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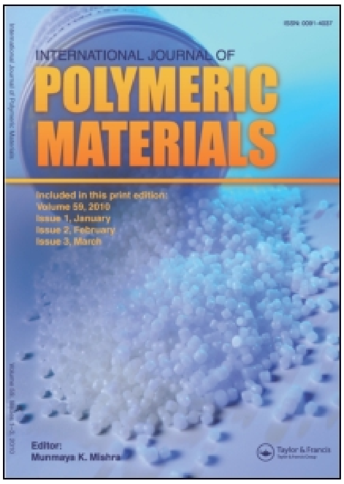

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Silane Grafting of Polyethylenes

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Silane Grafting of Polyethylenes

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Reactive extrusion is an attractive means of polymer processing since the shaping and reaction take place in a single operation. In this paper we report the silane grafting of polyethylenes in a single screw extruder. The optimum conditions for silane grafting, viz. temperature, shear rate, silane and DCP concentrations, were determined on a torque rheometer and then actual extrusion was performed using these conditions. The study shows that an optimum low level of grafting/crosslinking can be introduced into polyethylene during its extrusion for better mechanical behavior and/or thermal stability without affecting the processability.

Keywords: LDPE; LLDPE; Reactive extrusion; Silane grafting

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 grafts reactions may include intensive mixing sections and screw segments designed to expose the maximum surface area of polymer substrate to grafting agent [1–3].

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. Polyolefines grafted with vinyl silanes are readily crosslinked by moisture and the materials have a large commercial market as wire coating and pipe insulation [4–5].

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The crosslinking of polyethylene molecules by covalent bonds into three-dimensional networks leads to significant improvements of the materials properties, which greatly enlarge the application fields of these low-cost polyolefines. 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 ageing [6–7]. Also, crosslinked products can incorporate high amounts of fillers without a remarkable deterioration of the material properties. 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 [8–15].

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 [16–24]. In this paper 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.

EXPERIMENTAL

Materials

The grades of LDPE, LLDPE, DCP and silane used for the study are: (1) LDPE-Indothene 24FSO40; melt index 4 g/10 min; density 0.922 g/cm^3 (supplied by IPCL, Baroda). (2) LLDPE-Indothene LL20FSO10; melt index 1 g/10 min; density 0.920 g/cm^3 (supplied by IPCL, Baroda).

Dcp-Dicumyl peroxide used was commercial grade with 40% purity Silane-Si-69. Bis (3-(triethoxy silyl) propyl) tetrasulphide; yellow to brown liquid; pH; 7–8.

Reactive Extrusion

Conditions for reactive extrusion were first determined on a Brabender plasticorder mixer model PL3S equipped with roller type rotors, having a capacity of 40 g. 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 form 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.

Characterization and Testing

The gel content of the extrudate was determined from extraction in boiling toluene for 8 hrs according to ASTMD 2765. The tensile properties were determined both from compression molded sheets obtained from the material in the Brabender mixer and directly from the film obtained from the extruder according to ASTM D638, using a zwick tensile testing machine model 1445 using a stretching rate of 50 mm/min.

FTIR spectra of the compression molded films were taken in Nicolet Avatar 360 ESP FTIR spectrometer after extraction in toluene for 8 hours.

The rheological measurements were made with a Goettfert capillary rheometer using a die of 1-mm diameter and a L/D ratio 30. The extrudate emerging from the capillary was collected and the diameter of the extrudate was measured at various points. The extrudate swell ratio was calculated as the ratio of the diameter of the extrudate, De, to the diameter of the capillary die, D.

The thermogravimetric analysis were done on a Dupont 2000 thermal analyzer at a heating rate of 10°C/min in air, from room temperature to 700°C.

The densities of the polymer samples were measured by the method of displacement of liquid (ASTM D 792).

RESULTS AND DISCUSSION

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 stabilizes at a lower value. The extent of grafting/crosslinking may be estimated either from the maximum torque or the stabilized torque. Figure 1 shows the variation of stabilized torque

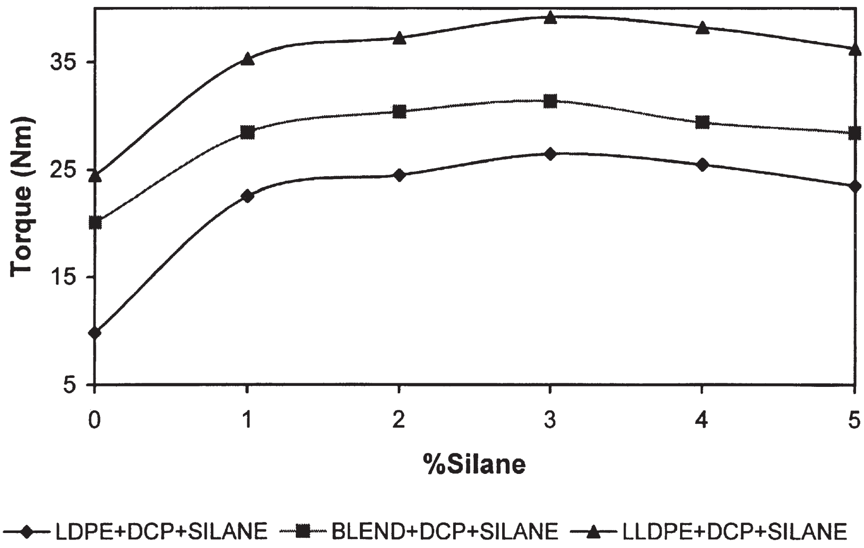


FIGURE 1 Variation to torque with silane content (190°C, 60 rpm).

with percentage silane content in the case of LDPE, LLDPE and LDPE/LLDPE blend, at 190°C and 60 rpm 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 give 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 create Si–O–Si bonds. The polymer is thus crosslinked. The highest value of stabilized 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 60 rpm is showm in Figure 2. Maximum tensile strength is obtained for 3% silane.

The variation of stabilized torque for LDPE, LLDPE and their blend, with DCP content at 190°C and 60 rpm keeping silane concentration constant at 3 phr is shown in Figure 3. Maximum torque is obtained for 4% DCP (percent of silane level) in all cases and hence 4% DCP was chosen as the optimum concentration. The optimum

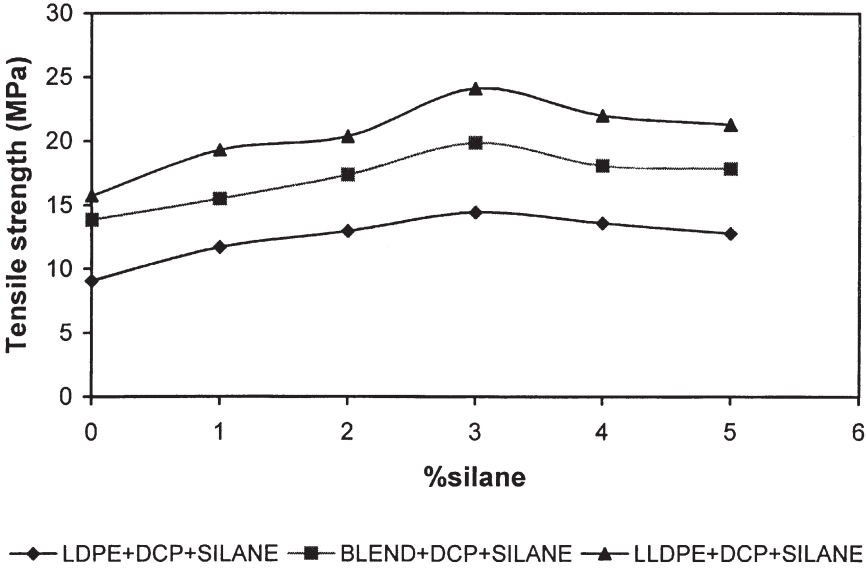


FIGURE 2 Variation of tensile strength with silane content (190°C, 60 rpm).

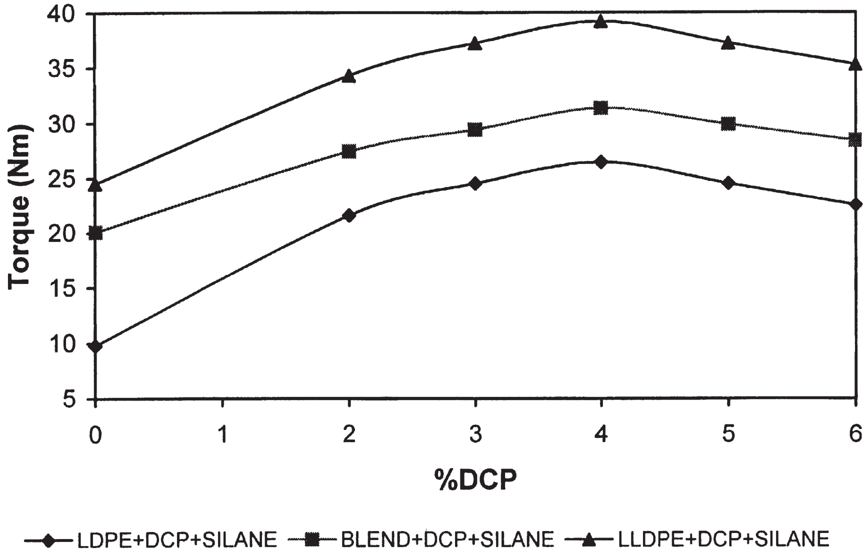


FIGURE 3 Variation of stabilized torque with DCP content (190°C, 60 rpm).

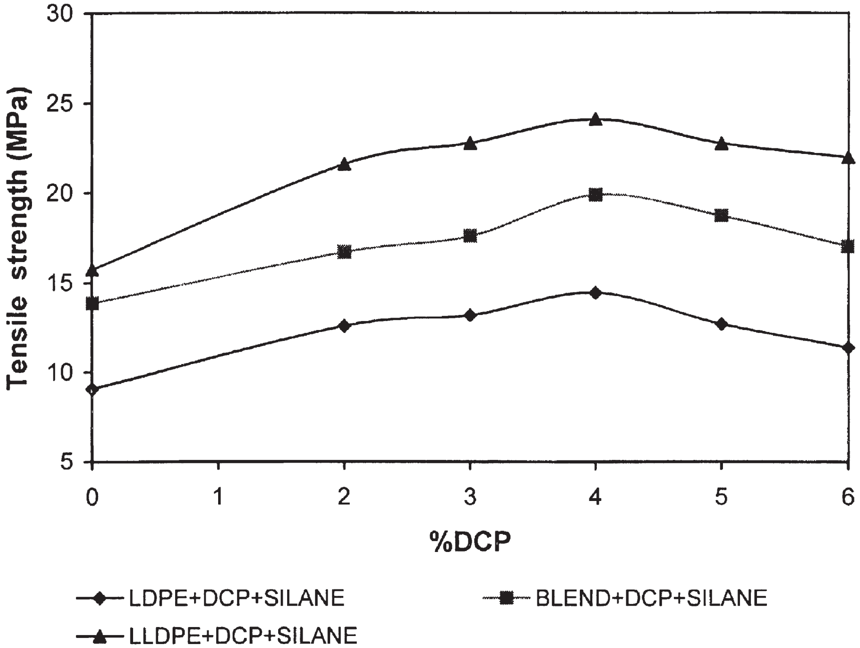


FIGURE 4 Variation of tensile strength with DCP content (190°C, 60 rpm).

percentage DCP content was also determined taking the tensile strength as the critical property. Figure 4 shows the variation of tensile strength for LDPE, LLDPE and their blend with percent DCP after processing at 190°C and 60 rpm. Maximum tensile strength is obtained for 4% DCP in all the cases. The increases in tensile strength is more pronounced in the case of LLDPE.

Figure 5 shows the variation of stabilized 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 60 rpm. This shows that the shear rate at this rpm is optimum for silane grafting.

Figure 6 shows the variation of stabilized torque with temperature at 60 rpm for unmodified polymers 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

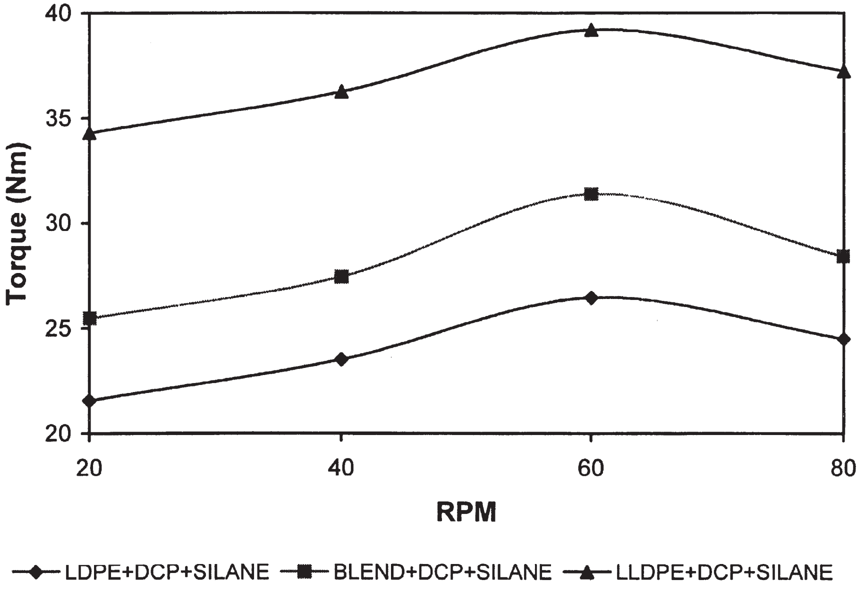


FIGURE 5 Variation of stabilized torque with rpm for silane grafted LDPE, LLDPE and their blend at 190°C.

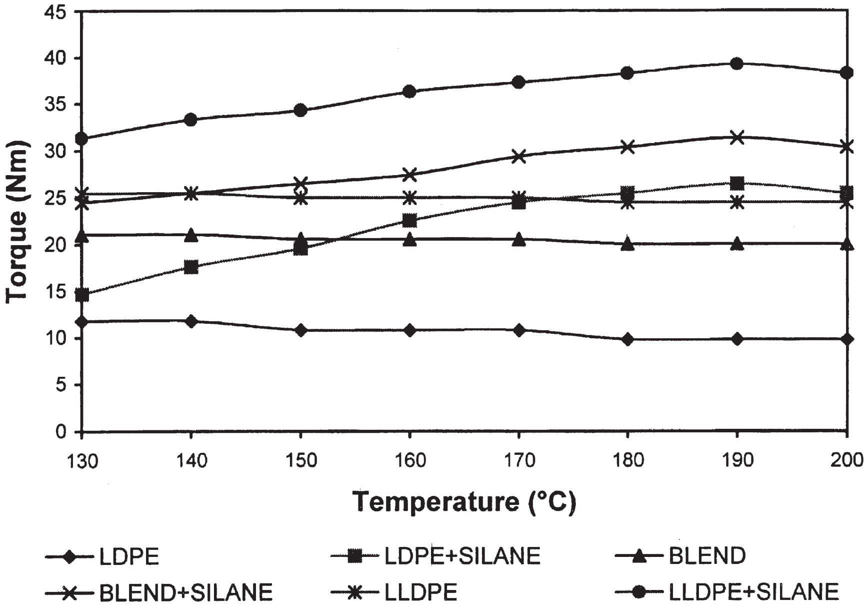


FIGURE 6 Stabilized torque vs temperature curves of unmodified and silane grafted LDPE, LLDPE and their blend at 60 rpm.

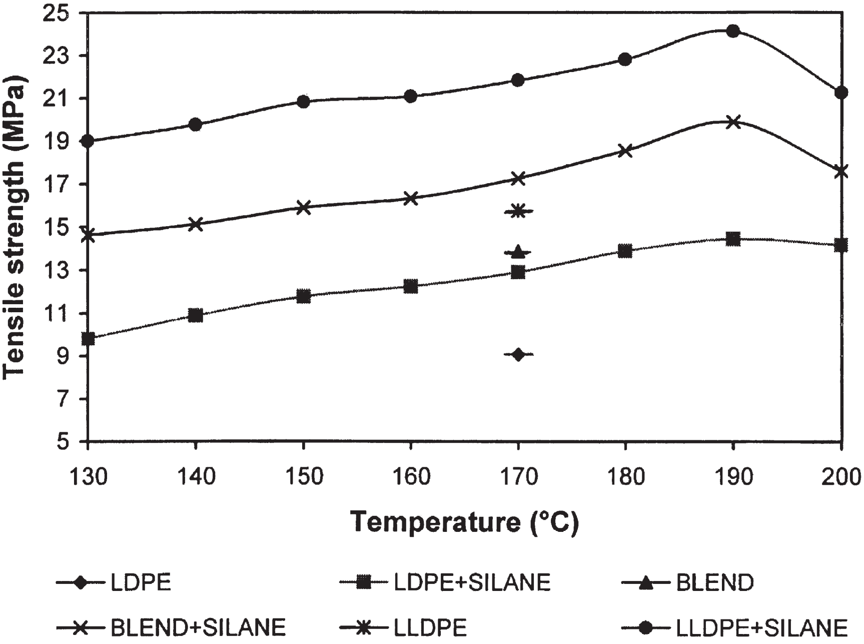


FIGURE 7 Tensile strength vs temperature curves of unmodified and silane grafted LDPE, LLDPE and their blend at 60 rpm.

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 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 Figure 7 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 Figure 8 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

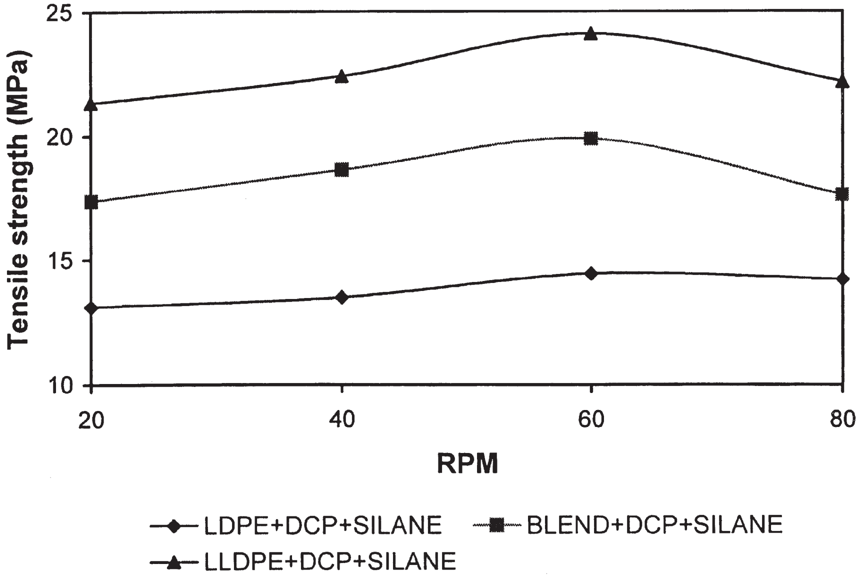


FIGURE 8 Tensile strength vs rpm in the case of silane grafted LDPE, LLDPE and their blend at 190°C.

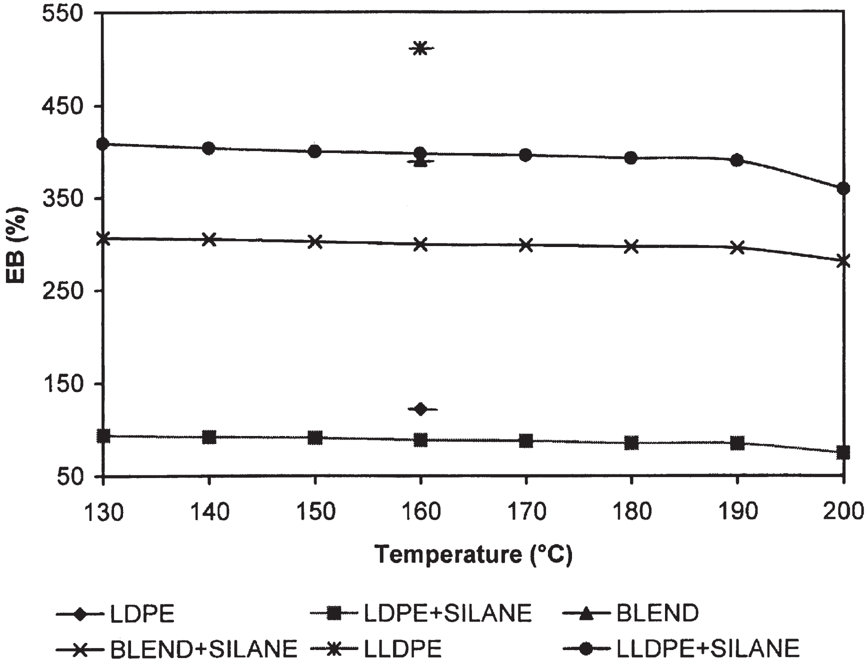


FIGURE 9 Variation of EB with temperature in the case of silane grafted LDPE, LLDPE and their blend.

is obtained at 60 rpm, in all the cases, further confirming that the shear rate/residence time at this rpm is the optimum.

Figure 9 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 EB values decreases on silane grafting and crosslinking as expected Figure 10 shows the variation of EB with % silane in the case of silane grafted LDPE, LLDPE and their blend. On silane grafting, EB values are found to be decreased. Figure 11 shows the variation of EB with % DCP in the case of silane grafted LDPE, LLDPE and their blend. As the DCP content increases, EB values are found to be decreased.

The silane grafting on the polymer chains was confirmed by FTIR spectra. The FTIR spectra of pure polymer and silane grafted LLDPE are shown in Figures 12 and 13. The IR spectra of silane grafted polymers show additional absorption band at 1081 cm^{-1}, which is characteristic of the Si–O–Si bonds. The absorption band at 2020 cm^{-1} is characteristic of Si–C bond.

Figure 14 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

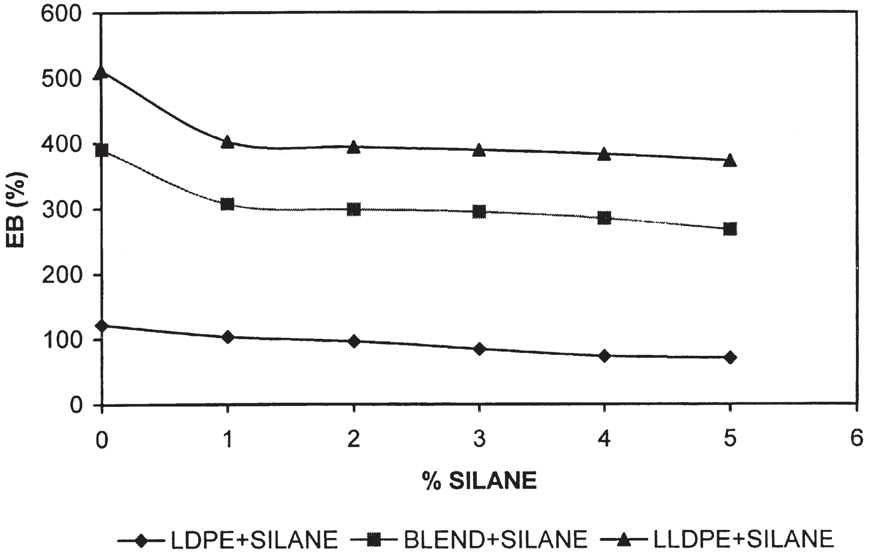


FIGURE 10 Variation of EB with % silane in the case of silane grafted LDPE, LLDPE and their blend.

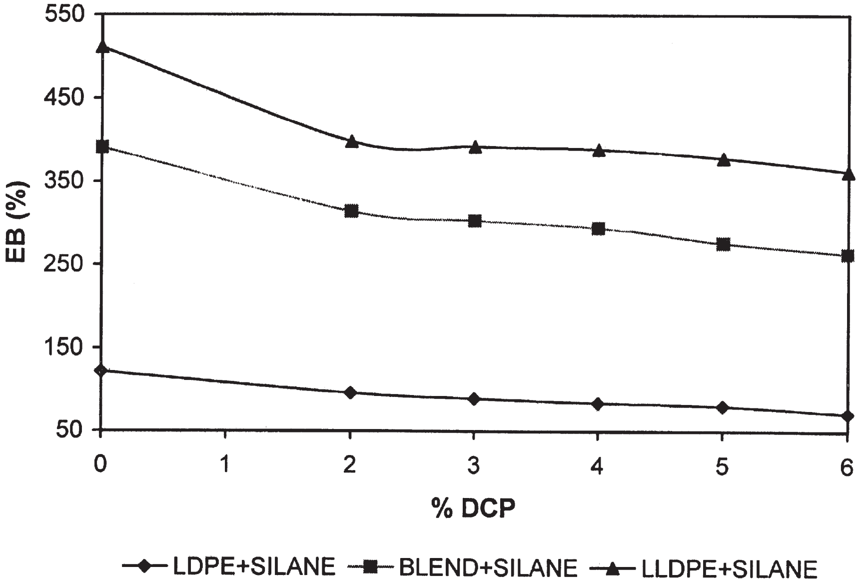


FIGURE 11 Variation of EB with % DCP in the case of silane grafted LDPE, LLDPE and their blend.

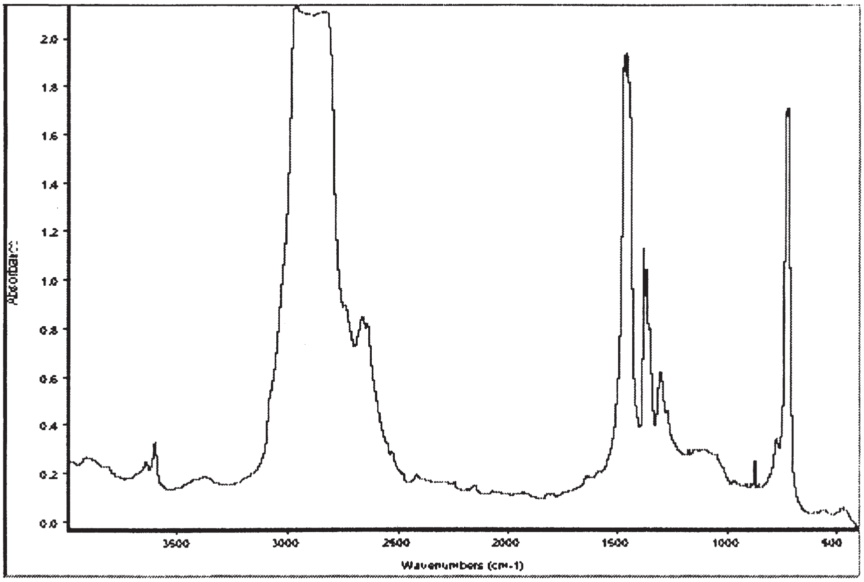


FIGURE 12 FTIR spectrum of blend.

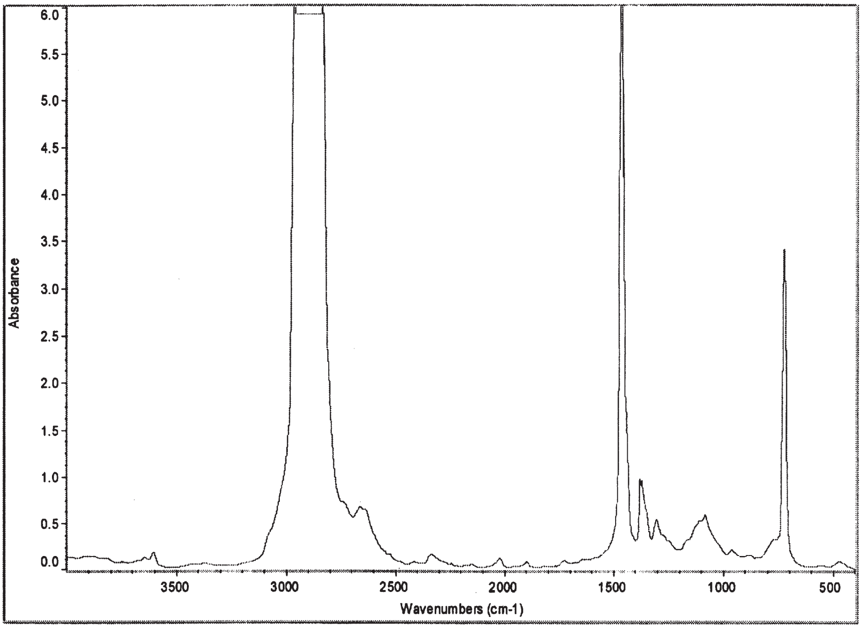


FIGURE 13 FTIR spectrum of silane grafted blend.

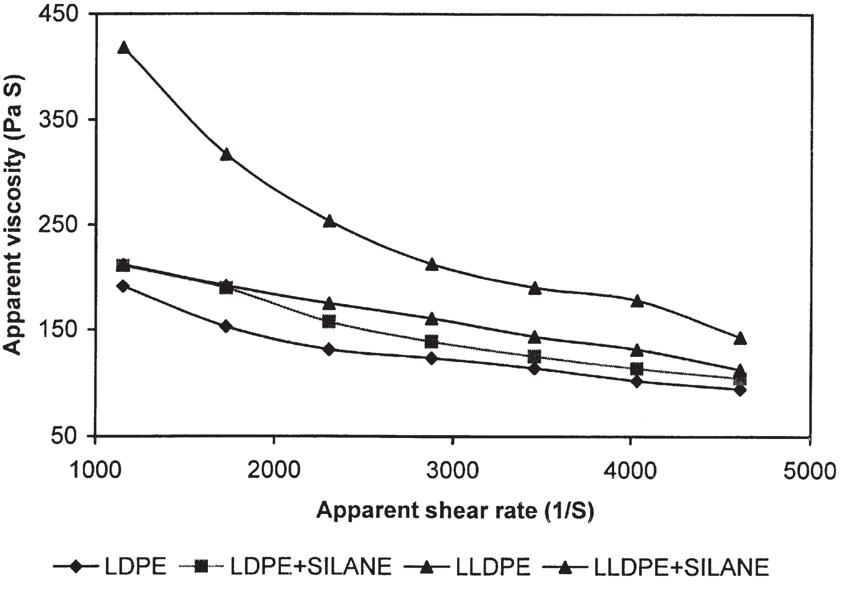


FIGURE 14 Flow curves of unmodified and modified LDPE and LLDPE.

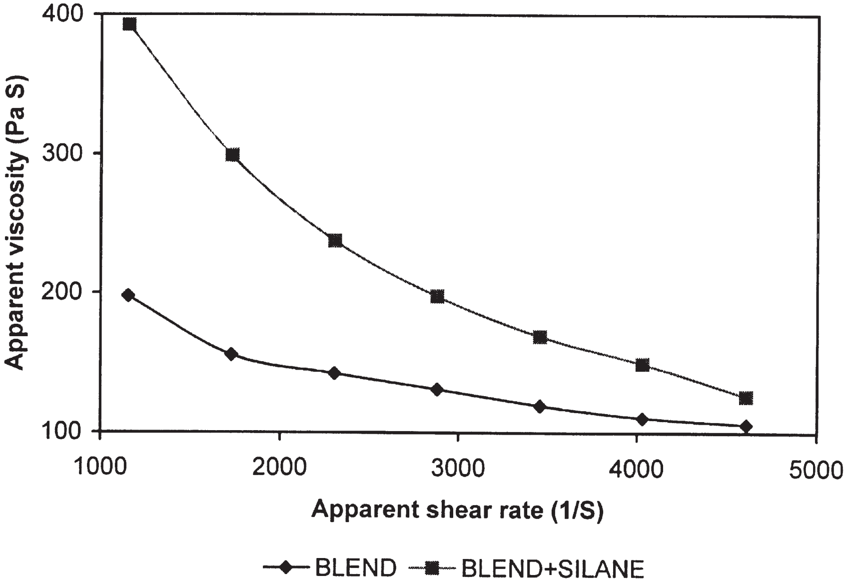


FIGURE 15 Flow curves of unmodified and modified blend.

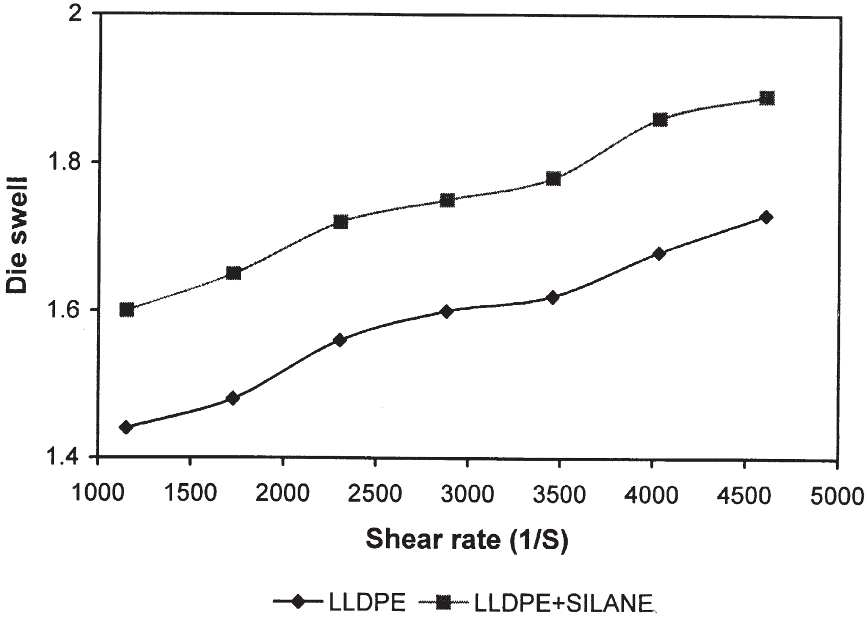


FIGURE 16 Extrudate swell ratio vs shear rate of unmodified and modified LLDPE.

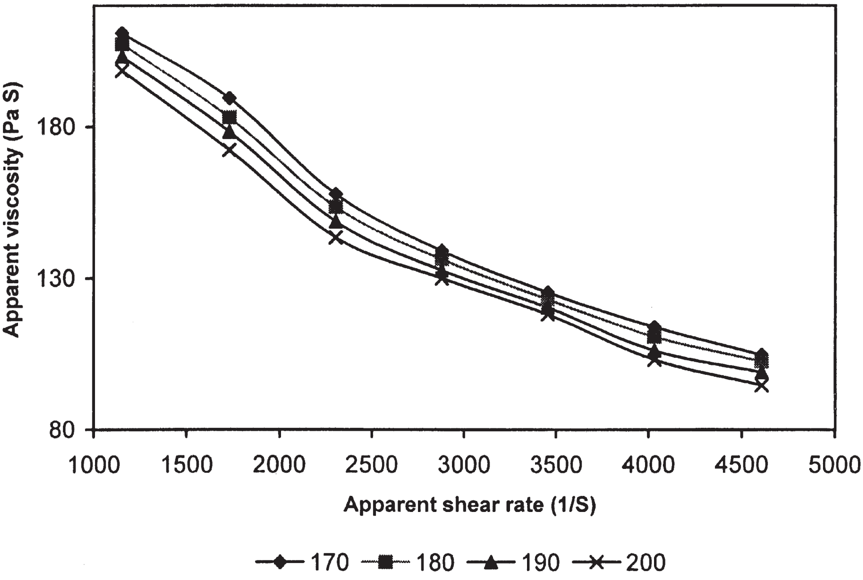


FIGURE 17 Flow curves of modified LDPE at different temperatures.

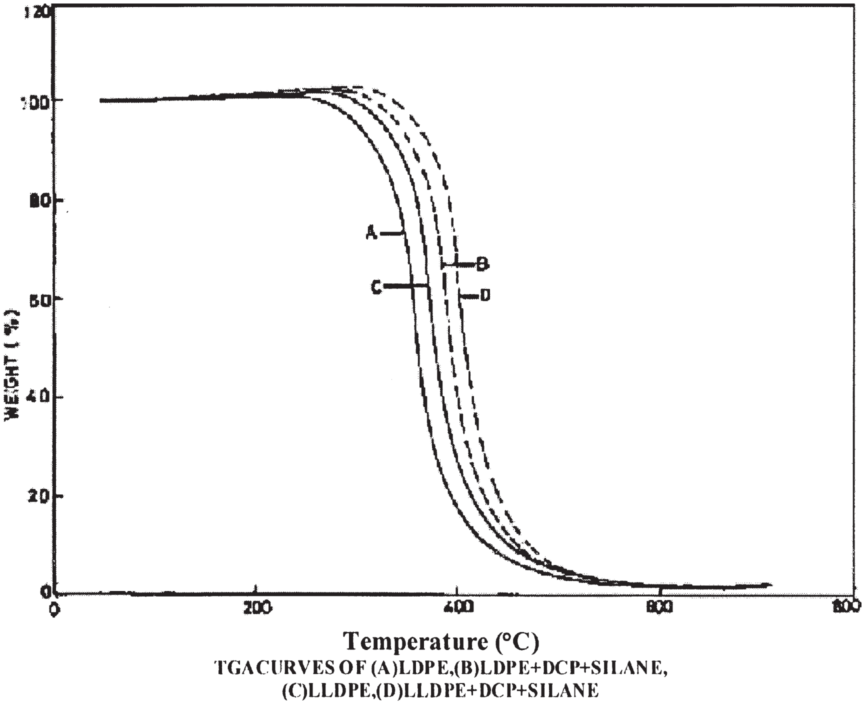
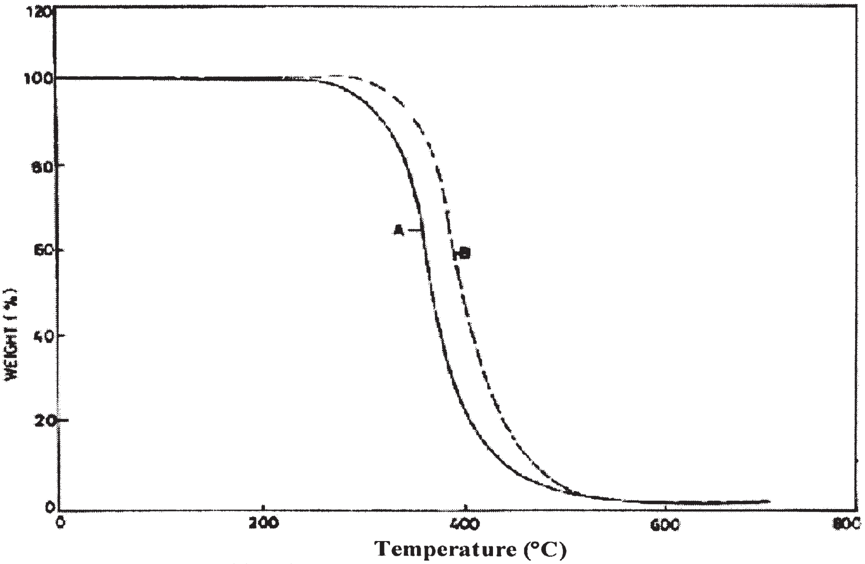


FIGURE 18 Thermogravimetric curves of unmodified and modified LDPE and LLDPE.

Si–O–Si links between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. Figure 15 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. Figure 16 shows the extrudate swell ratio vs shear rate of unmodified and silane grafted LLDPE. 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 silane grafting in all the cases. The increase in swell ratio may be due to crosslinking of the polymer and subsequent reduction in crystallinity. Figure 17 shows the variation of viscosity with temperature of silane grafted LDPE at different shear rates. The viscosity decreases with increase in temperature as expected.

The thermogravimetric curves of unmodified and silane grafted LDPE and LLDPE are shown in Figure 18. Silane grafting shows improvement in thermal stability as expected. The thermogravimetric curves of unmodified and silane grafted LDPE/LLDPE blend are



TGA CURVES OF (A) BLEND, (B)BLEND+DCP+SILANE

FIGURE 19 Thermogravimetric curves of unmodified and modified LDPE/LLDPE blend.

TABLE 1 The Temperature of Derivative Weight % Peak

Material	Peak tem (°C)
LDPE alone	373.8
LDPE + DCP + SILANE	386.1
Blend alone	380.3
Blend + DCP + SILANE	392.7
LLDPE alone	383.5
LLDPE + DCP + SILANE	397.3

shown in Figure 19. Silane grafted LLDPE and LDPE/LLDPE blend shows better thermal stability than silane grafted LDPE.

Decomposition temperatures are given in Table 1. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density. The gel content of silane grafted LDPE is compared with that of LLDPE and 50/50 LDPE/LLDPE blend in Table 2. 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 2 Gel Content Values at 190°C

Material	Gel content (%)
LDPE + DCP + SILANE	32.6
Blend + DCP + SILANE	38.2
LLDPE + DCP + SILANE	40.7

TABLE 3 Variation of Density with Modification

Material	Density
LDPE	0.973
LDPE + DCP + SILANE	0.959
BLEND	0.957
BLEND + DCP + SILANE	0.939
LLDPE	0.947
LLDPE + DCP + SILANE	0.923

The densities of unmodified and modified LDPE, LLDPE and their blend are shown in Table 3. The densities of the modified polymers are found to marginally reduce upon modification. This behavior can be attributed to reduction of crystallinity, because of network formation.

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 the 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 behavior and thermal stability.

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