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Characterization of elastomer compounds by thermal analysis

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Abstract

Thermal analysis provides very useful tools for the characterization and identification of both, elastomer compound and finished product. This investigation focuses on the use of different thermal techniques for compositional analysis, characterization of thermal, oxidative stability and glass-transition temperature (T_g) of different components present in the elastomeric systems. Thermogravimetry (TG) is critical for identification of composition. TG analysis of three compositions (S_1, S_2 and S_3) shows S_1 and S_2 are soft-oil extended compounds and S_3 is a hard compound, all comprising ethylene propylene diene rubber (EPDM). Energy dispersive X-ray analysis (EDAX) of the residues from TGA reveals the presence of mineral filler clay in sample (S_3) besides carbon black. The use of high-resolution TG has been found to give better resolution between overlapping weight loss steps leading to better quantification of various components compared to conventional TG. The coefficient of expansion of the rubber compound (from thermo-mechanical analysis – TMA) above T_g is correlated to the hardness of the samples. The use of differential scanning calorimetry (DSC) to determine oxidative stability identifies also the presence of similar antioxidants. Dynamic mechanical analysis (DMA) is found to be very sensitive for characterization of glass-transition temperature, visco-elastic properties and, in particular, the adhesion between the elastomer compound and coating. © 1998 Elsevier Science B.V.

Keywords: Adhesion; Coating; Dynamic mechanical analysis; Elastomer compound; Thermal analysis

1. Introduction

Elastomeric systems are highly complex formulations depending on their particular end-use application. In general, the elastomer formulation comprises a base elastomer, process oil, plasticizer, fillers (carbon black or mineral filler), and additives such as stabilizer or process aid and curatives. Such a complex heterogeneous system requires exact procedures for product characterization and analysis. A wide variety of procedures [1–3] for analyzing elastomeric vulcanizate are available but most of them are time-intensive because of the inextractible nature of the cross-linked system. Thermal analysis has the potential to provide quick information for characterization and identification of an elastomer composition, often an important quality-control requirement for rubber industry.

The importance and application of thermal analysis in rubber industry has been detailed by Turi [4], Maurer and Brazier [5]. Sircar [6] analyzed the composition of various rubber vulcanizates by TG–DTG

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techniques. Several authors [7,8] have used thermal analysis for elastomer research and development, particularly in composition analysis. The use of dynamic mechanical analysis (DMA) for characterization of visco-elastic properties of elastomers, thermoplastic elastomers [9,10] has been reported by various authors. It is very sensitive for characterization of glass-transition temperature in optical-fibre coating or adhesion between fibre and matrix [11] and, in particular, analysis of fibre in a vapour-laden atmosphere [12].

The present investigation focusses on the analysis of rubber compounds by thermal and dynamic mechanical analysis. The composition analysis of different vulcanizates was established by thermogravimetric analysis (TGA). Derivative thermogravimetry (DTG) was then used to identify the various components. DSC was used to determine the oxidative induction time (OIT) and the glass-transition temperature (T_g). Thermomechanical analysis (TMA) was used to confirm the glass-transition temperature (T_g) and to determine the coefficient of linear expansion ($\propto$). Finally, dynamic mechanical analysis (DMA) was used to evaluate the relaxation transitions and the visco-elastic properties over a range of temperatures. Combining such complementary thermal techniques permits detailed compositional analysis of the different elastomer compounds.

2. Experimental

For the analysis, three different rubber compounds received from Bridgestone TG Australia were used, being designated as S_1, S_2 and S_3. All instruments used for thermal analysis in this paper were manufactured by TA Instruments, USA.

2.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the samples was conducted using a TGA 2950 thermal analyzer (TA Instruments) using conventional (heating rate) and high-resolution modes operating from room temperature to 800°C at a heating rate of 10°C min^{-1}. In all analyses, a nominal, 20-mg sample was used. Conventional TG analysis was carried out under an atmosphere of either nitrogen or oxygen at a flow rate of 60 ml min^{-1}. Under nitrogen, the inert atmosphere was maintained from 30–500°C to monitor the weight loss of oil and polymer with temperature. At 500°C, the gas flow was changed from nitrogen to oxygen to observe the carbon-black degradation. The onset of degradation, the weight loss due to different ingredients and the residue remaining at 800°C were evaluated. The temperature, at which the rate of mass loss ($T_{\max}$) is at a maximum, was evaluated from the differential thermogravimetry (DTG) curves. High-resolution TG was carried out only under an atmosphere of oxygen. The ability to separate closely overlapping weight-loss peaks with greater resolution is unique to high-resolution TG.

2.2. Differential scanning calorimetry (DSC)

DSC was conducted using DSC 2920 from TA Instruments. The oxidative induction time (OIT) of different formulations was evaluated as a qualitative measure of material stability. A weighed amount of sample was analyzed from 30–300°C under nitrogen flow. All the runs were in triplicate. For glass-transition measurement, a weighed amount of sample prepared in a crimped aluminium pan was cooled in the cell to -150°C with liquid nitrogen and then heated at a constant rate of 10°C min^{-1} in nitrogen atmosphere to 600°C. The midpoint of the base-line shift was taken as the glass-transition temperature.

2.3. Thermomechanical analysis (TMA)

Thermomechanical analysis was carried out in TMA 2940 from TA Instruments. The macroexpansion probe was used both with, and without, a load of 5 g in the -100 to 350°C range at a heating rate of 5°C min^{-1}. The probe zero was adjusted after the sample was cooled. The penetration probe was used with a load of 5 g over the same temperature range for some sample.

2.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was carried out on the rubber samples in DMA 2980 (TA Instruments) operating in the tension mode from -150 to 100°C at a frequency of 1 Hz, at 0.08% strain amplitude with a programmed heating rate of 3°C min^{-1}. Liquid nitrogen was used to achieve the subambient temperature.

2.5. Energy dispersive X-ray Analysis (EDAX)

Energy dispersive X-ray analysis was conducted using Cam Scan CS44 scanning electron microscope (SEM) operating at an acceleration voltage of 20 kV with EDAX detector.

3. Results and discussions

3.1. Thermogravimetric analysis

Thermogravimetric analysis of the elastomer samples (S_1, S_2 and S_3) was carried out according to the standard procedures for elastomer vulcanizate. The weight-loss curves of sample S_1 in nitrogen (conventional mode) and oxygen (high-resolution mode) atmosphere are shown in Fig. 1. The TG curve consists of several steps. Under nitrogen there is no weight loss up to 200°C indicating the stability of the material in this temperature range. An initial weight loss occurs, between 200–400°C, due to the loss of volatile matter present in the composition. The T_{max} corresponding to this weight loss occurs near 340°C. Isothermal treatment for a certain time period above T_{max} will hasten oil volatilization, without any polymer degradation. The method developed by Maurer [13] and later used by Groves and Thomas [14] affirms assignment of the initial weight loss due to oil and extenders. The next weight loss occurs in the 450–490°C range, due to the medium volatile elastomeric components present in the composition. Table 1 summarizes the percent weight loss from the different ingredients in TGA. Table 2 shows the temperature at which the degradation/volatilization of an ingredient is maximum. The degradation occurs in a range with the maxima at T_{max}. The samples S_1 and S_2 show oil in the 23.6–25% range but S_3 shows only 9.6% oil. The temperature range through which this oil volatilizes, indicates that aromatic/naphthenic oils were used for compounding. Zeyen [15] observed that isothermal TG works very efficiently for both, aromatic/naphthenic oils and that paraffinic oils in molded rubber goods (particularly in EPDM – ethylene propylene diene rubber compound) co-volatilize with the rubber.

The experimental approach to alter the volatilization temperature of the oil, is to use reduced pressure

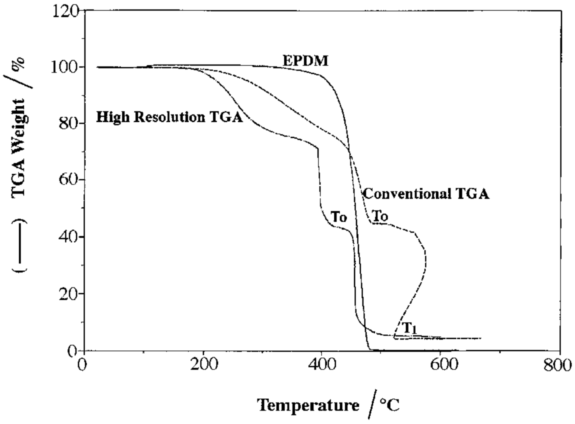

Fig. 1. Thermogravimetric analysis of sample S_1 (conventional and high-resolution mode) and EPDM rubber (conventional mode).

Table 2
DTG peak temperatures of S_1 for various ingredients

Ingredient	$T_{initial}$/°C	T_{mean}/°C	T_{final}/°C	Atmosphere (gas)
Oil	200	340	400	Nitrogen
Rubber	450	469	490	Nitrogen
Carbon black	520	570	575	Oxygen

Table 1
Compositional analysis of rubber vulcanizates by thermogravimetric analysis

Ingredient present in the composition	S_1/% (in N_2) [a]	S_1/% (in O_2)	S_2/% (in N_2) [a]	S_2/% (in O_2)	S_3/% (in N_2) [a]	S_3/% (in O_2)
Oil	25.01	24.18	25.28	23.65	9.6	10.43
Rubber	30.45	32.58	30.7	34.1	38.87	38.49
Carbon black	40.1	37.88	39.73	36.75	29.66	27.52
Residue (always in O_2)	4.25	5.3	4.08	4.9	21.86	22.85

[a] In all experiments with nitrogen (N_2) as purge gas, after polymer degradation, the purge gas has been switched to oxygen.

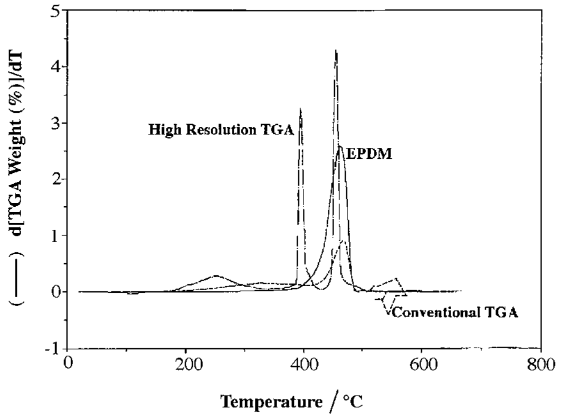

Fig. 2. High resolution and conventional DTG curves for sample S_1 and EPDM rubber.

to separate it from the polymer weight loss, arising from the presence of various low molecular weight components. However, in the present case, the two peaks on DTG plot (Fig. 2) are well separated which also confirms the non-paraffinic nature of the oil. Samples S_1 and S_2 reveal more or less the same oil content. Polymer degradation occurs in the same temperature range 450 to 490°C for all the samples. EPDM rubber compound is known to decompose in this range [4], with the gum compound showing decomposition at a higher temperature than any unsaturated diene rubber. Thermogravimetric evaluation of EPDM rubber (supplied by Japan Synthetic Rubber – JSR) under similar conditions, indicated that elastomer degradation occurs at 475°C, confirming the fact that the samples (S_1–S_3) consist of EPDM rubber. It is interesting to note from Table 1 that the polymer percentage is less than the carbon black residue for both samples S_1 and S_2. Often, the polymer leaves char after degradation in nitrogen and when the environment is switched from nitrogen to oxygen, such char also gets oxidized together with the carbon black, resulting in a higher estimate for the carbon black.

The characteristic TGA thermograms suggest that the temperature interval at which carbon-black weight loss in oxygen occurs varies significantly in the different formulations. Fig. 1 shows several features in this region:

(a) an initial area of low weight loss;
(b) a point (T_0) at which weight loss increases sharply;
(c) an intermediate region which may be either essentially linear or exhibits an inflection point; and
(d) a terminal region ending at T_1.

The characteristics of the terminal region suggest that at some point between T_0 to T_1 the heat of reaction increases the sample temperature at a much higher rate than the set programmed rate of the instrument. The ability to determine the amount of carbon black present in a composition together with the separation of closely overlapping weight-loss peaks is unique to high-resolution TG. The analysis (high-resolution) allows significant decomposition steps over a smaller temperature range because the heating rate is reduced once any significant weight loss commences. The derivative weight-loss peak is, consequently, narrower than with conventional TG allowing greater resolution to separate competing/overlapping weight losses.

Dynamic TGA, also referred to as high resolution TGA [16,17], is also effective in resolving the overshooting of the first derivative signals during carbon-black decomposition. High-resolution TGA of sample S_1 using dynamic heating rate in an oxygen atmosphere is shown in Fig. 1. The weight loss still occurs over three major steps. The overall weight loss associated with those three steps, however, reveals the difference in the thermo-oxidative stability of the oil, the elastomer and the carbon black in each sample. Table 1 shows the amount of carbonaceous residue obtained by pyrolyzing each compound. Compound S_3 shows the highest percentage (22.8%) of residue left at 800°C. Such a high amount of residue could only be the result of some inorganic filler present in the composition. Samples S_1 and S_2 have residues in the 4.9–5.3% range. Generally, the system containing mineral filler shows little or no weight loss after switching to oxygen gas flow. The residue left is a combination of mineral filler and ash. Sample S_3, therefore, is a highly filled (carbon black and mineral filler) and less oil-extended hard-rubber formulation while both S_1 and S_2 are carbon-black filled and highly extended soft compositions. The thermal stability of S_3 is highest due to its high filler level. A similar trend is noticed using conventional heating in nitrogen, except that the onset of degradation for all ingredients occurs at a higher temperature.

Table 3
Elemental compositions of TGA residues

Sample	Element/%									
	Ca	Zn	S	Si	Cl	Al	K	Fe	C	O
S_1	32.60	32.61	13.04	6.52	—	—	—	—	4.35	10.87
S_2	73.27	0.99	11.88	2.97	0.99	—	—	—	3.96	5.94
S_3	4.29	4.30	1.44	59.77	—	11.45	1.44	0.72	—	16.60

The residues of all samples following TG analysis were examined by scanning electron microscopy (SEM) using an attached EDAX facility to determine elemental composition [18]. Table 3 shows the elemental composition of the residue after EDAX analysis. Sample S_1 has higher levels of zinc (Zn) and calcium (Ca) indicating the presence of their oxides together with medium levels of sulphur (S). Normally for continuous vulcanization CaO is used as a desiccant. The presence of calcium in the present case may be for the similar reason or it could be due to talc. Sulphur is present as a curative. Sample S_2 exclusively has calcium together with a moderate level of sulphur. Sample S_3 has a high silicon (Si) level together with zinc (Zn) and aluminium (Al) indicating that not only zinc oxide but also clay is present in the compositions.

3.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the oxidative-induction time (OIT) of samples S_1 and S_3. Oxidative induction time [19] is a relative measure of a material's resistance to oxidative decomposition and is determined by the onset of exothermic oxidation in a material at a specified temperature in an atmosphere of oxygen. Valuable information can be derived from OIT values related to processing and service conditions. Each sample was heated isothermally at 170°C in an inert atmosphere, before switching to oxygen gas flow. The onset time for degradation is measured from the time gas flow is switched to oxygen, to the time at which degradation is first detected. Both samples S_1 and S_3 give OIT values of 3.48–3.44 min (Table 4), indicating that a similar type and amount of antioxidant is present. The TGA also showed onset of degradation under oxygen at the same temperature.

The glass-transition temperature (T_g) as obtained from DSC thermogram is recorded in Table 4 and shown in Fig. 3. The soft-rubber composition (S_1) shows a very broad T_g at −47.6°C which is probably due to presence of both fillers and cross-linking, both of which broaden the DSC curve. The T_g of hard rubber sample (S_3) could not be detected by DSC. The pure EPDM rubber run under similar condition (also shown in Fig. 3) reveals a T_g of −50°C. However, S_3

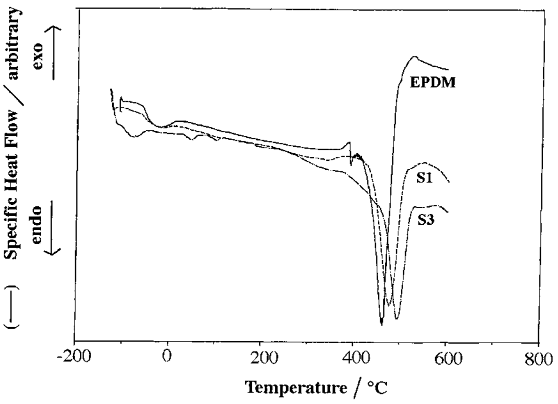

Fig. 3. DSC thermograms of different samples.

Table 4
TMA and DSC analyses of the samples

Sample	$\alpha\times10^4/(°C^{-1})$ ($<T_g$) (−50°C to −35°C)	$\alpha\times10^4/(°C^{-1})$ ($>T_g$) (12°C to 40°C)	T_g/°C (TMA)	T_g/° (DSC)	OIT/(min)
S_1	0.23	2.6	−26.9	−47.6	3.48
S_3	0.38	1.66	−19.7	(not visible)	3.44

shows two small endothermic transitions – at −100°C which could be due to the presence of silicone fluid in the composition (also highest amount of Si was detected for S_3 in EDAX) and at 45°C due to melting (T_m) of the rubber. Brazier and Nickel [20] reported that EPDM of ethylene content >60% exhibits an endothermic transition at 47°C. The endotherm could well be due to the ethylene content exceeding 60% ethylene in the EPDM rubber. At high temperatures (>460°C) an endotherm appears in the compositions resulting from EPDM rubber degradation confirming the base polymer content.

3.3. Thermomechanical analysis (TMA)

Thermomechanical analysis (TMA) with macroexpansion probe was performed using the soft-rubber (S_1) and the hard-rubber (S_3) compositions to measure the T_g, co-efficient of linear expansion ($\propto$) and bulk dimensional changes. A typical TMA curve shown in Fig. 4 represents the free expansion thermograms associated with sample S_1. The slope of this curve measured by derivative offset from zero is the rate of expansion at any given temperature. The results of TMA are reported in Table 4. The glass-transition temperature, T_g, has been detected at −26.9°C from the derivative curve of sample S_1. An apparent shrinkage occurs in the elastomer composition as it passes through the T_g region. Such shrinkage is actually due to the mass of the probe (non-zero). Although sample S_1 was analyzed without load to avoid significant indentation, the hard-rubber composition (S_3) was analyzed by using the macroexpansion probe with a load of 5 g. The T_g for this sample shifts to −19.7°C which is in good agreement with the compositional analysis, as this sample contains a higher amount of carbon black and mineral filler, both of which affect the relaxation behaviour. Above T_g, the slope depends on the competition between indentation and thermal expansion. The behaviour is directly related to the different hardness of the two samples. Both samples show characteristic thermograms above T_g.

The soft sample (S_1) when analyzed using a penetration probe shows a T_g (Fig. 5) at same temperature as observed using the macroexpansion probe, following which a little dimensional change occurs. At temperatures of 200°C and 340°C, two sharp steps occur, associated with shrinkage which is mainly due to the loss of volatiles and oily components present in this composition.

The different TMA experiments provide information about shrinkage, thermal history and elasticity effects of these rubber compounds. Brazier and Nickel [20] reported the use of various TMA modes (expansion and penetration) and data to evaluate the coefficient of linear expansion of elastomer systems. Maurer [21] has reported the use of vulcanized elastomer standards of known expansion coefficient in calibrating TMA instrument. However, in the present case, indium standard was used for calibration to measure the apparent expansion coefficient above, and below, T_g. The expansion coefficient obtained using a penetration probe on the soft composition (S_1) is lower than that obtained using a macroexpansion probe. The free

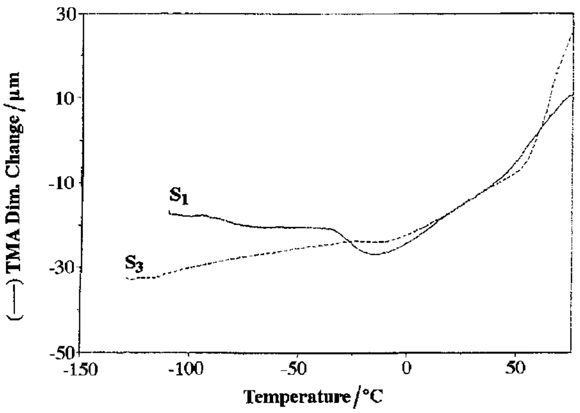

Fig. 4. TMA curves of sample S_1 and S_3 using macroexpansion probe.

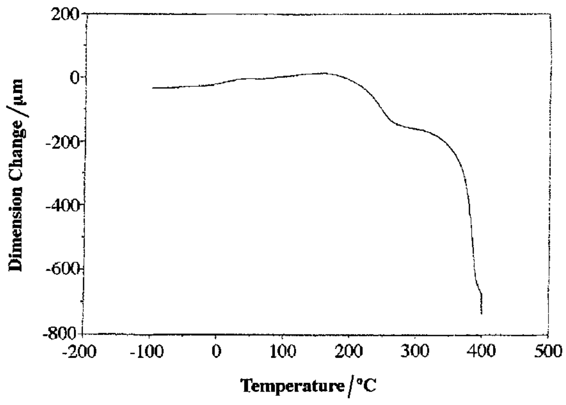

Fig. 5. TMA curve of sample S_1 using penetration probe.

expansion experiment shows similar shrinkage behaviour due to loss of volatiles, but at an earlier onset temperature. It is interesting to note that below T_g, the coefficient of thermal expansion (Table 4) for both hard and soft compositions, namely S_3 and S_1, show little dimensional changes in the 0.38–0.23 range due to restricted chain motion in the glassy state irrespective of the probe used. Above T_g, the free volume considerably increases, and the extent of indentation varies with the hardness of the compound.

3.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out on both, soft- (S_1, S_2) and hard-rubber samples (S_3). Fig. 6 and 7 show the representative plot of the effect of temperature on dynamic elastic (E'), loss (E'') moduli, and damping factor (tan δ). In Fig. 6, the characteristic sigmoidal variation of elastic modulus with temperature is observed for the sample S_1. It passes from the glassy to the rubbery state through different regions with the decrease in the stiffness of the samples. The loss modulus and damping sharply increase, attaining a maxima and then dropping off with the rise in temperature. Table 5 compares the storage modulus of samples S_1, S_2 and S_3 over a −50 to 50°C range. Of the two soft samples, S_1 shows higher modulus than S_2. As expected, the hard-rubber sample S_3 shows the highest modulus. The modulus for all samples decreases with temperature as the samples pass from the glassy to the rubbery state.

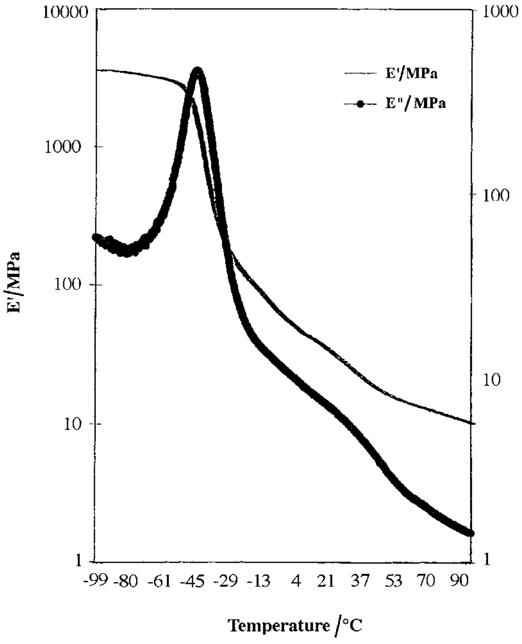

Fig. 6. Effect of temperature on storage modulus (E') and loss modulus (E'') for sample S_1.

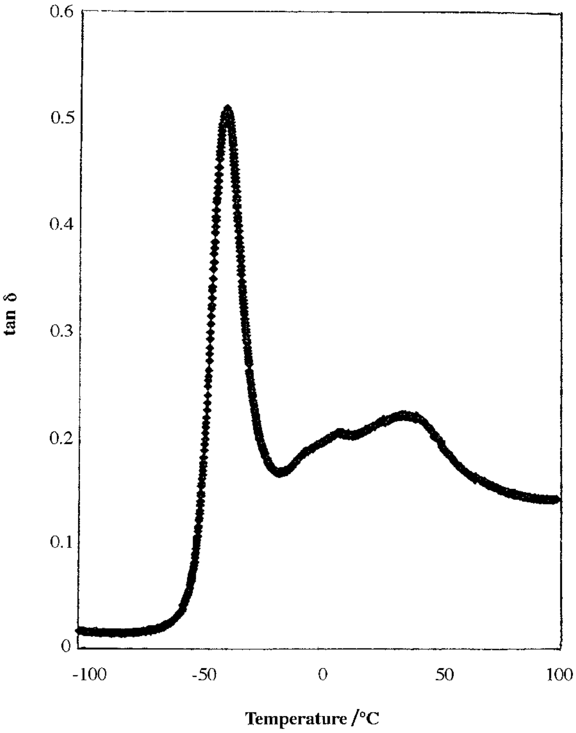

Fig. 7. Effect of temperature on damping factor tan δ for sample S_1.

Fig. 7 shows the representative plot of temperature dependence of tan δ for the sample S_1. Seen here are three distinct transition relaxation peaks for both systems. The loss modulus E'' follows a trend similar to tan δ. Specific details relating to the tan δ peak temperatures and peak values for all the samples are collated in Table 6. The T_g value has been selected from the peak position of tan δ as a function of temperature. It is interesting to note that there are three transitions in both the soft-rubber compositions S_1 and S_2 (both tan δ and E'' curves) designated as T_{g_1}, T_{g_2} and T_{g_3} in the tan δ curve and E''_1, E''_2 and E''_3 from the E'' curve. The low temperature transition T_{g_1} is due to filled EPDM rubber which occurs in the −37.6 to −38.3°C range for both the samples. The

Table 5
Comparison of storage modulus (E') values at different temperatures

Composition	E'/MPa at −50°C	E'/MPa at −25°C	E'/MPa at 0°C	E'/MPa at 25°C	E'/MPa at 50°C
S_1	2475.90	146.09	58.17	31.18	16.53
S_2	2302.27	120.82	50.15	24.24	14.30
S_3	2580.40	611.10	181.30	58.50	20.10

Table 6
Dynamic mechanical properties of the samples

Sample	T_{g_1}/°C	T_{g_2}/°C	T_{g_3}/°C	tan δ_1	tan δ_2	tan δ_3	E_1''/°C	E_2''/°C	E_3''/°C
S_1	−37.6	10.1	37.4	0.508	0.192	0.212	−44.2	10	38
S_2	−38.3	2.3	30	0.519	0.2	0.212	−44.4	1.5	29
S_3	−23.5	—	31.5	0.212	—	0.243	−31.5	—	25.3

sharp peak due to EPDM is followed by two broad shoulders at 10.1° and 37.4°C, respectively. Near room temperature, two similar transitions occur for S_2 corresponding to the relaxation of two components believed to be primary and secondary coatings on the rubber compositions. Boast [11], while analyzing coated optical-fibre system using DMA, observed a broad shoulder associated with two transitions at 27° and 50°C due to a soft primary- and tough outer-coating, respectively. Table 6 shows that these transitions in both the tan δ and E'' (E_2'' and E_3'') curves occur almost at the same temperature for both the samples (whereas the first transition temperature T_{g_1} differs from E_1''). In the transition region, E' decreases sharply with temperature. As these parameters are related by tan $\delta=E''/E'$, the difference in the tan δ and E'' peak temperatures will be controlled by how much E' changes with temperature. The heights of different tan δ peaks are, more or less, the same for both samples. Sample S_3, however, shows only two transitions, the low temperature transition due to rubber is at −23.5°C (indicates presence of high level of filler) and the other transition is at 31.5°C. This indicates the absence of primer coating. The height of the tan δ_1 peak is reduced by 58% from that of S_1 and tan δ_3 increases marginally.

The high value of modulus of S_1, compared to that of S_2, at all temperatures coupled with the three T_g values strongly suggests that both elastomer samples S_1 and S_2 are coated systems. Differences between both samples are due to the differences in coating thickness, and in the adhesion of the coating to the rubber substrate through primer coating, which affects the storage modulus values at all temperatures.

4. Conclusions

TG analysis shows that S_1 and S_2 are carbon-black filled, highly extended EPDM based soft-rubber compositions while S_3 is a highly loaded and hard EPDM rubber formulation. EDAX analysis of the TGA residue reveals the presence of mineral filler clay besides carbon black in this sample.

T_g values, measured from DSC and TMA for S_1 and S_3, are consistent with the compositional analysis from TGA. Oxidative induction time using DSC shows each sample contains a similar level of the same antioxidant. The dimensional changes revealed by TMA (above T_g) in samples S_1 and S_3 are related to the different hardness of each sample.

The DMA results of both the soft-rubber compositions, S_1 and S_2, clearly reveal three transitions in the tan δ curve. The modulus values are different though the samples are more or less similar in composition. These results indicate that soft compositions are coated systems and adhesion of coating to rubber surface is enhanced using a primer coating. The modulus data indicate that sample S_1 will perform better than S_2 even though the base rubber formulation is the same. The differences arise with variation in the thickness of the primer and coating layers. Thus, thermal analysis offers a rapid, potent and precise approach to identify and assess complicated elastomer compositions.

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References

[1] Annual Book ASTM Standard, Pt 37, D-297-81, 1982.

[2] N.K. Dutta, D.K. Tripathy, Kautschuk+Gummi Kunststoffe 43 (1990) 880.

[3] A.K. Bhowmick, D. Mangaraj, in: A.K. Bhowmick, M.M. Hall, H.A. Benarey (Eds.), Rubber Products Manufacturing Technology, Marcel Dekker, New York, 1994, p. 315.

[4] E.A. Turi, Thermal Characterization of Polymeric Materials, 2nd edn., Academic Press, New York, 1997.

[5] J.J. Maurer, D.W. Brazier, Kautschuk+Gummi Kunststoffe 36 (1983) 37.

[6] A.K. Sircar, Rubber Chem. Technol. 65 (1992) 503.

[7] A.K. Sircar, T.G. Lamond, Rubber Chem. Technol. 45 (1972) 329.

[8] Compositional Analysis by TG, ASTM Std., E 1131-93, p. 693.

[9] N.K. Dutta, D.K. Tripathy, J. Appl. Polym. Sci. 44 (1992) 1635.

[10] N. Roy Choudhury, A.K. Bhowmick, Thermochim. Acta 176 (1991) 149.

[11] R. Boast, IUPAC International Symposium on Polymer Materials, Polymer '91, Melbourne, Australia, 10–14 Feb, 1991, p. 36.

[12] D.M. Price, Thermochim. Acta 294 (1997) 127.

[13] J.J. Maurer, Rubber Chem. Technol. 42 (1969) 110.

[14] I. Groves, L. Thomas, Res. Dev., February 1988.

[15] R.L. Zeyen, Kautschuk+Gummi Kunststoffe 41 (1988) 974.

[16] High Resolution TGA – Manual, TA Instruments, USA.

[17] I.F. Groves, R.S. Whitehouse, J. Thermal Anal. 40 (1993) 587.

[18] J.I. Goldsmith, D.E. Newbury, P. Echlin, D.C. Joy, C. Fiori, E. Lifshin, Scanning Electron Microscopy and X-Ray Microanalysis, Plenum Press, New York, 1981.

[19] R. Boast, P. Latoszynski, Polymer 85 (1985) 165.

[20] D.W. Brazier, G.H. Nickel, Thermochim. Acta 26 (1978) 399.

[21] J.J. Maurer, in: E.A. Turi (Ed.), Thermal Characterization of Polymer Material, Academic Press, Chap. 6, New York, 1981, p. 571.