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Plasticization of an ionic thermoplastic elastomer based on EPDM by diethylene glycol

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Zinc sulfonated EPDM of high (75 wt%) ethylene content behaves as an ionic thermoplastic elastomer. Diethylene glycol plasticizes the ionic domains of zinc sulfonated EPDM, without affecting the hydrocarbon backbone. Studies include measurement of physical properties, processability studies in a Monsanto processability tester (MPT), dynamic mechanical analyses (d.m.a.) and dielectric thermal analyses (d.e.t.a.). Copyright © 1996 Elsevier Science Ltd.

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Introduction

Ionomers are microphase separated polymers containing low levels of ionic functional groups[1–3]. Because of the interionic electrostatic forces, as well as the high degree of thermodynamic incompatibility between the polar ionic groups and the non-polar hydrocarbon polymer matrix, the ionic groups aggregate in the bulk and form physical crosslinks[4,5]. Zinc sulfonated EPDM, hereafter abbreviated as SEPDM is an ionic thermoplastic elastomer[6]. The presence of zinc sulfonate groups provides strong physical crosslinks at ambient temperatures, but the elastomer becomes thermoplastic at elevated temperatures permitting melt processing[7–9]. It has been reported that dimethyl sulfoxide (DMSO) acts as an ionic plasticizer in SEPDM and it causes reduction in melt viscosity and improvement in melt processability[6]. The effect of diethylene glycol, hereafter abbreviated as DEG, on properties of SEPDM has not been investigated so far. The objective of this work is to study the plasticization effect of DEG on SEPDM.

Experimental

Materials. Polymers used in this study are: (i) thermoplastic EPDM (M_n: 52 000 and M_w: 151 000) containing 75% ethylene, 20% propylene and 5% 5-ethylidine-2-norbornene and, (ii) SEPDM (level of sulfonation, 30 meq/100 g polymer) formed by the sulfonation of the pendent unsaturation in the thermoplastic EPDM, followed by neutralization of the resultant EPDM sulfonic acid using the procedure described by Makowski *et al.*[10]. Both polymers were supplied by the Exxon Research & Engineering Company, New Jersey, USA. DEG of density 1.118 g cm^{-3} and boiling point 245°C, was obtained from E. Merck (India) Ltd., Bombay.

Sample preparation. Rubber compounds were prepared in a Brabender Plasticorder (model PLE-330) using a cam-type rotor. Mixing was done for 6 min at a rotor speed of 80 rev min^{-1} and at a temperature of 150°C. The neat polymers were also masticated under the same conditions. Test specimens were prepared by moulding in an electrically heated hydraulic press for 5 min at 160°C under a pressure of 10 MPa.

Determination of physical properties. The stress–strain properties were determined at 25°C, according to ASTM D412 (1987) using dumb-bell specimens in a Zwick Universal Testing Machine (UTM), model 1445, using a cross-head speed of 500 mm min^{-1}. The tear resistance was determined as per ASTM D624 (1986) using unnicked 90° angle test pieces (die C) at 25°C at a cross head speed of 500 mm min^{-1} in Zwick UTM model 1445. The hysteresis loss was determined under strain mode according to ASTM D412 (1980) by stretching dumb-bell specimens to a strain level of 200% in Zwick UTM model 1445.

Determination of processability. The processability studies were carried out using a Monsanto Processability Tester (MPT) at the shear rates of 36, 90, 181 and 289 s^{-1} and a temperature of 170°C. The capillary length (29.77 mm) to diameter (1.50 mm) ratio was 20 with a compound entrance angle of 45 and 60°. The preheat time for each sample was 10 min.

Dynamic mechanic analysis. Dynamic mechanical properties were measured in a Rheovibron DDV-III-EP viscoelastometer at a frequency of 3.5 Hz and a strain amplitude of 0.0025 cm. The measurements were carried out over a temperature range of $-100°$ to $+200°$C at a heating rate of 1°C min^{-1}.

Dielectric thermal analysis. Dielectric thermal analyses were done in a Du Pont DEA 2970 Dielectric

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Table 1 Physical properties at 25°C

Composition of the mix	Modulus at 300% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN m^{-1})	Hysteresis loss (J m^{-2}) 10^3
EPDM	2.7	11.0	1036	63	82
SEPDM	7.3	23.0	691	115	146
SEPDM + DEG 2.5 phr[a]	5.0	19.9	745	112	140
SEPDM + DEG 5 phr	4.3	16.0	851	102	131
SEPDM + DEG 7.5 phr	3.7	12.6	973	84	127

[a] phr stands for parts by weight per hundred parts of rubber

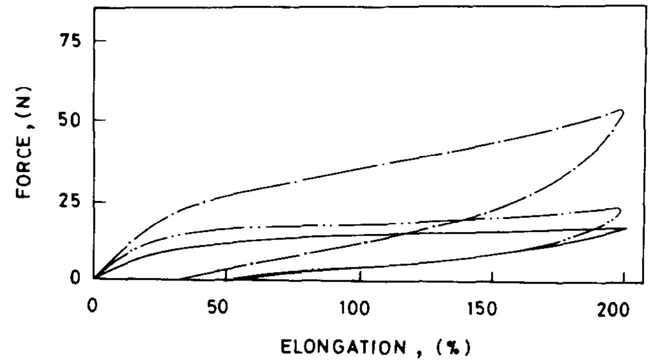

Figure 1 Hysteresis plots at 25°C of EPDM (——), SEPDM (— • —), and SEPDM + 5 phr DEG (— •• —)

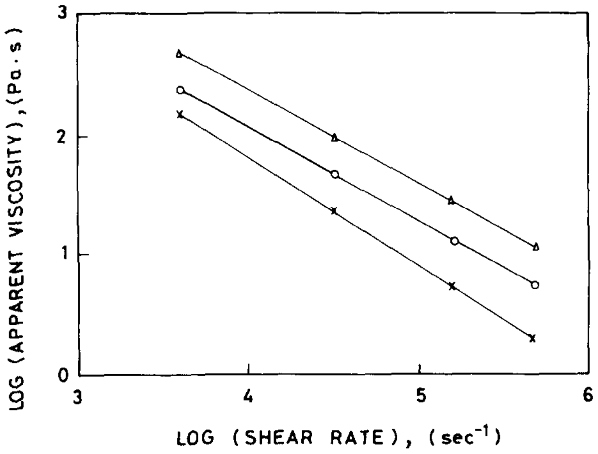

Figure 2 Apparent viscosity vs shear rate at 170°C of EPDM (–×–×–), SEPDM (–△–△–), and SEPDM + DEG 5 phr (–○–○–)

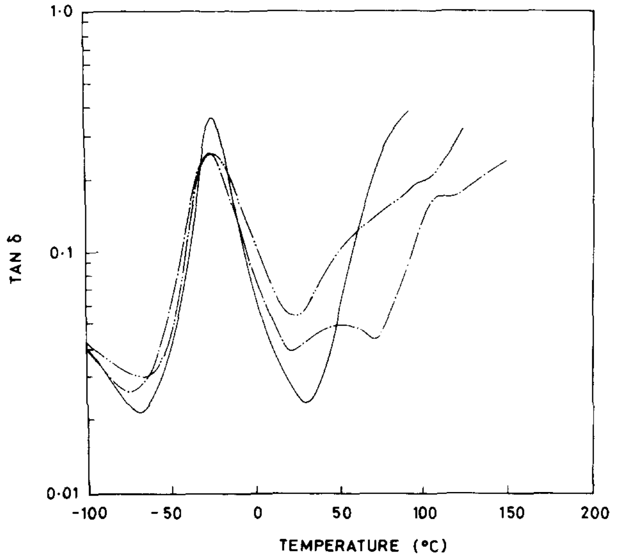

Figure 3 Semilogarithmic plots of tan δ vs temperature from dynamic mechanical analyses of EPDM (——), SEPDM (— • —) and SEPDM + DEG 5 phr (— •• —)

Analyser in a nitrogen environment. Square shaped specimens of 25 mm side and 0.5 mm thickness were used. The measurements were carried out over a frequency range of 1–100 000 Hz and temperature range of 20–200°C at a heating rate of 5°C min^{-1}.

Results and discussion

Physical properties. The physical properties of the neat polymers and the SEPDM compounds containing 2.5 phr (that is, parts by weight per hundred parts of rubber), 5 and 7.5 phr DEG are shown in *Table 1*. Bleeding was observed in a compound containing 10 phr DEG. However, no bleeding was observed when the DEG dosage was up to 7.5 phr. SEPDM, because of the presence of ionic domains, which act as physical crosslinks[11], showed higher modulus and tensile strength and lower elongation at break, as compared to the control thermoplastic EPDM. Incorporation of DEG caused gradual decrease in modulus and tensile strength and an increase in elongation at break.

SEPDM showed higher tear strength and hysteresis as compared to the thermoplastic EPDM. The higher tear strength of SEPDM could be attributed to the presence of ionic domains, which may be acting as tear deviators or arrestors[12,13]. The higher hysteresis (*Figure 1*) shown by SEPDM, could be attributed to the additional energy dissipation mechanisms, arising out of the ionic aggregates, which may be considered to behave as ultrafine reinforcing filler particles in the host polymer in addition to acting as multifunctional crosslinks[3,13]. Incorporation of DEG caused gradual decrease in tear strength and hysteresis of SEPDM. It is thus apparent that DEG acts as a plasticizer for SEPDM.

Processability. The log–log plots of apparent viscosity *versus* shear rate are shown in *Figure 2*. At all shear rates SEPDM showed higher viscosity than the thermoplastic EPDM. The SEPDM compound containing 5 phr DEG showed lower viscosity compared with neat SEPDM. The results show that DEG plasticizes SEPDM.

Table 2 Results of dynamic mechanical analyses

Composition of the mix	T_g[a] (°C)	Tan δ at T_g (tan δ_{max})	Transition due to ionic aggregates[b] (T_i), (°C)	Tan δ at T_i	Transition due to melting of crystallites[b] (°C)
EPDM	−26	0.365	—	—	[c]
SEPDM	−26	0.257	+27 to +80	0.040	+119
SEPDM + DEG 5 phr	−25	0.259	—	—	+109

[a] From (tan δ)$_{max}$ in the plot of tan δ vs temperature
[b] From tan δ vs temperature plot
[c] Not detectable

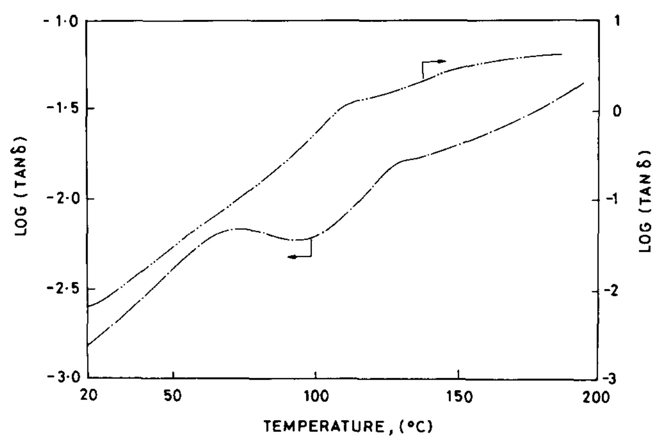

Figure 4 Semilogarithmic plots of dielectric loss tangent, tan δ vs temperature for SEPDM (— • —), and SEPDM + DEG 5 phr (— •• —)

Dynamic mechanical properties. Figure 3 shows the plot of loss tangent (tan δ) against temperature obtained from the dynamic mechanical analyses of thermoplastic EPDM, SEPDM and the SEPDM compound containing 5 phr DEG. The glass–rubber transition temperature (T_g) occurred around −26°C in the case of EPDM and SEPDM. Apart from T_g SEPDM showed two other transitions, one at +119°C, which is believed to be due to the melting of the crystalline zone of the polyethylene block, and another broad transition in the temperature range of +27 to +80°C, which is ascribed to the ionic aggregates. The transition due to ionic aggregates (T_i) has been found to occur in the similar temperature range, in the case of rubbery ionomers[14,15]. In the case of crystalline ionomers, transition due to ionic aggregates has been reported to occur at a temperature lower than the crystalline melting temperature[16–18]. The lower tan δ_{max} (that is, tan δ value at T_g) in the case of SEPDM, as compared to EPDM, is due to the stiffening of the matrix imparted by ionic domains in the former[19].

Incorporation of DEG causes no reduction in T_g of SEPDM and the tan δ_{max} remains almost constant, indicating that the backbone hydrocarbon chains are not plasticized by the DEG. However, in the presence of DEG, the high temperature transition due to the ionic aggregates (T_i) is not observed, which suggests that DEG causes dissolution or solvation of the ionic aggregates present in SEPDM. The melting of the crystallites is observed at a lower temperature in the presence of DEG. Results of dynamic mechanical analyses are shown in *Table 2*.

Dielectric thermal properties. The variation of log(tan ϵ) with temperature observed from the dielectric thermal analyses of SEPDM and SEPDM compounds containing 5 phr DEG is shown in *Figure 4*. SEPDM shows two transitions, the one at +123°C is believed to be due to the melting of the crystalline polyethylene block, and the lower temperature transition at +57°C is believed to be due to the ionic aggregates (T_i)[16–18]. The low temperature transition due to the ionic aggregates (T_i) is not observed in the presence of DEG, indicating that DEG plasticizes the ionic domains, probably through the solvation of ions.

Conclusions

SEPDM shows improved physical properties as compared to thermoplastic EPDM. DEG reduces the physical properties of SEPDM. Processability studies in a Monsanto processability tester indicates reduction in melt viscosity of SEPDM in the presence of DEG. Results of dynamic mechanical analyses show the occurrence of an ionic transition in addition to the glass–rubber transition in SEPDM. The results suggest that DEG does not affect the main chain glass–rubber transition, but disrupts the high temperature transition due to ionic aggregates. Results of dielectric thermal analyses support those of dynamic mechanical analyses, confirming the role of DEG as an ionic plasticizer in SEPDM.

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