CHAPTER 4

SILANE GRAFTING OF POLYETHYLENES
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4.1. 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. Free radical initiators and less commonly air or ionizing radiation have been used to initiate the reaction. Extruder reactors for performing graft reactions may include intensive mixing sections and screw segments designed to expose the maximum surface area of polymer substrate to grafting agent.1-6

Grafting of vinylsilanes to polyolefin substrates in the presence of peroxide is the most common example of a graft reaction performed in extruder reactors. The sole purpose of the peroxide is to initiate the grafting reaction. Polyolefins grafted with vinyl silanes are readily crosslinked by moisture and the materials have a large commercial market as wire coating and pipe insulation.7-15

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 polyolefins. Compared with the untreated material, crosslinked polyethylene especially shows enhanced impact strength, better thermal performance and higher chemical resistance. Further, considerable improvements can be found in the resistance to wear, creep and ageing16-24. Also, crosslinked products can
incorporate high amounts of fillers without a remarkable deterioration of the material properties.

Dialkyl or diaralkyl peroxides are the most commonly used radical donors for the organosilane grafting. The sole purpose of the peroxide is to initiate the grafting reaction. They degrade, due to the instability of their O-O bond, to free radicals, when exposed to higher temperatures. The service temperature of crosslinked polyethylene can be extended to significantly higher temperatures than those of thermoplastic polyethylene. For example, an important application of peroxide crosslinked polyethylene is in hot water piping installations where the combination of high temperatures and pressures has caused failure of thermoplastic polyethylene and polypropylene.

In addition to the disadvantage of high cost special equipment necessary for the production of peroxide crosslinked piping, and coatings in the wire and cable industry, other production methods (e.g., injection moulding and blow moulding) are still unavailable or uneconomical. A more versatile technology developed by Dow Corning for manufacturing crosslinked polyethylene products using conventional thermoplastic processing techniques is recently becoming important. Polyethylene reacted with an organosilane in a compounding extruder gives silane grafted polymer containing Si-OR groups.

Currently, different techniques are in use for the production of crosslinked polyethylene whereby the thermally initiated peroxide method, the
crosslinking via γ or β radiation and the silane method are by far the most important.\textsuperscript{44-50} The silane method, differs from the other crosslinking techniques when considering the processing procedure. Compounding of such a mixture in the melt at a high temperature causes decomposition of the peroxide and grafting of alkoxy silyl groups to the polyolefine chains. In a first step, during the processing of the polymer, H atoms are abstracted from the macromolecules by free radicals, which are generated from thermally degradable organic peroxides. Silane can link up to these activated sites whereby the radical character is transferred to the linking element. The actual crosslinking takes place subsequently to the grafting step. The functional end groups saponize to silanoles in a hydrolysis reaction with water molecules. The generated OH groups then condense with adjacent Si-O-H groups to main Si-O-Si bonds. The polymer is thus crosslinked.\textsuperscript{7}

The use of extruders as continuous reactors for processes such as polymerization, polymer modification or compatibilization of polymer blends involves technologies that are gaining increasing popularity and compete with conventional operations with respect to efficiency and economics. In this chapter the optimum conditions for silane grafting viz: temperature, shear rate, silane and DCP concentrations were determined on a torque rheometer in the case of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and their blend and then actual extrusion of these polymers was performed using these conditions in a laboratory extruder. Silane grafting of low density polyethylene (LDPE) in the presence of peroxide was performed with and without addition of water.
4.2. EXPERIMENTAL

Reactive Extrusion

Comparison of single step and double step silane grafting

Conditions for reactive extrusion were first determined on a Brabender plasticorder mixer model PL3S equipped with roller type rotors, having a capacity of 40g. Changes in torque obtained are a measure of the changes in the melt viscosity of the polymer. Different mixing conditions were generated by varying the temperature and rpm. The dosage of silane was varied from 1-5% of the total weight of the polymer. Dicumyl peroxide (DCP) at concentrations of 2-6% of the silane was added along with the polymer. Reactive extrusion was done on a laboratory general purpose plastic extruder attached to a Brabender plasticorder model PL2000 with an L/D ratio of 25, 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.

Reactive extrusion was performed both in a single step and double step process. In the single step process, silane, DCP and the polymer were added to the hopper of the extruder and extrusion was performed in one stage. In the double step process, the extruded material collected from the ribbon die was cut in to small pieces and again fed into the hopper of the extruder.
4.3. RESULTS AND DISCUSSION

On addition of LDPE, DCP and silane to the Brabender mixer, the torque rises due to melting/crosslinking/grafting, reaches a maximum value and then stabilises at a lower value. The grafting/crosslinking may be estimated either from the maximum torque or the stabilised torque. Fig 4.1 shows the variation of stabilised torque with silane content at 190°C and 60rpm in the torque rheometer keeping the level of DCP content at 4% of the silane level. An initial increase in torque is observed on silane grafting/crosslinking as expected. Polyethylene reacted with the oraganosilane in the compounding extruder gives silane grafted polymer containing Si-OR groups. Water molecules cause hydrolysis of Si-OR groups and formation of Si-O-Si crosslinks by condensation. The highest value of stabilised torque is obtained for 3% silane, which shows that under the conditions maintained, the maximum extent of grafting/crosslinking occurred at this concentration of silane; hence 3% silane was chosen for further trials. The optimum percentage of silane content was also verified from the variation of tensile strength of the samples. The variation of tensile strength with percentage silane after processing at 190°C at 60rpm is shown in Fig 4.2. Maximum tensile strength is obtained for 3% silane.
Fig 4.1 Variation of stabilised torque with silane content at 190°C

Fig 4.2 Variation of tensile strength with silane content at 190°C
The variation of stabilised torque with DCP content at 190°C and 60rpm keeping silane concentration constant at 3phr is shown in Fig 4.3. Maximum torque is obtained for 4% DCP (percent of silane level) and hence 4% DCP was chosen as the optimum concentration. The optimum percentage DCP content was also determined taking the tensile strength as the critical property. Fig 4.4 shows the variation of tensile strength with percent DCP after processing at 190°C and 60rpm. Maximum tensile strength is obtained for 4% DCP. Fig 4.5 shows the variation of stabilised torque with rpm at 190°C for modified and unmodified LDPE. In the case of silane grafted polymer maximum torque is obtained at 60rpm. This shows that the shear rate at this rpm is optimum for silane grafting.

Fig 4.6 shows the variation of stabilised torque with temperature at 60rpm for pure LDPE and LDPE containing 3% silane and 4% DCP with and without addition of water. In presence of water, torque increases indicating a higher crosslinking. The torque rises when the temperature of the mixer increases from 130°C to 190°C indicating progressive improvement in grafting/crosslinking after which the torque decreases. This result suggests that there is an optimum radical concentration to promote grafting efficiency, beyond which the graft content levels off and termination reactions become prominent.
Fig 4.3 Variation of stabilised torque with DCP content at 190° C

Fig 4.4 Variation of tensile strength with DCP content at 190° C
Fig 4.5 stabilised torque vs rpm at 190° C

Fig 4.6 Stabilised torque vs temperature
Fig 4.7 shows the effect of residence time for the onset of grafting/crosslinking at different temperatures, at 60 rpm, measured as the time for attaining the maximum torque. It may be observed that the time for the onset of grafting/crosslinking decreases with increase in temperature as expected. The time for the onset of crosslinking at 190°C is about 1 minute.

The optimum conditions obtained from the torque rheometer have been adopted for reactive extrusion. Silane grafting of polyethylene was carried out in the laboratory extruder by using the optimum temperature (190°C) and optimum concentrations of silane (3%) and DCP (4% of silane) as per the results obtained from the torque rheometer. Further, the average residence time for the extrudate was found to be about 1 min. at 190°C, at 60 rpm. Hence 190°C and 60 rpm were tried as the optimum extruder parameters for the grafting/crosslinking. To verify whether these conditions are the optimum, reactive extrusion was conducted at other temperatures and rpms also. Fig 4.8 shows the variation of tensile strength with temperature in the case of single step and double step processing. There is an increase in tensile strength on silane grafting and the maximum value is obtained at 190°C for the single stage as expected. Tensile strengths from double step processing are higher than the single step values at lower temperatures, and increases with increasing temperature, but less than the single stage rate of increase. They coincide at 180°C.
Fig 4.7 Variation of time for the onset of grafting/crosslinking at different temperatures at 60 rpm

Fig 4.8 Tensile strength vs temperature
Fig 4.9 shows the variation of tensile strength with rpm for single stage and double stage processing. The tensile strength increases with rpm and a maximum value of tensile strength is obtained at 60rpm, further confirming that the shear rate/residence time at this rpm is the optimum.

Fig 4.10 shows the gel content variation with temperature for single step and double step processing. Maximum gel content is obtained at 190°C confirming the earlier observations for the other characteristics. The gel content values for double step are less than for single step. Fig 4.11 shows the variation of viscosity of unmodified and modified LDPE at different shear rates at 170°C. An increase in viscosity is obtained on silane grafting since the melt viscosity is sensitive to peroxide initiated C-C branching reactions and silane grafting. Again, this can be explained by a reduction of the chain mobility due to silane grafting and by peroxide initiated branching effects. Product obtained from single stage grafting shows higher viscosity than the one obtained from double stage process. It may be concluded that under the conditions employed, single stage grafting is sufficient. Fig 4.12 shows the thermogravimetric curves of unmodified LDPE and silane grafted LDPE. Silane grafting shows improvement in thermal stability.
Fig. 4.9 Tensile strength vs rpm

Fig. 4.10 Gel content vs temperature
Fig 4.11 Flow curves of unmodified and modified LDPE

Fig 4.12 TGA curves of (A) LDPE, (B) LDPE + SILANE
From the foregoing studies on silane grafting of LDPE under the conditions employed, it was found that single step grafting is sufficient since the double step process does not show much improvement in properties. Further, silane grafting was done on LLDPE and LDPE/LLDPE blend and the optimum conditions for silane grafting were determined.

**Silane grafting of LDPE, LLDPE and their blend**

On addition of polymer, DCP and silane to the Brabender mixer, the torque rises due to melting/crosslinking/grafting, reaches a maximum value and then stabilises at a lower value. The grafting/crosslinking may be estimated either from the maximum torque or the stabilised torque. Fig 4.13 shows the variation of stabilised torque with silane content in the case of silane grafted LDPE, LLDPE and LDPE/LLDPE blend, at 190°C and 60rpm in the torque rheometer keeping the level of DCP content at 4% of the silane level. An initial increase in torque is observed on silane grafting/crosslinking as expected. Polyethylenes reacted with the oraganosilane in the compounding extruder gives silane grafted polymer containing Si-OR groups. Water molecules cause hydrolysis of Si-OR groups and the generated OH groups then condense with adjacent Si-OH groups to main Si-O-Si bonds. The polymer is thus crosslinked. The highest value of stabilised torque is obtained for 3% silane, which shows that under the conditions maintained, the maximum extent of grafting/crosslinking occurred at this concentration of silane; hence 3% silane was chosen for further trials.
The optimum percentage of silane content was also verified from the variation of tensile strength of the samples. The variation of tensile strength for LDPE, LLDPE and their blend, with percentage silane after processing at 190°C at 60rpm is shown in fig 4.14. Maximum tensile strength is obtained for 3% silane.

The variation of stabilised torque for LDPE, LLDPE and their blend, with DCP content at 190°C and 60rpm keeping silane concentration constant at 3phr is shown in fig 4.15. Maximum torque is obtained for 4% DCP (percent of silane level) in all the cases and hence 4% DCP was chosen as the optimum concentration. The optimum percentage DCP content was also determined taking the tensile strength as the critical property.
Fig 4.14 Variation of tensile strength with DCP content at 190° C

Fig 4.15 Variation of stabilised torque with DCP content at 190° C
Fig 4.16 shows the variation of tensile strength for LDPE, LLDPE and their blend with percent DCP after processing at 190°C and 60rpm. Maximum tensile strength is obtained for 4% DCP in all the cases. The increase in tensile strength is more pronounced in the case of LLDPE. Fig 4.17 shows the variation of stabilised torque with rpm at 190°C for modified (3% silane and 4% DCP) LDPE, LLDPE and their blend. In all the cases maximum torque is obtained at 60rpm. This shows that the shear rate at this rpm is optimum for silane grafting.

Fig 4.18 shows the variation of torque with temperature at 60rpm for unmodified and modified LDPE, LLDPE and their blend containing 3% silane and 4% DCP. For pure polymers, the torque is almost parallel to the x-axis as expected. In the case of silane grafted polymers the torque rises when the temperature of the mixer increases from 130°C to 190°C indicating progressive improvement in grafting/crosslinking after which the torque decreases. This result suggests that there is an optimum radical concentration to promote grafting efficiency, beyond which the graft content levels off and the termination reactions become prominent.

The optimum conditions obtained from the torque rheometer have been adopted for reactive extrusion. Silane grafting of polyethylenes was carried out in the laboratory extruder by using the optimum temperature (190°C) and optimum concentrations of silane (3%) and DCP (4% of silane) as per the results obtained from the torque rheometer. Hence 190°C and 60rpm were tried as the optimum extruder parameters for the grafting/crosslinking. To verify whether these conditions are the optimum, reactive extrusion was conducted at other temperatures and rpms also.
Fig 4.16 Variation of tensile strength with DCP content at 190°C

Fig 4.17 Variation of stabilised torque with rpm at 190°C
Fig 4.18 Variation of torque with temperature at 60 rpm

Fig 4.19 shows the variation of tensile strength with temperature at 60 rpm in the case of unmodified and silane grafted LDPE, LLDPE and their blend containing 3% silane and 4% DCP. There is an increase in tensile strength on silane grafting and the maximum value is obtained at 190°C, in all the cases, as expected. Fig 4.20 shows the variation of tensile strength with rpm, at 190°C for silane grafted LDPE, LLDPE and their blend. The tensile strength increases with rpm and a maximum value of tensile strength is obtained at 60 rpm, in all the cases, further confirming that the shear rate/residence time at this rpm is the optimum.
Fig 4.19 Tensile strength vs temperature at 60 rpm

Fig 4.20 Tensile strength vs rpm at 190°C
Fig 4.21 shows the variation of elongation at break (EB) with temperature, in the case of unmodified and silane grafted LDPE, LLDPE and their blend. It is found that the EB values decreased on silane grafting and crosslinking as expected.

![Graph showing variation of EB with temperature](image)

**Fig 4.21 Variation of EB with temperature**

Fig 4.22 shows the variation of EB with percent silane in the case of silane grafted LDPE, LLDPE and their blend at 190° C. On silane grafting, EB values are found to be decreased. Fig 4.23 shows the variation of EB with DCP content in the case of silane grafted LDPE, LLDPE and their blend at 190° C. As the percent of DCP increases, EB values are found to be decreased.
Fig 4.22 Variation of EB with silane content at 190° C

Fig 4.23 Variation of EB with DCP content at 190° C
The silane grafting on the polymer chains was confirmed by FTIR spectra. The FTIR spectra of unmodified LDPE, LLDPE, silane grafted LDPE, LDPE/LLDPE blend and LLDPE are shown in figures 4.24-28. The IR spectra of silane grafted polymers show additional absorption band at 1081 cm$^{-1}$ which is characteristic of the Si-O-Si bonds. Fig 4.29 shows the IR spectrum of silane grafted LDPE with addition of water. The bands are much pronounced in this spectrum. The absorption band at 2020 cm$^{-1}$ is characteristic of Si-C bond.

Fig 4.24 FTIR spectrum of LDPE
Fig 4.25 FTIR spectrum of LLDPE

Fig 4.26 FTIR spectrum of silane grafted LDPE
Fig 4.27 FTIR spectrum of silane grafted blend

Fig 4.28 FTIR spectrum of silane grafted LLDPE
Fig 4.29 FTIR spectrum of silane grafted LDPE with addition of water

Fig 4.30 shows the variation of viscosity at different shear rates, at 170°C, in the case of LDPE, silane grafted LDPE, LLDPE and silane grafted LLDPE. An increase in viscosity is obtained on silane grafting as expected. The increase in viscosity is due to the introduction of Si-O-Si links between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. Fig 4.31 shows the variation of viscosity at different shear rates, at 170°C, in the case of blend, and silane grafted blend. Here also silane grafting shows increase in viscosity.
Fig 4.30 Flow curves of unmodified and modified LDPE and LLDPE

Fig 4.31 Flow curves of unmodified and modified blend
Figs 4.32-34 show the extrudate swell ratio vs shear rate of unmodified and silane grafted LDPE, LLDPE and their blend. It can be seen from the figures that the extrudate swell ratio ($D_e/D$) 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 silane grafting in all the cases. The increase in swell ratio may be due to crosslinking of the polymer and subsequent reduction in crystallinity.

![Fig 4.32 Extrudate swell ratio vs shear rate](image-url)
Fig 4.33 Extrudate swell ratio vs shear rate

Fig 4.34 Extrudate swell ratio vs shear rate
Fig 4.35-37 show the variation of viscosity with shear rate at different temperatures for silane 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 unmodified and silane grafted LDPE, LLDPE and their blend are shown in figures 4.38-40. The slope of these lines is proportional to the activation energy for viscous flow.

Fig 4.35 Variation of viscosity with shear rate at different temperatures for silane grafted LDPE
Fig 4.36 Variation of viscosity with shear rate at different temperatures for silane grafted blend

Fig 4.37 Variation of viscosity with shear rate at different temperatures for silane grafted LLDPE
Fig 4.38 Temperature dependence of viscosity of silane grafted LDPE

Fig 4.39 Temperature dependence of viscosity of silane grafted blend
The activation energy values are shown in Table 4.1. The silane grafted polymers show marginally higher activation energy as expected. The difference in activation energy with crosslinking gradually increases with LLDPE content. This is likely to be due to the higher crosslink density in LLDPE than in LDPE.

Table 4.1 Variation of activation energy of the polymers at different shear rates.

<table>
<thead>
<tr>
<th>Shear rate (1/s)</th>
<th>LDPE</th>
<th>LDPE + SILANE</th>
<th>BLEND</th>
<th>BLEND + SILANE</th>
<th>LLDPE</th>
<th>LLDPE + SILANE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1152</td>
<td>0.89</td>
<td>1.22</td>
<td>0.92</td>
<td>1.24</td>
<td>1.04</td>
<td>1.47</td>
</tr>
<tr>
<td>1728</td>
<td>0.92</td>
<td>1.50</td>
<td>1.05</td>
<td>1.39</td>
<td>1.18</td>
<td>1.68</td>
</tr>
<tr>
<td>2304</td>
<td>1.34</td>
<td>1.72</td>
<td>1.28</td>
<td>1.80</td>
<td>1.48</td>
<td>1.90</td>
</tr>
<tr>
<td>2880</td>
<td>1.60</td>
<td>1.92</td>
<td>2.15</td>
<td>2.56</td>
<td>2.26</td>
<td>2.88</td>
</tr>
<tr>
<td>3456</td>
<td>1.81</td>
<td>2.75</td>
<td>2.56</td>
<td>3.27</td>
<td>2.59</td>
<td>3.10</td>
</tr>
<tr>
<td>4032</td>
<td>2.23</td>
<td>3.28</td>
<td>2.97</td>
<td>3.38</td>
<td>3.12</td>
<td>3.85</td>
</tr>
<tr>
<td>4608</td>
<td>3.35</td>
<td>3.91</td>
<td>3.35</td>
<td>5.79</td>
<td>3.46</td>
<td>3.99</td>
</tr>
</tbody>
</table>
The thermogravimetric curves of unmodified and silane grafted LDPE and LLDPE are shown in fig 4.41. Silane grafting shows improvement in thermal stability as expected.

**FIG 4.41 TGACURVES OF (A) LDPE, (B) LDPE + DCP + SILANE, (C) LLDPE, (D) LLDPE + DCP + SILANE**

The thermogravimetric curves of unmodified and silane grafted LDPE/LLDPE blend are shown in fig 4.42. Silane grafted LLDPE and LDPE/LLDPE blend shows better thermal stability than silane grafted LDPE.
FIG 4.42 TGA CURVES OF (A) BLEND, (B) BLEND+DCP+SILANE

Decomposition temperatures are given in table 4.2. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density.

Table 4.2 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 + SILANE</td>
<td>386.1</td>
</tr>
<tr>
<td>BLEND</td>
<td>380.3</td>
</tr>
<tr>
<td>BLEND + DCP + SILANE</td>
<td>392.7</td>
</tr>
<tr>
<td>LLDPE</td>
<td>383.5</td>
</tr>
<tr>
<td>LLDPE + DCP + SILANE</td>
<td>397.3</td>
</tr>
</tbody>
</table>
The gel content of silane grafted LDPE is compared with that of LLDPE and 50/50 LDPE/LLDPE blend in table 4.3. 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.

Table 4.3 Gel content values at 190° C

<table>
<thead>
<tr>
<th>Material</th>
<th>Gel Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE + DCP + SILANE</td>
<td>32.6</td>
</tr>
<tr>
<td>BLEND + DCP + SILANE</td>
<td>38.2</td>
</tr>
<tr>
<td>LLDPE + DCP + SILANE</td>
<td>40.6</td>
</tr>
</tbody>
</table>

The densities of unmodified and modified LDPE, LLDPE and their blend are shown in table 4.4. The densities of the modified polymers are found to get marginally reduced upon modification. This behaviour can be attributed to reduction in crystallinity, because of network formation.

Table 4.4 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 + SILANE</td>
<td>0.959</td>
</tr>
<tr>
<td>BLEND</td>
<td>0.957</td>
</tr>
<tr>
<td>BLEND+DCP + SILANE</td>
<td>0.939</td>
</tr>
<tr>
<td>LLDPE</td>
<td>0.947</td>
</tr>
<tr>
<td>LLDPE + DCP + SILANE</td>
<td>0.923</td>
</tr>
</tbody>
</table>
4.4. CONCLUSIONS

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


