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Studies on dynamic mechanical and mechanical properties of vinyloxyaminosilane grafted ethylene propylene diene terpolymer/linear low density polyethylene (EPDM-g-VOS/LLDPE) blends

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Abstract

The dynamic mechanical properties of vinyloxyaminosilane grafted ethylene propylene diene terpolymer/linear low density polyethylene (EPDM-g-VOS/LLDPE) blends have been evaluated with special reference to the effect of blend ratio. It has been found that increasing the proportion of LLDPE in the blends decreases the T_g values and increases the storage modulus (E') and loss modulus (E'') due to increase in crystallinity. A gradual increase in the values of tan δ_{max} is observed for the blends with increase in EPDM-g-VOS concentration, which indicates that no phase inversion occurs. But however the higher increase in tan δ_{max} after 50 wt.% of EPDM-g-VOS composition is due to small change in crystallinity and is ascertained by SEM micrographs. Mechanical properties such as tensile strength, Young's modulus and hardness increase with increases in LLDPE concentration in the blends and with dicumyl peroxide (DCP) concentration whereas the values of elongation at break are decreased with increase in LLDPE and DCP concentration.

Keywords: EPDM-g-VOS/LLDPE blends; Loss modulus; Storage modulus; Mechanical properties

1. Introduction

Thermoplastic elastomers are materials having the processing characteristics of thermoplastics and mechanical properties of vulcanized elastomers. Polyolefin elastomer blends obtained by physical blending gained considerable attention and importance due to the simple method of preparation. The effect of blend ratios and dynamic cross-linking of the elastomer phase on the mechanical properties, processing characteristics and failure properties of polyolefin thermoplastic elastomers have been reviewed by several authors [1–9]. The main disadvantage of polyolefin–elastomer blend is the lower service temperature, which is dependent on the crystalline melting temperature of the polyolefin component.

Garfasegna [10] prepared low-voltage and medium-voltage cable insulant using vinyltrimethoxysilane (VTMO) grafted and moisture cross-linked ethylene–propylene copolymer and ethylene–propylene–diene terpolymer (EPDM). Tanida et al. [11] prepared heat shrinkable tubes by grafting VTMO with EPDM. Bustin et al. [12] synthesized VTMO grafted EPDM and polyethylene using Brabender mixer. Kawada et al. [13] prepared heat resistant silane grafted polymers with EPDM and other α-olefin polymers. Umeda et al. [14] prepared composites exhibiting better processability and thermal stability than original elastomers using silane grafted EPDM and the other α-olefins with silica, stearic

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acid, antioxidant, zinc oxide and dicumyl peroxide (DCP). Weing et al. [15] studied the interaction of PP with EPDM in their blends by using differential scanning calorimetry, dynamic mechanical analysis and X-ray scattering. Schaefer et al. [16] investigated the mechanical properties, storage modulus and loss modulus of ternary polymer system consisting of polypropylene, EPDM using different types of inorganic fillers like kaolin and $BaSO_4$.

An attempt has been made in the present study to evaluate dynamic mechanical and mechanical properties of EPDM-g-vinyloxyaminosilane/LLDPE blends with reference to blend ratio on storage modulus (E'); loss modulus (E''); and loss tangent ($\tan\delta$) at different temperatures and the effect of LLDPE and DCP concentrations on mechanical properties in order to assess the suitability of these blends for engineering applications for better performance than unmodified EPDM.

2. Experimental

2.1. Materials

The EPDM (ENB) rubber employed in this study was a commercial grade (Nordel IP 5750R) (ethylene/propylene/5-ethylidene-2-norbornene = 71/20/9 by wt.%, with Mooney viscosity, $ML_{(1+4)}$, of 50 at 125 °C and specific gravity of 0.88) of Du Pont Dow Elastomers, USA. The vinyloxyaminosilane (VOS) ($M_w = 313$, specific gravity = 0. 988, viscosity = 11.5 cP and b.p. = 300 °C) was procured from Wacker-Chemie, Germany. LLDPE (ethylene–1-octene) used was commercial grade (Engage 8003) with Mooney viscosity, $ML_{(1+4)}$, of 22 at 121 °C, MFI = 1.0 dg/min and density = 0.880 g/cc of DuPont Dow Elastomers, USA. DCP (99% assay with m.p. = 30 °C) was obtained from Concord Chemical Industrial Co., Taiwan.

2.2. Preparation of EPDM-g-VOS

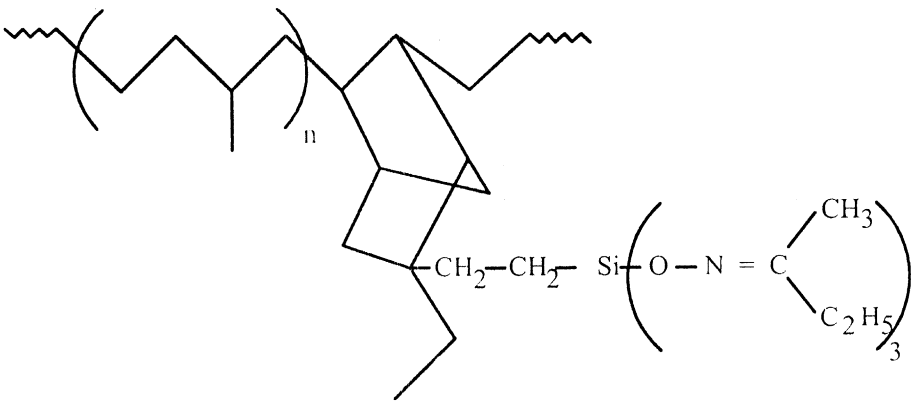
The EPDM-g-VOS has been synthesized in toluene using DCP as initiator. Using the optimum efficiency conditions obtained from solution grafting, EPDM-g-VOS has been prepared by melt mixing technique. The EPDM (ENB) semicrystalline granules were coated with 0.2 wt.% DCP initiator dissolved in the 2.0 wt.% VOS based on 100 g of EPDM. The treated polymer was processed in a Haake Rheocord-90, torque rheometer at 160 °C for 6 min at mixer rotation speed of 30 rpm. Since the DCP concentration was low, the grafting of VOS is probably the dominating reaction than the co-cross-linking of EPDM in the presence of VOS and DCP. The structure of EPDM-g-VOS and its possible cross-linking mechanisms using hot water are given in Schemes 1 and 2 respectively.

2.3. Preparation of EPDM-g-VOS/LLDPE blends

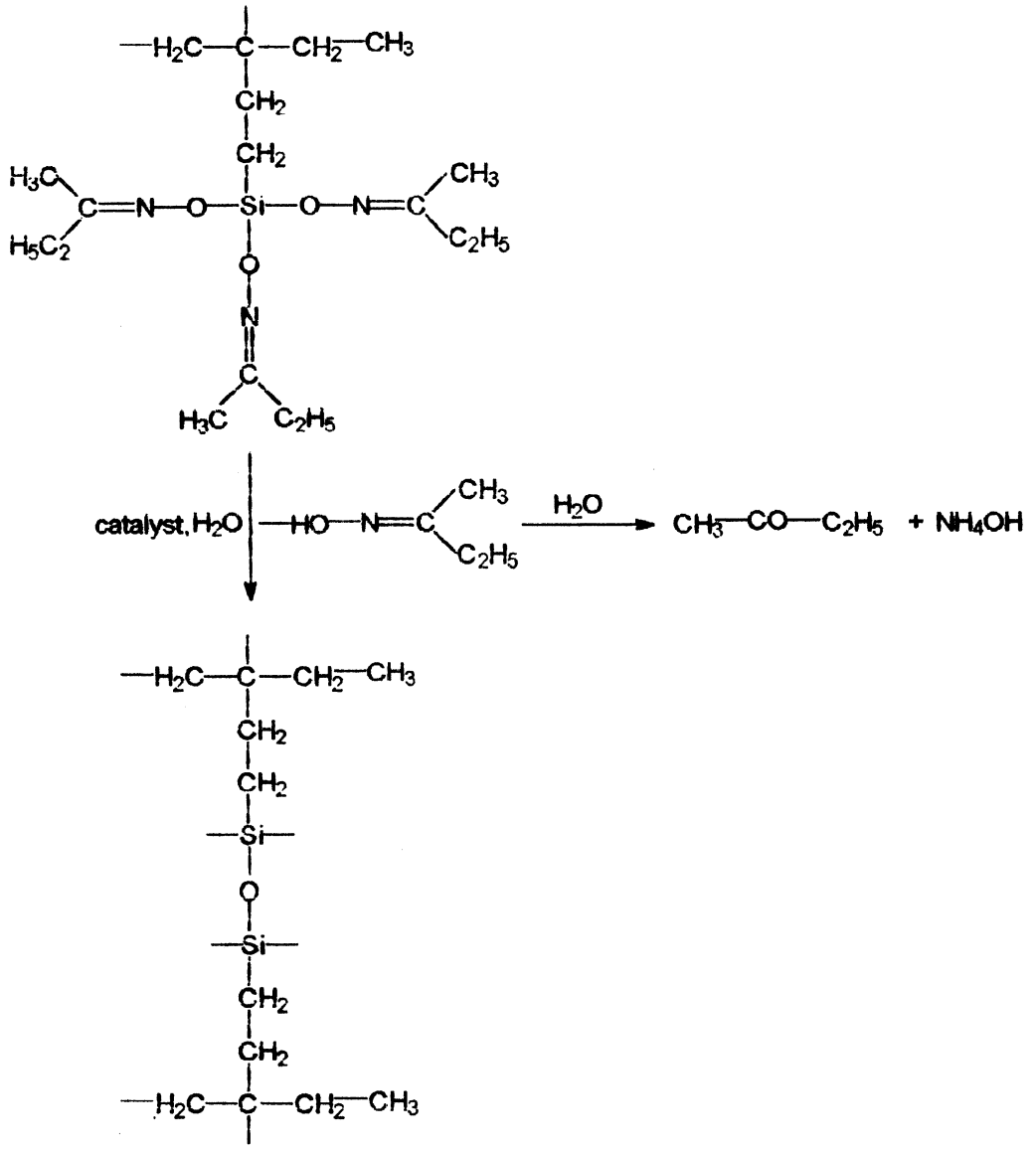
The EPDM-g-VOS, 0.1 wt.% dibutyl tindilaurate and fixed amount of DCP (1.0, 2.0 and 3.0 wt.%, based on the amount of EPDM-g-VOS) were preblended in a two roll mill at 80 °C for 10 min. Blends of EPDM-g-VOS with LLDPE were prepared on a two roll mixing mill (Nishimura 84.301 Type, Japan). The LLDPE was blended with EPDM-g-VOS with the various concentrations of DCP in the molten state at 180 °C for 15 min. The linear blends (i.e., uncross-linked) were also prepared and characterized. The compounding recipe of the blends are presented in Table 1.

2.4. Preparation of test specimen

The blends were processed in the form of 3 mm sheets using compression moulding at 180 °C for 10 min using 10 kg/cm^2 pressure. The compression moulded EPDM-g-VOS and EPDM-g-VOS/LLDPE blends were cured



Scheme 1. Structure of VOS grafted EPDM.



Scheme 2. Schematic representation of cross-linking mechanism of EPDM-g-VOS.

by immersion in boiling water for 2 h. The test specimens were prepared from the compression molded sheets using punching technique as per ASTM standards.

2.5. Dynamic mechanical properties

The ability of a polymeric material to withstand loads at elevated temperatures is one of the key aspects of engineering performance to be studied. Dynamic mechanical analysis is a method that measures the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. The loss tangent is a sensitive indicator of cross-linking in the polymer skeleton. The dynamic mechanical properties of linear and cross-linked EPDM-g-VOS, LLDPE and EPDM-g-VOS/LLDPE blends were measured using a dynamic mechanical thermal analyser (Polymer Laboratories DMTA MK-II) at a dynamic strain amplitude of 0.325 cm and a frequency of 35 Hz. Moulded samples of dimensions $80 \times 15 \times 10$ mm^3 were used for testing. The temperatures of testing were in the range between −100 and 120 °C at the heating rate of samples was 1 °C/min.

Table 1
Compounding recipe for EPDM-g-VOS/LLDPE blends

Composition	EPDM-g-VOS	LLDPE	DCP[a]
$E_{90}X_{10\,(L)}$	90	10	0
$E_{75}X_{25\,(L)}$	75	25	0
$E_{50}X_{50\,(L)}$	50	50	0
$E_{25}X_{75\,(L)}$	25	75	0
$E_{10}X_{90\,(L)}$	10	90	0
$E_{90}X_{10\,(V)}$	90	10	1
$E_{75}X_{25\,(V)}$	75	25	1
$E_{50}X_{50\,(V)}$	50	50	1
$E_{25}X_{75\,(V)}$	25	75	1
$E_{10}X_{90\,(v)}$	10	90	1
$E_{90}X_{10\,(V)}$	90	10	2
$E_{75}X_{25\,(V)}$	75	25	2
$E_{50}X_{50\,(V)}$	50	50	2
$E_{25}X_{75\,(V)}$	25	75	2
$E_{10}X_{90\,(v)}$	10	90	2
$E_{90}X_{10\,(V)}$	90	10	3
$E_{75}X_{25\,(V)}$	75	25	3
$E_{50}X_{50\,(V)}$	50	50	3
$E_{25}X_{75\,(V)}$	25	75	3
$E_{10}X_{90\,(v)}$	10	90	3
$E_{(W)}$	100	0	0
$X_{(L)}$	0	100	0
$X_{(*)}$	0	100	1
$X_{(*)}$	0	100	2
$X_{(*)}$	0	100	3

E: EPDM-g-VOS, X: LLDPE, (L): Linear (uncross-linked), (V): Cross-linked by both DCP and hot water, (*): Cross-linked by DCP, (W): Cross-linked by hot water only.

[a] DCP concentration is based on 100 phr of EPDM-g-VOS.

2.6. Mechanical properties

Tensile properties of the samples were studied at 25 ± 2 °C according to ASTM D 412-87 test method using dumb-bell shaped test pieces at a cross head speed of 500 mm/min using an Universal Testing Machine (ZWICK-1484). The hardness of the samples was measured according to ASTM D 2240-86 and expressed in Shore Å units.

2.7. Morphology

For studying the morphology of the blends, LLDPE was preferentially extracted from the linear blends of EPDM-g-VOS/LLDPE using xylene. The cryogenically fractured edge of the sample was kept immersed in xylene for about 48 h at ambient temperature for preferential extraction of LLDPE. The samples were dried in an air oven at 120 °C for 24 h and preserved in a desiccator. The solvent extracted samples were sputter coated with gold (Au) and SEM observations were made using Hitachi model S 2400 scanning electron microscope.

3. Results and discussion

3.1. Effect of temperature on loss tangent

The loss tangent ($\tan\delta$) values of the linear EPDM-g-VOS, LLDPE and EPDM-g-VOS/LLDPE blends of different composition at 35 Hz as a function of temperature (−100 to 120 °C) are presented in Fig. 1. The

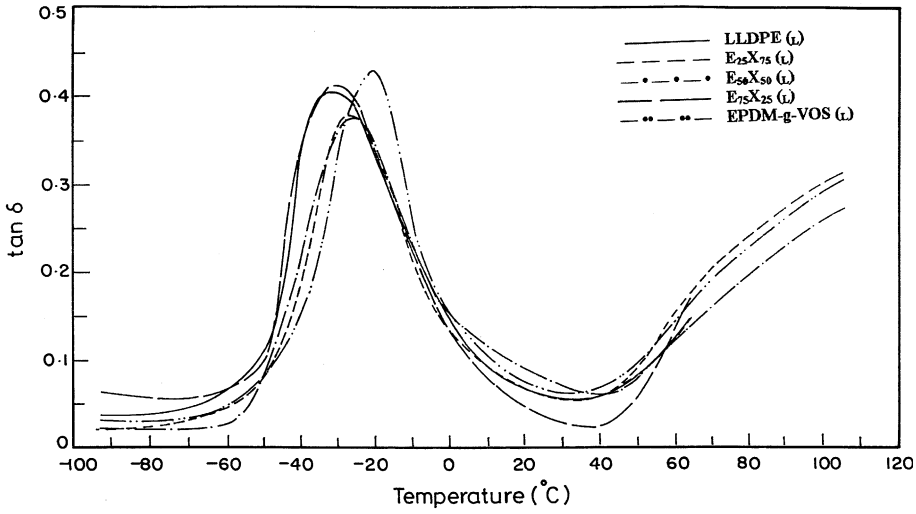


Fig. 1. The effect of temperature on tan δ values of linear EPDM-g-VOS/LLDPE blends.

values of glass transition temperature (T_g) is obtained from the temperature corresponding to peak tan δ_{max}. In the present investigation, the difference in T_g values of components involved in the blend formation viz., EPDM-g-VOS (−25 °C) and LLDPE (−38.6 °C) respectively is less than 20 °C and hence miscibility of the blends cannot be ascertained using this T_g values. Further it is observed that the values of T_g decreased with increase in concentration of LLDPE due to miscibility of the blends.

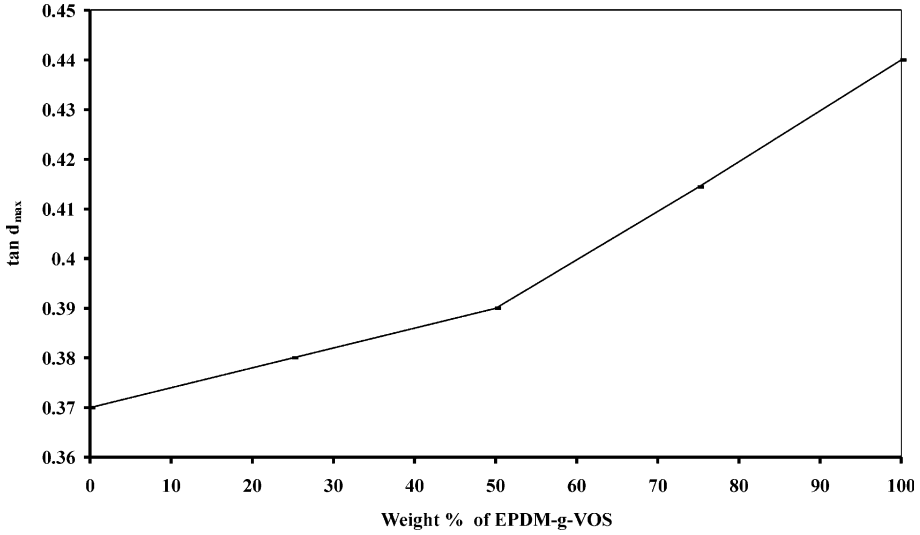


Fig. 2. Variation of tan δ with weight percentage of EPDM-g-VOS.

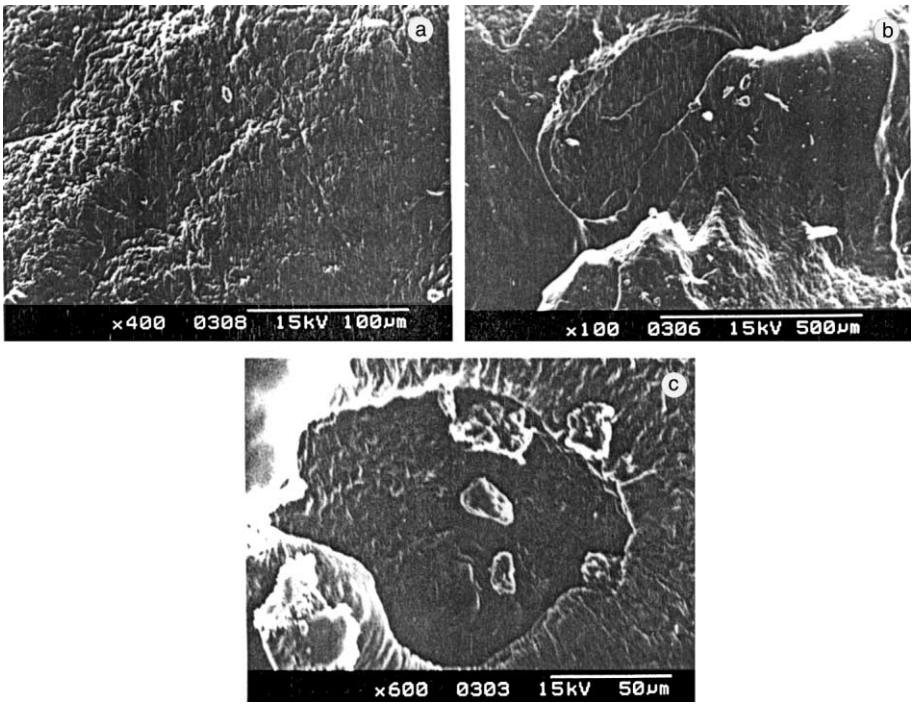


Fig. 3. Scanning electron micrographs of EPDM-graft-VOS/LLDPE blends: (a) $E_{25}X_{75}$, (b) $E_{50}X_{50}$, and (c) $E_{75}X_{25}$.

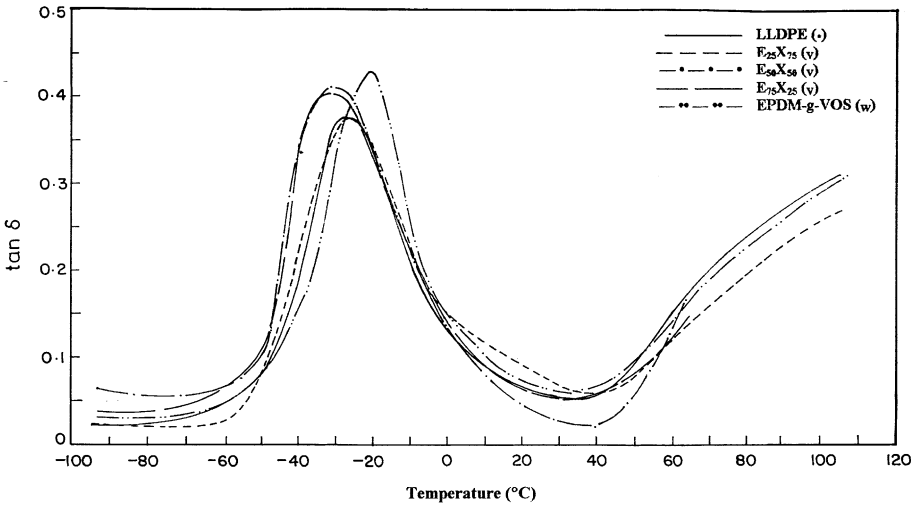


Fig. 4. The effect of temperature (−100 to 100 °C) on tan δ values of cross-linked EPDM-g-VOS/LLDPE blends.

3.2. Effect of EPDM-g-VOS concentration loss tangent (tan δ)

The values of peak $\tan\delta_{max}$ obtained for linear EPDM-g-VOS, LLDPE and EPDM-g-VOS/LLDPE blends as a function of concentration of EPDM-g-VOS are presented in Fig. 2. It is observed that the value of $\tan\delta_{max}$ increases gradually with increase in wt.% of EPDM-g-VOS in EPDM-g-VOS/LLDPE blends which indicates that no phase inversion occurs as the composition increases. It is also known that no phase inversion will occur when two amorphous polymers form a polymer blend. Since both EPDM-g-VOS and LLDPE are amorphous, they are compatible in all compositions. However a change in height occurs from 50 wt.% composition due to the small change in crystallinity and is ascertained from SEM micrographs presented in Fig. 3(a)–(c). In the blend $E_{25}X_{75}$, EPDM-g-VOS phase remains as dispersed particles in the LLDPE matrix, which is observed as black spots in Fig. 3(a). These black spots are formed due to the extraction of LLDPE from the blends. In the blend $E_{75}X_{25}$, LLDPE is in the dispersed phase and EPDM-g-VOS is in continuous phase (Fig. 3(c)). In the $E_{50}X_{50}$ blend, both EPDM-g-VOS and LLDPE form continuous phases as shown by continuous, narrow white layers followed by thick black layers in Fig. 3(b).

3.3. Effect of cross-linking

The $\tan\delta_{max}$ values of hot water cross-linked EPDM-g-VOS, DCP cross-linked (2 wt.%) LLDPE and both hot water and DCP (2 wt.%) cross-linked EPDM-g-VOS/LLDPE blends of different composition as a function of temperature (−100 to 100 °C) are presented in Fig. 4. The T_g values of both hot water and DCP cross-linked blends are higher than linear EPDM-g-VOS/LLDPE blends due to network molecular structure.

The T_g values of linear and cross-linked blends are presented in Table 2. In the case of linear blends for every 25 wt.% increase in EPDM-g-VOS, the values of T_g is increased to 8%. Similarly, 13% increase in the value of T_g is observed for every 25 wt. % increase of EPDM-g-VOS in the cases of cross-linked blends. The increase in T_g values of cross-linked blends are due to restriction of chain flexibility.

Table 2
T_g of linear and cross-linked EPDM-g-VOS/LLDPE blends at 35 Hz

Composition	Linear blends	Cross-linked blends
	T_g (°C)	T_g (°C)
$E_{(L)}$	−25.0	–
$X_{(L)}$	−38.6	–
$E_{75}X_{25\,(L)}$	−28.0	–
$E_{50}X_{50\,(L)}$	−30.0	–
$E_{25}X_{75\,(L)}$	−34.2	–
$E_{75}X_{25\,(V)}$	–	−23.0
$E_{50}X_{50\,(V)}$	–	−25.0
$E_{25}X_{75\,(V)}$	–	−31.2
$E_{(W)}$	–	−21.0
$X_{(*)}$	–	−32.9

(V): Cross-linked by both DCP and Hot water, (W): Cross-linked by hot water only, (*): Cross-linked by DCP only.

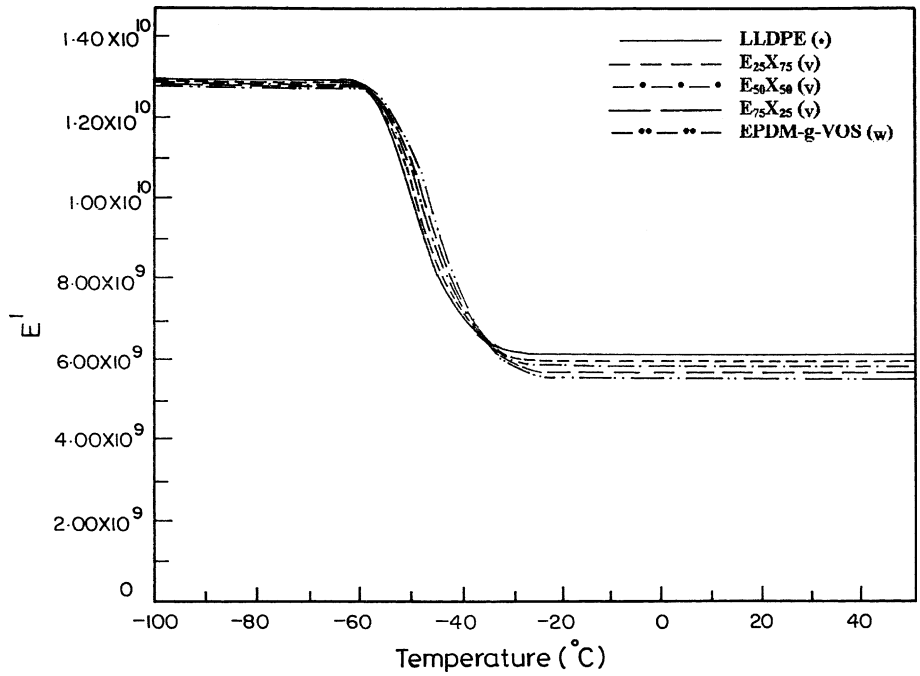


Fig. 5. The effect of temperature (−100 to 50 °C) on the storage modulus of cross-linked EPDM-g-VOS/LLDPE blends.

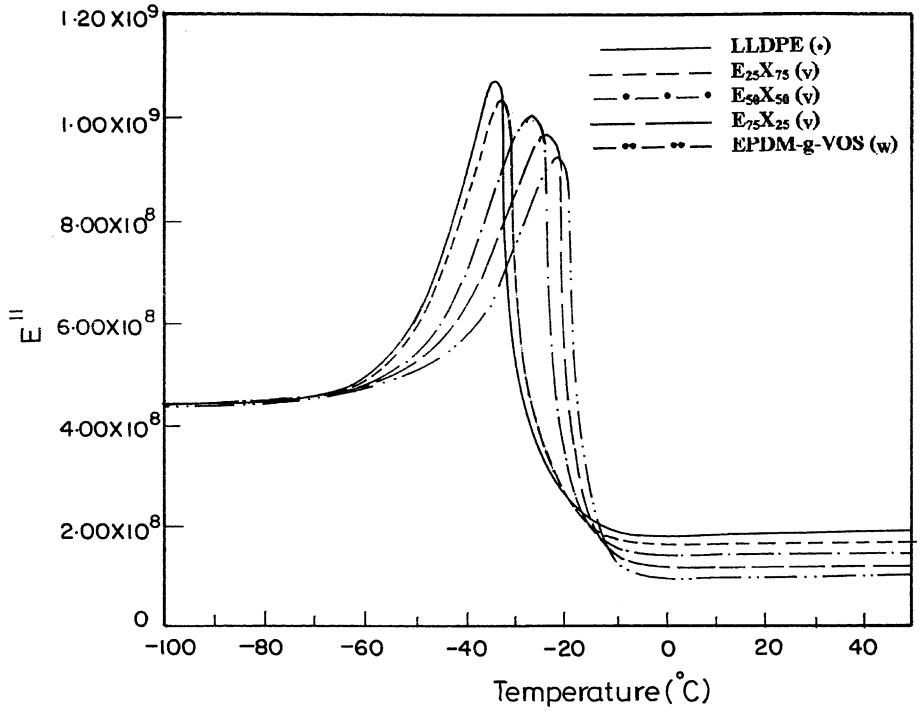


Fig. 6. The effect of temperature (−100 to 50 °C) on the loss modulus of cross-linked EPDM-g-VOS/LLDPE blends.

3.4. Effect of temperature on storage modulus (E′) and loss modulus(E″)

The influence of temperature (−100 to 50 °C) on storage modulus (E') and loss modulus (E'') of cross-linked EPDM-g-VOS, LLDPE and EPDM-g-VOS/ LLDPE blends of different compositions are presented in Figs. 5 and 6 respectively. The EPDM-g-VOS, LLDPE and EPDM-g-VOS/ LLDPE blends of different composition exhibit nearly the same moduli of 1.3×10^{10} Pa in the low temperature region or glassy region due to the similarity in the crystalline character.

3.5. Effect of LLDPE concentration on storage modulus (E′) and loss modulus(E″)

The values of storage moduli and loss moduli of cross-linked EPDM-g-VOS, LLDPE and EPDM-g-VOS/ LLDPE blends of different compositions are presented in Figs. 5 and 6. It is observed that the storage moduli and loss moduli of blends are increased with increase of LLDPE concentration due to increase of crystalline structure. This fact is further supported by the observations made by Murayama [17] for PP/EPDM blends.

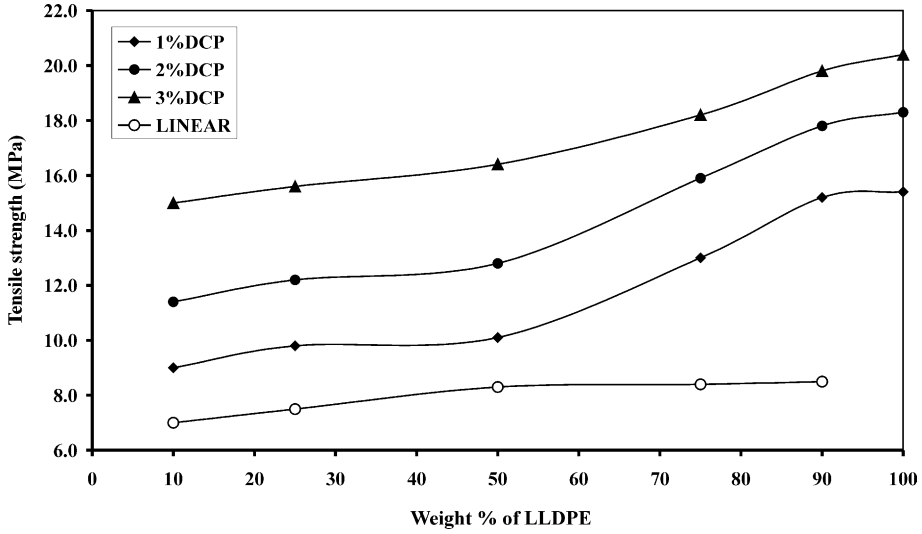


Fig. 7. Variation of tensile strength as a function of weight percentage of LLDPE in the cross-linked blends.

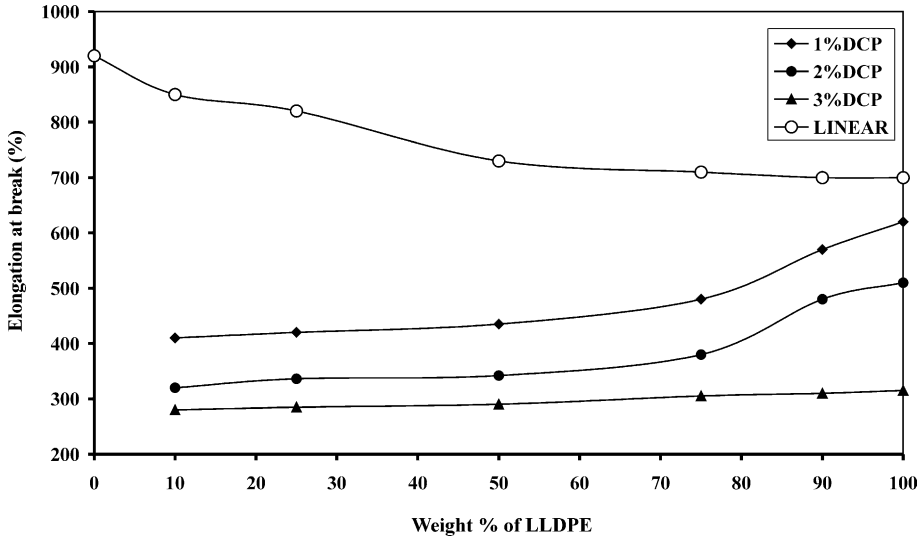


Fig. 8. Variation of elongation at break as a function of weight percentage of LLDPE in the cross-linked blends.

3.6. Mechanical properties of linear blends

3.6.1. Effect of LLDPE concentration

The mechanical properties such as tensile strength, elongation at break, Young's modulus and hardness of linear EPDM-g-VOS/LLDPE blends are presented in Figs. 7–10 respectively. Unmodified LLDPE and LLDPE rich EPDM-g-VOS/LLDPE blends show higher values of tensile strength, Young's modulus and hardness than those of EPDM-g-VOS rich blends. EPDM-g-VOS exhibit typical uncross-linked elastic behaviour. The blend comprising 75 wt.% EPDM-g-VOS and 25 wt.% LLDPE $(E_{75}X_{25})_{(L)}$ possess a similar tensile and modulus values as those observed for EPDM-g-VOS. In the case of $E_{50}X_{50(L)}$ blend it is observed that the tensile and modulus behaviour are intermediate to those of blends having compositions between $E_{10}X_{90(L)}$ and $E_{90}X_{10(L)}$. The values of elongation at break are increased with increase in concentration of EPDM-g-VOS due to branching and molecular flexibility and decreased with increase in LLDPE concentration due to the contribution of crystalline domains by LLDPE.

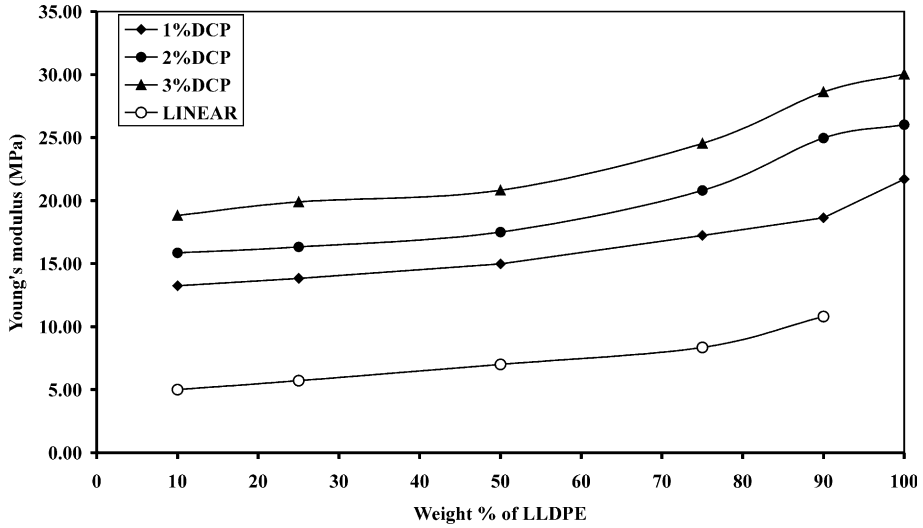


Fig. 9. Variation of Young's modulus as a function of weight percentage of LLDPE in the cross-linked blends.

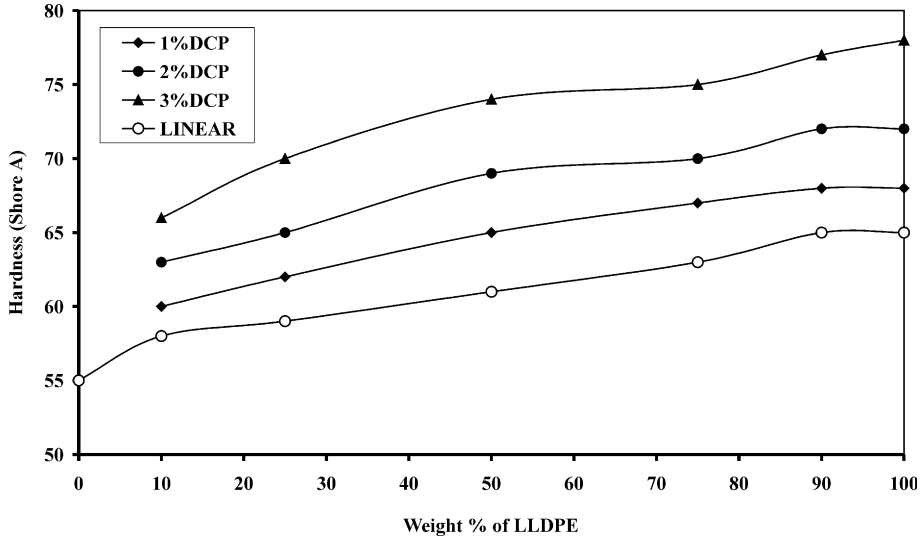
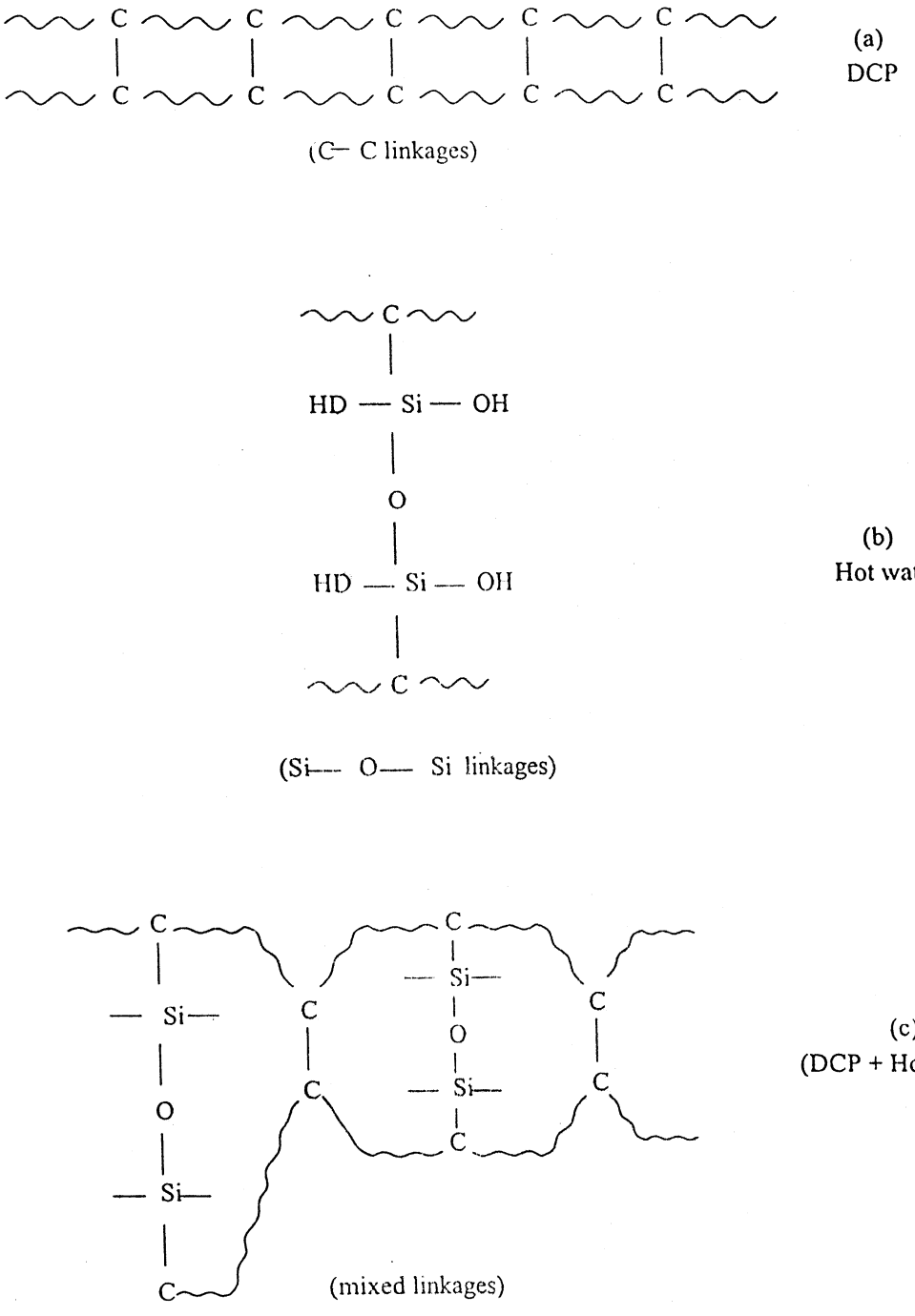


Fig. 10. Variation of hardness as a function of weight percentage of LLDPE in the cross-linked blends.



Scheme 3. Schematic representation of cross-linking reactions: (a) DCP, (b) hot water and (c) DCP and hot water.

3.7. Mechanical properties of cross-linked blends

3.7.1. Effect of LLDPE concentration

The mechanical properties such as tensile strength, elongation at break, Young's modulus and hardness of cross-linked EPDM-g-VOS/LLDPE blends with increase in LLDPE composition are presented in Figs. 7–10 respectively. The increase in tensile values may be explained due to the influence of crystalline domains of LLDPE. An observation similar to tensile behaviour of

Table 3
Young's modulus and cross-link density of EPDM-g-VOS/LLDPE blends

Sample code	Young's modulus (MPa)	Cross-link density ($\times 10^4$) g mol/cc
E (W)	18.64	2.86
$E_{90}X_{10}$ (V)	18.82	2.93
$E_{75}X_{25}$ (V)	19.90	2.99
$E_{50}X_{50}$ (V)	20.82	3.07
$E_{25}X_{75}$ (V)	24.53	3.28
$E_{10}X_{90}$ (V)	28.62	3.44
X (*)	30.04	3.69

EPDM-g-VOS/LLDPE blends are also noticed in the case of the values of Young's modulus and hardness (Figs. 9 and 10). The value of elongation at break is also increased with increase in LLDPE and decreased with increase in concentration of EPDM-g-VOS (Fig. 8). This behaviour may be explained due to the formation of hybrid polyolefin thermoplastic elastomer comprising flexible and rigid domains.

3.7.2. Effect of DCP concentration

The influence of increase in concentration of DCP on mechanical properties of different EPDM-g-VOS/LLDPE cross-linked blends are presented in Figs. 7–10. The mechanical properties of blends are increased with increase in concentration of peroxide due to increases in cross-link density. It is observed that for every 1% increase in concentration of DCP, the value of tensile strength and Young's modulus in the blends are increased to about 18–25% and 19–20% respectively. Further, the values of elongation at break decreased with increase in concentration of peroxide. To relate the mechanical properties with respect the formation of network structure, a tentative schematic representation of the nature of cross-links formed in EPDM-g-VOS by hot water, cross-links in LLDPE by DCP and EPDM-g-VOS/LLDPE blends by both hot water and DCP are presented in Scheme 3.

The linkages present in different blend systems are C–C, Si–O, Si–O–Si and Si–C. The blend systems having high concentrations of EPDM-g-VOS possess higher proportion of Si–O–Si linkage than C–C linkage that lowers the values of tensile strength and Young's modulus with enhanced elongation at break are due to its free rotation and flexibility.

The values of cross-link density are measured by swelling method [18] for different blend systems using 2 wt.% DCP along with values of Young's modulus are presented in Table 3. The values of cross-link density of the blends are increased with increase in concentration of LLDPE due to co-cross-linking. It is also observed that for 50 wt.% increase of LLDPE, the cross-link density is increased to 10% (Table 3).

4. Conclusions

Data obtained from dynamic mechanical analysis provides the evidence for decreased values of T_g with increase in concentration of LLDPE in the linear blends due to miscibility and the T_g values of cross-linked blends are higher than linear blends due to chain entanglement. The values of $\tan\delta_{max}$ increases gradually with increase of EPDM-g-VOS concentration in the blends which indicates no phase inversion. The values of storage modulus (E') and loss modulus (E'') of blends are increased with increase in LLDPE concentration. The mechanical properties such as tensile strength, Young's modulus and hardness of linear and cross-linked EPDM-g-VOS/LLDPE blends are increased with increase in concentration of LLDPE. The value of elongation at break in the case of linear blends is increased with increase in LLDPE concentration, whereas in the case of cross-linked blends it is decreased with increase in LLDPE concentration. Based on the results obtained from experimental studies, it is suggested that LLDPE rich EPDM-g-VOS/LLDPE blends can be used as a viable competitive products in the field of automotive industry for gaskets, oil seals, radiator hoses. Further, it is also suggested that the results of glass transition temperature, $\tan\delta_{max}$, storage modulus, loss modulus and mechanical properties of the blends having high concentration of EPDM-g-VOS indicate that these blends could be used for low temperature applications especially for submarine cables.

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