activation energy with grafting increases with LLDPE content. This is likely to be due to the higher crosslink density in LLDPE than in LDPE.

<table>
<thead>
<tr>
<th>Shear rate (1/s)</th>
<th>LDPE</th>
<th>LDPE + DCP + MA</th>
<th>BLEND</th>
<th>BLEND + DCP + MA</th>
<th>LLDPE</th>
<th>LLDPE + DCP + MA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1152</td>
<td>0.899</td>
<td>1.421</td>
<td>0.929</td>
<td>1.519</td>
<td>1.042</td>
<td>1.891</td>
</tr>
<tr>
<td>1728</td>
<td>0.924</td>
<td>1.603</td>
<td>1.054</td>
<td>1.716</td>
<td>1.186</td>
<td>2.042</td>
</tr>
<tr>
<td>2304</td>
<td>1.340</td>
<td>1.949</td>
<td>1.281</td>
<td>2.057</td>
<td>1.486</td>
<td>2.457</td>
</tr>
<tr>
<td>2880</td>
<td>1.601</td>
<td>2.305</td>
<td>2.154</td>
<td>2.786</td>
<td>2.269</td>
<td>3.104</td>
</tr>
<tr>
<td>3456</td>
<td>1.819</td>
<td>3.593</td>
<td>2.565</td>
<td>3.649</td>
<td>2.599</td>
<td>3.959</td>
</tr>
<tr>
<td>4032</td>
<td>2.234</td>
<td>4.086</td>
<td>2.977</td>
<td>4.124</td>
<td>3.128</td>
<td>4.304</td>
</tr>
</tbody>
</table>
The thermogravimetric curves of unmodified and MA grafted LDPE and LLDPE are shown in fig 5.27. MA grafting introduces improvement in thermal stability as expected. The thermogravimetric curves of unmodified and MA grafted LDPE/LLDPE blend are shown in fig5.28. MA grafted LLDPE shows better thermal stability than modified LDPE.

Fig 5.27. TGA Curves of (A) LDPE, (B) LDPE + DCP + MA, (C) LLDPE, (D) LLDPE + DCP + MA
Fig 5.28. TGA Curves of (A) BLEND, (B) BLEND + DCP + MA

Decomposition temperatures are given in table 5.3. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density.

Table 5.3. The temperature of derivative weight % peak

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak temp(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>373.8</td>
</tr>
<tr>
<td>LDPE + DCP + MA</td>
<td>388.3</td>
</tr>
<tr>
<td>BLEND</td>
<td>380.3</td>
</tr>
<tr>
<td>BLEND + DCP + MA</td>
<td>396.1</td>
</tr>
<tr>
<td>LLDPE</td>
<td>383.5</td>
</tr>
<tr>
<td>LLDPE + DCP + MA</td>
<td>403.3</td>
</tr>
</tbody>
</table>
The densities of unmodified and modified LDPE, LLDPE and their blend are shown in table 5.4. The densities of the MA grafted polymers are found to get marginally reduced upon modification. This behaviour can be attributed to reduction in crystallinity, because of network formation.

Table 5.4 Variation of density with modification

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>0.973</td>
</tr>
<tr>
<td>LDPE+DCP+MA</td>
<td>0.949</td>
</tr>
<tr>
<td>BLEND</td>
<td>0.957</td>
</tr>
<tr>
<td>BLEND+DCP+MA</td>
<td>0.924</td>
</tr>
<tr>
<td>LLDPE</td>
<td>0.947</td>
</tr>
<tr>
<td>LLDPE+DCP+MA</td>
<td>0.912</td>
</tr>
</tbody>
</table>

5.4. CONCLUSIONS

The study shows that maleic anhydride can be grafted to polyethylenes through reactive extrusion, on a single screw extruder and that the optimum parameters of reactive extrusion can be obtained from torque rheometer studies. The low level of grafting/crosslinking introduced does not seem to affect the processing of the material, but marginally improves its mechanical behaviour and thermal stability.
REFERENCES


