

Application of Differential Scanning Calorimetry and Differential Thermogravimetry Techniques to Determine the Ratio of Blend Components in Reactive Chlorinated Elastomer Blends

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ABSTRACT: Quantitative and qualitative analyses of chlorine-containing elastomer blends, like neoprene rubber/chlorosulfonated polyethylene and neoprene rubber/nitrile–polyvinyl chloride, with carbon black and other fillers, are complex and confusing because the blends contain the same carbon–chlorine moiety. Various interfering phenomena by fillers, co-curing by the common ingredients, and uncertainty in functional group analysis make the determination of the ratio of component elastomers in chlorine-containing elastomer blends very difficult or sometimes almost impossible by Fourier transform infrared and thermogravimetric analysis techniques. However, differential scanning calorimetry (DSC) and supportive differential thermogravimetry (DTG) are very useful techniques to assess such complex materials. Enough flexibility associated with specific heat (from DSC) and response zone (from DTG) can avoid the interfering effects. The DSC–DTG technique thus can be an effective tool to determine the ratio of component polymers in chlorine-containing elastomer blends. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 937–948, 2002

Key words: differential scanning calorimetry (DSC); differential thermogravimetry (DTG); chlorine-containing polymer; specific heat; blend ratio; standard deviation (σ)

INTRODUCTION

Neoprene rubber (CR) has several different applications and has been widely used for many years in products like tubing (e.g., suction, fueling, and de-fueling) for conveying oils [e.g., lubricating, vegetable (inedible), and transformer oils, and oil with low aromatic content] because of its excellent oil, weather, ozone, and flame resistance

properties in a wide temperature range (-50 – 100 °C). The presence of chlorine (Cl) in the backbone of CR makes CR suitable for mixing with the elastomers of similar polarity and elastomers with Cl in the polymeric structure. The long and short ranges of dipole–dipole interactions as well as the common Cl moiety, have enabled at least a technological compatibility in the Cl-containing elastomer blends. In fact, there is enough scope of blending of CR with other Cl-containing elastomers [e.g., nitrile–polyvinyl chloride (NBR–PVC, commercially available), plasticized polyvinyl chloride (PVC), chlorosulfonated polyethylene (CSM), etc.] to provide not only improvement in

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properties such as less swelling in saline water and resistance to solvents, weather, flame, heat, oil, chemicals, etc., but also a decrease in the product cost in many cases. Therefore, it is common to use CR as a blend partner with natural rubber (NR, as practiced in industry) with the elastomers just mentioned. This type of blending is also true when CSM, a high-cost elastomer, is used as the base elastomer. If application is highly stringent, the blend may not achieve trouble-free operation in the long run. Therefore, determination of the blend ratio in the Cl-containing elastomers is necessary to have a trouble-free product.

Identification of Cl-containing polymers is possible by the copper wire test (Beilstein test), but problems occur when all the blend partners contain Cl in their polymeric structure. Moreover, chemical analysis following the color change in the American Society for Testing and Materials (ASTM) solutions (as per ASTM D 297 -1998) is pH dependent. If the compound contains basic or alkaline materials, like CaCO_3 or Barytes (BaSO_4), as the ingredient, color change analysis cannot ensure even the identification of the polymer itself. Therefore, determination of the blend ratio by the change of the refractive index is absolutely impossible by following the color change in the ASTM solutions. There are few reports¹ of the determination of the CR/PVC blend ratio by the extraction method. However, this process is time consuming and difficult to reproduce. Moreover, it has limited implications when the reactive carbon black-containing CR/PVC blend is considered because of a strong carbon black–elastomer interaction. Fourier transform infrared spectroscopy (FTIR), another technique for polymer identification (as per ASTM D 3677- 1995), is also a futile exercise in the case of Cl-containing elastomer blends with the same carbon–Cl bond frequencies irrespective of the polymer types. According to ASTM D 6370 - 1999, thermogravimetric analysis (TGA) can be used for the blend ratio determination. In fact, the percentage weight loss in the TGA graph depends on the overall compound rather than the individual elastomer. The semicrystalline polar moiety degrades faster than the mere hydrocarbon at relatively lower temperature. Sircar et al.² has worked on the analysis of vulcanizates based on binary blends by a thermogravimetric analysis (TGA)–differential thermogravimetry (DTG) technique. The potential of the TGA-DTG procedure for quantitative analysis of binary elastomer vulcanizates was also investi-

gated by Maurer^{3, 4} for the ethylene-propylene-diene monomer (EPDM)/NR blend and by Brazier and Nickel⁵ for NR/butyl rubber (IIR), NR/butadiene rubber (BR), NR/styrene-butadiene rubber (SBR), etc. blends. In fact, there is hardly any report on blend ratio determination in the Cl-containing elastomer blends in the literature. Perhaps, the common Cl moiety in CR and CSM degrades in a particular temperature range regardless of the types of elastomer in a co-curing system, even at the very slow heating rate. High-temperature differential scanning calorimetry (DSC) has been used by Rugo et al.⁶ for the analysis of a *cis*-polybutadiene rubber compound and the components, particularly extent of curing, has been analyzed by his group by determining the amount of reacted and unreacted sulfur and accelerators. DSC measures the heat flux with respect to a 'reference' with the temperature so that any minor change in the compounding can easily be understood from the exotherm or endotherm in a typical DSC thermogram. In this paper, we have attempted to establish a technique to determine the elastomer ratio in the blends of Cl-containing elastomers, like CR/CSM, CR/NBR–PVC, etc., in the commercial product itself by a statistical technique (from the high-temperature DSC study), and subsequently the best curve fit will be considered for some of the unknown samples of the aforementioned types. The physical properties were measured so that performance would be ascertained in the prepared blends. The inconveniences of FTIR and TGA have already been discussed in this paper, so the high-temperature DSC technique is used for blend ratio determination for Cl-containing elastomer blends promptly.

EXPERIMENTAL

Neoprene (CR) of grade Skyprene B-30 was from Toya Soda, Japan. Chlorosulfonated polyethylene (CSM) of grade Hypalon 40 was from DuPont and nitrile–polyvinyl chloride (NBR–PVC) of 70:30 was from Imperial Water Proofing, India. The CR/CSM and CR/NBR–PVC blends are prepared in an open, two-roll, laboratory-size mixing mill at 55 °C for 0.5 h as per formulations given in Table I. The compounding formulations were chosen on the basis of the industrial practice of using neoprene tubing. Blends were prepared and kept at room temperature for at least 24 h to attain saturation. The blends, A to J, were molded at 160 °C in a hydraulic press as per t_{90} , obtained from

Table I Compounding Formulations

Parameter	A	B	C	D	E	F	G	H	I	J
Skyprene (B-30)	100	80	70	30	20	—	85	75	60	—
Hypalon 40	—	20	30	70	80	100	—	—	—	—
NBR-PVC (70 : 30)	—	—	—	—	—	—	15	25	40	100
MgO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	—
ZnO	5.0	5.0	5	1.0	1.0	1.0	5.0	5.0	5.0	5.0
St. acid	1.0	1.0	1.0	—	—	—	1.0	1.0	1.0	1.5
Hard clay	—	—	—	50	50	50	—	—	—	50
Barytes	—	—	—	50	50	50	—	—	—	50
DOP	—	—	—	10	10	10	—	—	—	10
FEF	30	30	30	30	30	30	30	30	30	30
Ppt. silica	15	15	15	—	—	—	15	15	15	—
Sulfur	—	—	—	—	—	—	—	—	—	5.0
Ppt. CaCO ₃	50	50	50	—	—	—	50	50	50	—
Aromatic oil-710	10	10	10	—	—	—	10	10	10	—
4020	1.0	1.0	1.0	—	—	—	1.0	1.0	1.0	1.0
ETU	0.5	0.5	0.5	—	—	—	0.5	0.5	0.5	—
MBTS	—	—	—	—	—	—	—	—	—	1.5
TMTD	—	—	—	1.5	1.5	1.5	—	—	0.5	1.0
Tetron-A	—	—	—	1.0	1.0	1.0	—	—	—	—
<i>t</i> ₂ , min.	2.0	1.13	1.0	2.25	2.25	2.75	2.13	2.25	2.13	1.5
<i>t</i> ₉₀ , min @ 160°C	34	32	26	20	15	6.5	25	22	22	2.4
Maximum torque (lb.in)	53.5	51.5	49	47	51	51	48	45	56	50.6
% Volume change in fuel B (at RT, 24 h)	54	57	56	57	56	55	41	43	36	11

the Monsanto Rheometer (R-100). The physical properties of the blends were studied using Zwick machine -1445, Germany, at room temperature at 50 cm/min of strain rate. The aging of each blend was performed in an air-circulated oven for 24 h at 70 °C. The percentage of volume change in Fuel B (70:30, isooctane/toluene) for all blends was studied for 24 h at room temperature.

FTIR was performed in a Perkin Elmer Paragon - 1000 model from the pyrolysates as per ASTM D 3677- 1995 for individual blend. TGA was carried out from 250 to 600 °C, except for PVC blends (from 200 °C), at a heating rate of 2 °C/min in nitrogen atmosphere with the help of a Perkin Elmer TGA-7. High-temperature DSC was performed from room temperature to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere using a Perkin Elmer DSC-7.

RESULTS AND DISCUSSION

Physical Properties

The physical properties were studied in all blend systems. Properties of blends A–F both before and

after aging are shown in Table II. It is noted here that the possibility of blending in commercial products is either 80:20 in blend B or 20:80 in blend E; otherwise, a higher proportion would easily be understood in the physical performance itself. According to the results shown in Table II, the physical properties of the blends A and F change very little both before and after aging.

The variations in the properties of the CR/NBR-PVC (G to J) blends are depicted in Table III. The aged samples show inferior physical properties because of the PVC. The higher the NBR-PVC ratio in G, H, and I blends, the more is the amount of NBR and, consequently, the physical properties of these blends are improved accordingly.

Swelling in Fuel B

The percentage volume swelling in Fuel B was studied in all blends. The percentage volume change is almost the same in all cases regardless of the blend ratio (Table I). The blends G, H, I, and J give the lower volume of swelling because of the presence of NBR in the blend itself. It should

Table II Physical Properties

Blends (CR/CSM)	Hardness (Shore A)		Tensile Strength (kg/cm ²)		E.B. (%)	
	Before Aging	After Aging (70°C, 72 h)	Before Aging	After Aging (70°C, 24 h)	Before Aging	After Aging (70°C, 24 h)
A (100 : 0)	75	75	130	136	320	310
B (80 : 20)	73	73	132	134	330	330
C (70 : 30)	74	74	138	134	360	350
D (30 : 70)	75	75	134	146	310	300
E (20 : 80)	74	74	132	151	320	300
F (0 : 100)	75	75	165	175	270	260

be remembered that the proposed blend system is designed for use as the outer cover for an NBR-based inner tube. Thus, use of NBR-PVC in a CR blend is more beneficial than other Cl-containing elastomers from both the cost and properties points of view.

FTIR Analysis

FTIR spectroscopy has become an important tool for polymer identification. The ASTM, BS (British Standard) have already recognized this instrument for the analysis of unknown polymers. FTIR simply gives the plots of wave numbers (cm⁻¹) versus percentage transmittance/absorbance of the corresponding stretching, bending, rocking frequencies, etc. of the functional groups. Here, all of the elastomers contain Cl in the structure, and the carbon-chlorine (C-Cl) stretching frequencies at 819, 746, and 700 cm⁻¹ are seen, along with 1376 cm⁻¹ for gem-dimethyl groups in all cases (Figure 1). In the case of blends from A-F (Table I), the aforementioned peaks are available (Figure 1). The blends B and E were considered here because they are 80:20 and 20:80

ratios of CR and CSM, respectively, which are highly probable ratios for a commercial product. Wave numbers at 1376 cm⁻¹ and 1204-1177 cm⁻¹ were detected for SO₂Cl in CSM along with the aforementioned C-Cl bond frequencies (Figure 1). But 1376 cm⁻¹ for gem-dimethyl is the same as 1376 cm⁻¹ for SO₂Cl, and peaks at 1204-1177 cm⁻¹ fail to appear in most of the cases. Therefore, it is impossible to identify CR/CSM blend quantitatively by the FTIR technique. Moreover, the detection of polymers in the commercial products is also a difficult job because of very low percentage of polymer in the highly filled situation. FTIR analysis of CR/NBR-PVC blends (Figure 1) is also equally difficult because of the carbon black and crosslinking in the polymer matrix. The functional group C-Cl in PVC or CR again gives a misleading interpretation. The -C≡N in NBR corresponds to 2240 cm⁻¹ in blend G, because of low concentration of NBR-PVC, the -C≡N peak intensity is very weak. Therefore, identifying the CR/NBR-PVC blend is also a difficult proposition. Blend G shows the wave numbers corresponding to C-Cl bond along with 1376 cm⁻¹ of gem dimethyl. So it is not easy

Table III Physical Properties

Blends CR/NBR-PVC	Hardness (Shore A)		Tensile Strength (kg/cm ²)		E.B. (%)	
	Before Aging	After Aging (70°C, 72 h)	Before Aging	After Aging (70°C, 24 h)	Before Aging	After Aging (70°C, 24 h)
A (100 : 0)	75	76	130	136	320	310
G (85 : 15)	75	79	114	113	330	310
H (75 : 25)	80	83	97	102	240	230
I (60 : 40)	85	87	115	115	200	200
J (0 : 100)	95	96	180	200	60	55

E.B. = elongation at break.

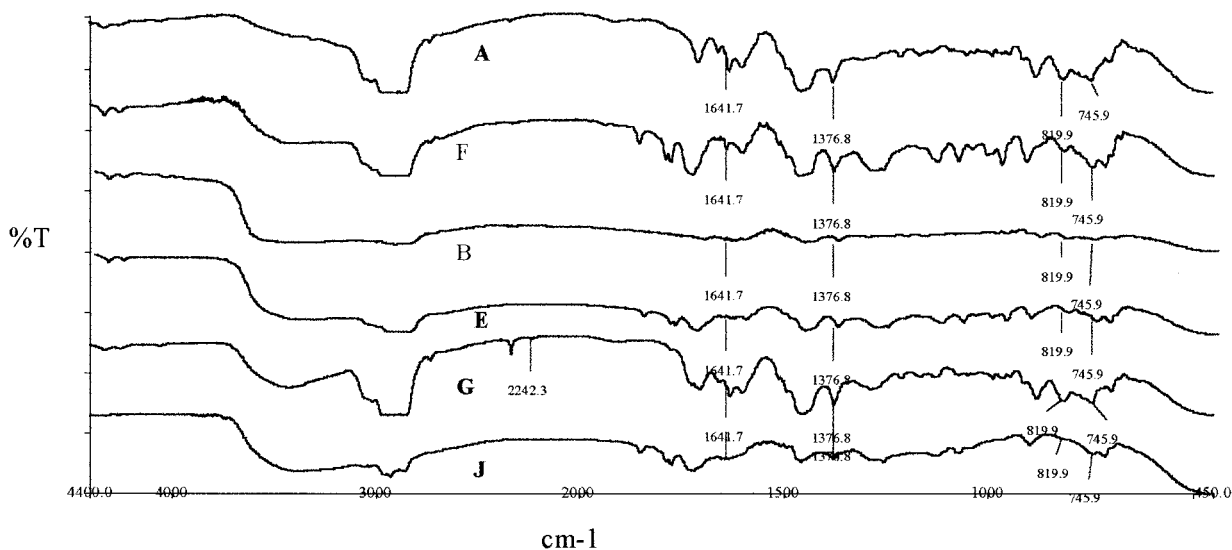


Figure 1 FTIR spectra of various blends in study.

to identify the PVC in a CR blend, particularly at lower percentage of PVC in the blend. The presence of 745, 819, 1376, and 1641 cm^{-1} (Figure 1) suggests a C—Cl bond along with gem dimethyl and the aliphatic double bond in the polymer, but to which polymer these peaks belong cannot be ascertained. Therefore, the identification of Cl-containing elastomer following the FTIR method is not so easy in such highly filled blend systems. It is to be noted here that interference of several functional groups, fillers like carbon black and subsequent vulcanization process jeopardize the identity of the elastomer itself, especially, the functional group like (C—Cl), which responds in the Fingerprint region of FTIR analysis ($<1000 \text{ cm}^{-1}$).

Probable Crosslinking Mechanism

Based on the mechanism reported^{7, 8} and the chemical affinity of the C—Cl bond in the Cl-containing elastomers towards metal oxide at the elevated temperature, the crosslinking reaction may occur in the following manner (see Scheme 1). The dehalogenation takes place where the metal oxide scavenges the Cl ion and forms the metal chloride. The carbon—oxygen—carbon (—C—O—C—) linkage is ultimately formed using the MgO in CR and CSM, and ZnO in the NBR—PVC.

Thermogravimetric Analysis (TGA)

Generally, all commercial elastomers degrade between 300 and 550 °C in a usual TGA because of

their hydrocarbon nature and each degradation step can be attributed to the characteristics feature of the individual polymer and its specific architecture. In the TGA run, with the increase in temperature, the thermal degradation of filled polymer systems takes place through various steps. Low boiling materials decompose first, followed by the decomposition of plasticizers, polymers, and fillers, respectively. The crystalline polar polymer degrades later than the amorphous one. This result is equally true for nonreactive polymers also. In fact, in the halogen-containing polymers particularly, at lower blend ratio, dehalogenation takes place at a lower temperature because of the labile nature of Cl, and then hydrocarbon degrades because of its inertness. Here, the decomposition of the crosslinked portion (—C—O—C—; as shown in the mechanism) (Scheme 1) takes place in a particular temperature region irrespective of the polymer type. As per the mechanism suggested, there is every possibility of the interference of all halogen-containing elastomers in the same temperature region.

Thermal degradation of CSM was reviewed by Maurer,⁹ and the first DTG curve on CSM was constructed manually. Smith et al.^{10, 11} assigned the three stages of weight loss observed to, respectively, the loss of the —SO₂Cl group, dehydrochlorination, and the thermal breakdown of the hydrocarbon chain residue in the CSM vulcanizates. These three events occur with maximum rates at 220, 340, and 470 °C, respectively. Neoprene elastomer also exhibits three stages of weight loss: Sircar and Lamond¹² calculated that

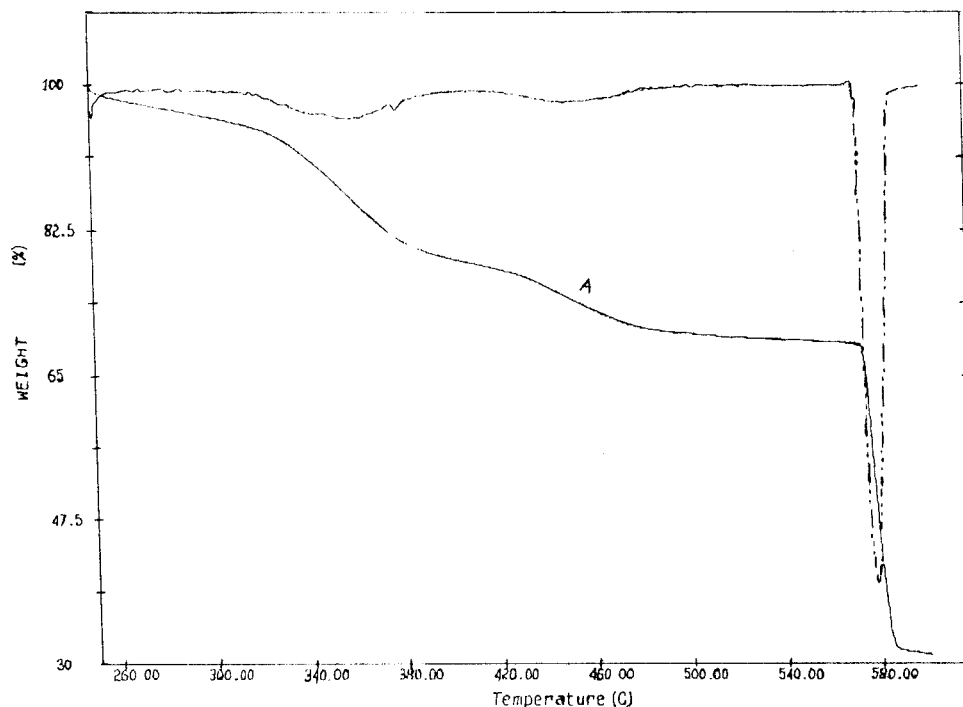


Figure 2 TGA-DTG thermogram of sample A.

dehydrochlorination accounted for 41% of the original sample of CR. They also suggested that the estimation of the Cl-containing elastomers in carbon black-containing vulcanizates requires the subtraction of the carbonaceous residue, found at 550 °C, from the total residue.

We studied the TGA-DTG scans of individual polymers at a very low heating rate of 2 °C/min (Figures 2–7). The TGA-DTG scan of blend A (Figure 2) shows more than one degradation step, and maximum weight losses at 360, 435, and 560 °C are observed, although 100% CR as the elastomer (Table I) was in original compound. The degradation steps of blend F are equally interesting because of more than four degradation steps from 300 to 450 °C (Figure 3) even though it has 100% CSM as elastomer. The TGA-DTG scan of blend J (Figure 4) shows four degradation steps between 200 and 550 °C. Because PVC degrades below 300 °C, the degradation pattern can easily be understood, but the degradation of the NBR part occurs above 300 °C, which is again a multistep degradation process. The TGA-DTG scan (Figure 5) of blend B provides three degradation steps with different weight percentages at 370, 520, and 570 °C, which are in no way related to the elastomer ratio in blend B. The same observation is also obtained for blend E (Figure 6), but the percent

weight loss is not at all comparable to the respective original elastomer contents of 32% CSM and 8% CR in the compound (Table I). The TGA-DTG scan for blend I shows four-step degradation between 260 and 580 °C (Figure 7), although it is the CR/NBR–PVC blend. The weight loss results in Figures 2–7 cannot ascertain the corresponding polymer content at the respective temperature of the individual elastomer. The wide temperature decomposition range as well as multistep decomposition in all blends will give not only the erroneous blend composition but also lead to unnecessary confusion. The decomposition, particularly that at >550 °C (in all cases observed here), and the carbonaceous fraction cumulated from the carbon black as well as from elastomers, prevent proper estimation of the blend ratio. In fact, we found (a) an abrupt shifting of the decomposition temperature, (b) abnormal weight loss compared with the elastomer taken in the blend, and (c) multiple decomposition steps, including the 100% elastomer itself. In this situation, if imagined in the multi-partner blends, the TGA-DTG scans will surely complicate the analysis. Further, the common crosslinked moiety of $-\text{C}-\text{O}-\text{C}-$ in the Cl-containing elastomer blends in the presence of reactive carbon black system will lead to an uncertain conclusion.

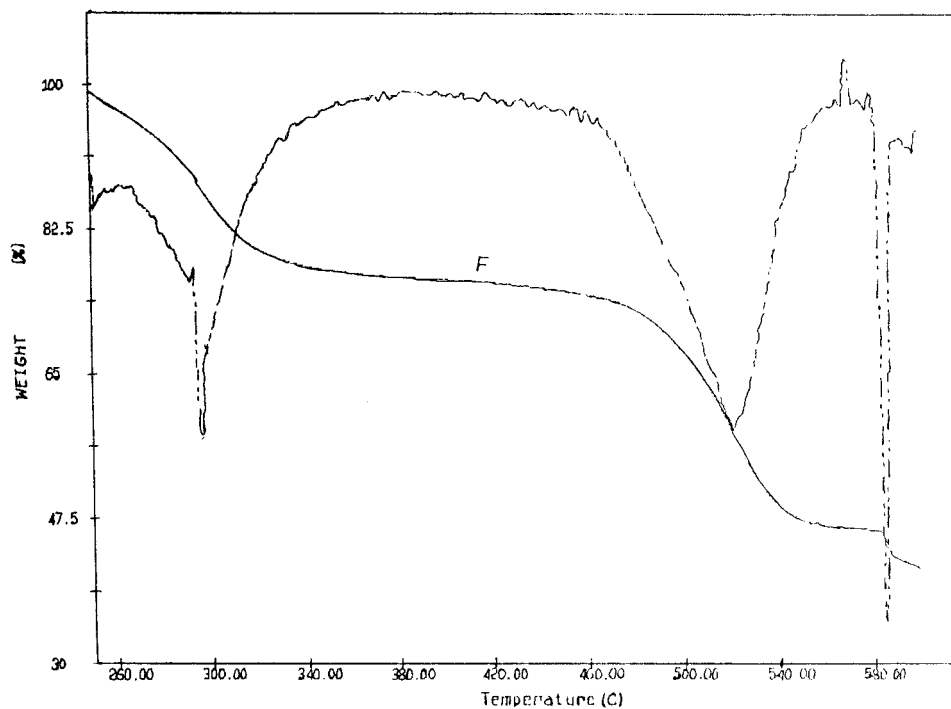


Figure 3 TGA-DTG thermogram of sample F.

Differential Scanning Calorimetry (DSC) Analysis

High-temperature DSC was performed on all blends at a heating rate of 10 °C/min from room

temperature to 600 °C in a nitrogen atmosphere so that the effect of oxygen was overcome. The heat change (ΔH) versus temperature (°C) was plotted in the original graph. Using the software,

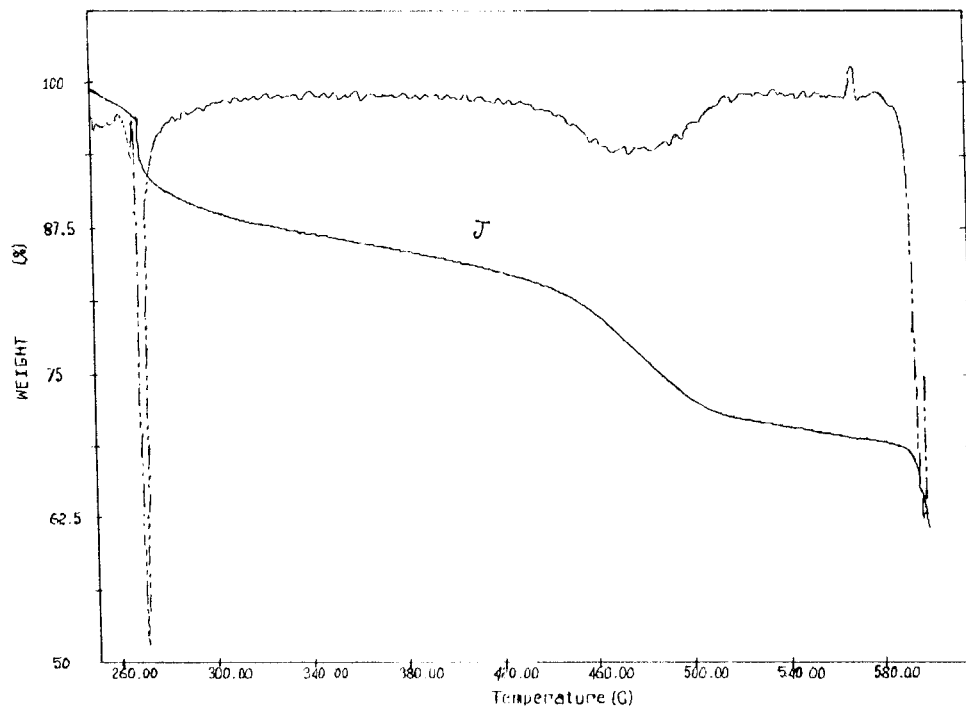


Figure 4 TGA-DTG thermogram of sample J.

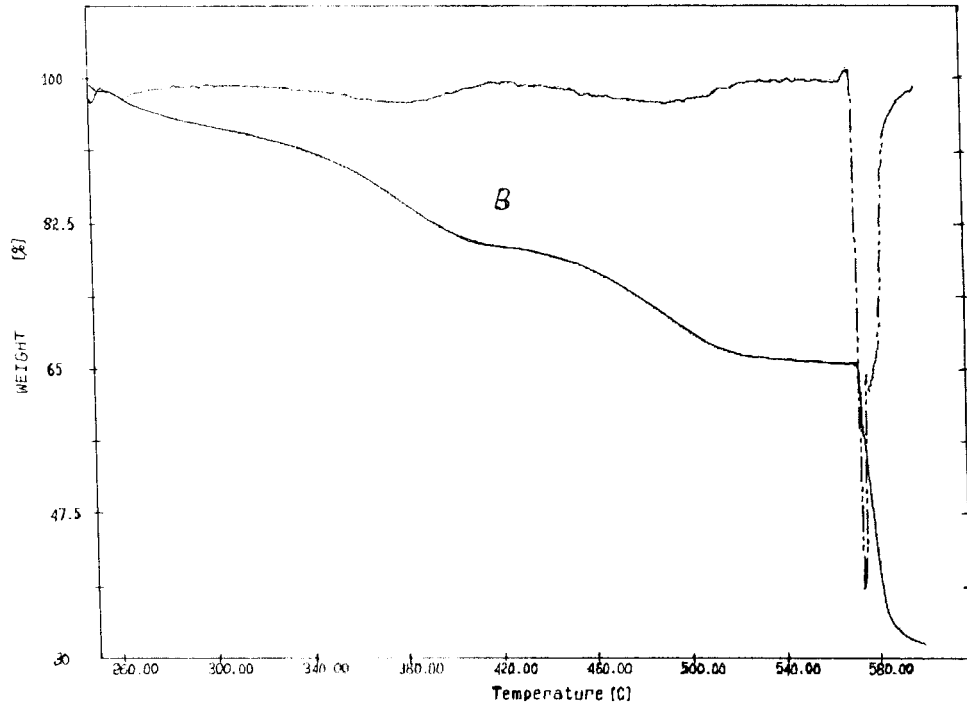


Figure 5 TGA-DTG thermogram of sample B.

fitted in the DSC-7, the heat change per gram of material has been calculated for each blend system from the area calculation. The higher heating

rate of 10 °C/min in the DSC scan than the 2 °C/min in the TGA is deliberate so the DSC procedure can be used commercially. The measure-

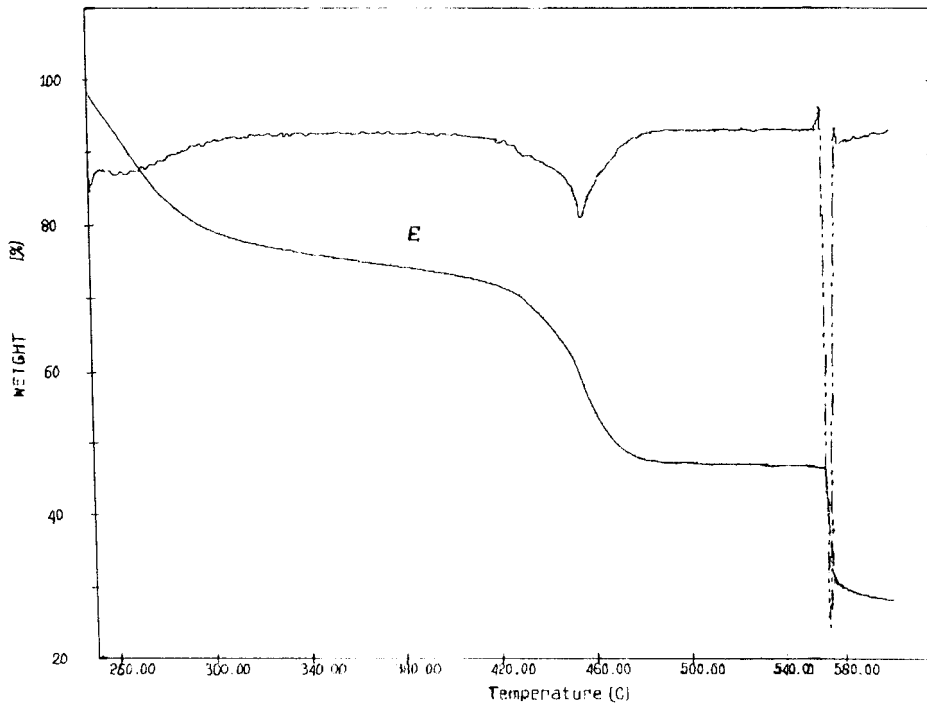


Figure 6 TGA-DTG thermogram of sample E.

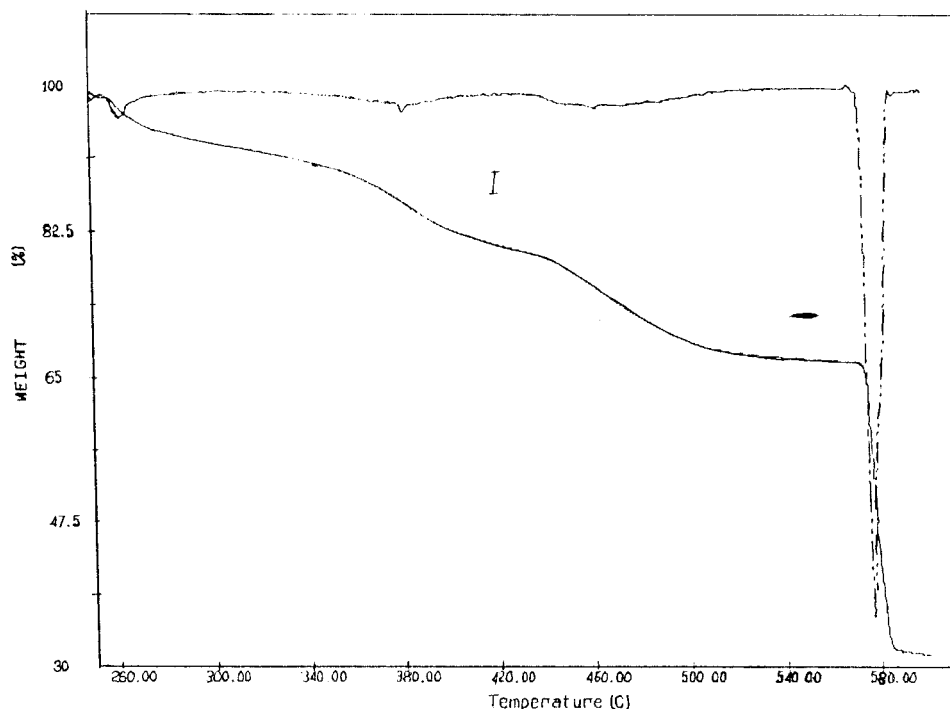


Figure 7 TGA-DTG thermogram of sample I.

ment of specific heat (J/g) at each decomposition temperature will substantiate any change or any reaction among the reactive chemical constituents more conveniently. Furthermore, any error that occurred or minor change that happened in the sample will be overcome by the conversion factor of gram (1000 mg), because the sample is taken at the milligram level for the DSC study. The calculation of specific heat also covers the temperature range (area under the curve); hence, the cumulative effect of the crosslinking that arises from the blend partners will be well accounted for in the DSC, which is not possible in the typical TGA thermogram. The exotherm in the cases of CR and NBR-PVC and the endotherm in case of CSM were obtained in the standard graph of the DSC measurement. Each of the blends was studied at least three times under the same conditions so that the standard deviation (σ) can be measured. The blends A, F, and J are 100% in the respective elastomers, and the $\Delta H/g$ (J/g) or specific heat for these samples are considered here as "Actual" as well as "Observed" for the sake of calculation. Subsequently, the $\Delta H/g$ (J/g) of the blends from B to E and G to I have been taken in DSC. The $\Delta H/g$ is calculated considering the blend ratio in the respective blend as well as $\Delta H/g$ obtained in the actual blend by the DSC.

Here the effect of ingredients has been taken as negligible because at the high temperature (>300 °C) only the elastomer or high boiling material are decomposed. The effect of crosslinking is ignored, because the crosslinking is corresponding to $-C-C$, $-C-O$, $-C-H$, or $-C-Cl$ bonds, which break at high temperature only. If there is any effect of crosslinking in the measurement, the area is measured over a temperature range, therefore, the temperature shifting has no effect in the area calculation. The enthalpy change per unit gram of the material also provides enough flexibility to encounter any change due to physical mixing during the blending. Here, the "Standard Deviation" has been added to the minimum "Observed" values of $\Delta H/g$ and compared with the "Calculated" values to have the best curve fit so that blend ratio of any unknown sample of a particular blend can easily be determined. The " σ ", " $\sigma + \text{Observed}$ " value, and "Calculated" value of $\Delta H/g$ for A to F blends are shown in Figure 8. The curve fit reveals that there is hardly any difference between the calculated and observed values of the $\Delta H/g$ in CR/CSM blends. As the CSM increases in the blend, the $\Delta H/g$ value changes from exo- to endotherm. Using this curve manually or by computer, the blend ratio can be determined within 2–3% deviation in the CR/CSM blend. The

variation of the $\Delta H/g$ versus blend ratio in the CR/NBR–PVC blend is shown in Figure 9. Both CR and NBR–PVC give an exotherm on degradation, perhaps, because of the dechlorination. The data fitting both in “Calculated” and the “Observed + σ ” values follow the same trend of the increasingly higher value of $\Delta H/g$ as the PVC amount is increased in the blend. The presence of NBR in the blends will certainly change the exotherm pattern. The specific heat measured at the lower percentage of NBR–PVC in the CR/NBR–PVC blend will obviously be less because of the lower amount of PVC and the endotherm of the NBR decomposition. As the amount of NBR–PVC increases with higher ratio of NBR–PVC in the blend, the high value of exotherm is observed (Figure 9). It is very interesting that the DSC curve in the blend from G to J shows an exotherm, which is exactly the amount of PVC present in the blend. This phenomenon can easily be understood because the PVC degrades relatively at lower temperature (230–260 °C). Here also, the curve fitting (Figure 9) provides the blend ratio with minimum error. However, the curve fit in both CR/CSM and the CR/NBR–PVC blend can estimate the blend partners easily in such co-curing reactive polymer amidst of reactive carbon black in the vulcanizates. The multistep decomposition and apparent difficulty in determining the blend ratio in the product itself by TGA now will find solution in the comparatively higher heating rate, high-temperature DSC method for such reactive blends. These observations regarding DSC are supported by the response zone, which is the zone corresponding to the decomposition of unit mass

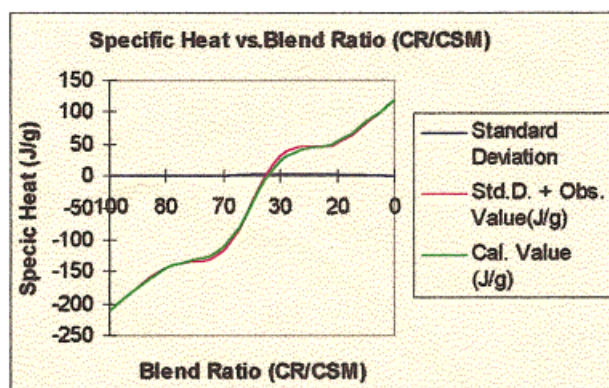


Figure 8 Specific heat (obtained from DSC) versus blend ratio (CR/CSM). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

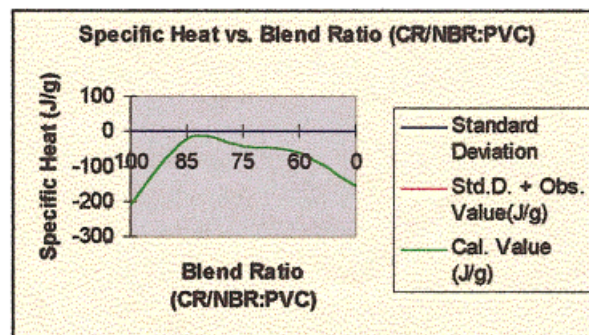


Figure 9 Specific heat (obtained from DSC) versus blend ratio (CR/NBR–PVC). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the materials at highest rate as observed in the DTG thermogram.²

CONCLUSION

Determination of the blend ratio, in the case of the Cl-containing elastomer blends (e.g., CR/CSM and CR/NBR–PVC) by FTIR and TGA-DTG techniques is very difficult or impossible because of the common moiety of chloride as well as amorphous hydrocarbon structure of the aforementioned elastomers. Polymer identification in the product, using the ASTM solutions, is a futile exercise in Cl-containing elastomer blends like CR/CSM, CR/NBR–PVC etc. mentioned above, particularly when compounds contain alkali ingredients like CaCO_3 and Barytes as fillers. The high-temperature DSC technique can successfully be used in this type of blend for the economic determination of the blend ratio instead of determining this ratio from the usual glass transition temperature by low-temperature DSC. The concept of best curve fit, as stated in this paper, would be utilized successfully, with minimum error, for the blend ratio determination of the unknown commercial samples containing highly polar functional groups in the presence of reactive carbon black as filler.

REFERENCES

1. Wake, W.C.; Tidd, B.K.; Loadman, M.J.R. 1983. Analysis of rubber and rubber like polymers, 3rd ed.; Applied Science Publishers: New York., 3rd Ed. (1983).

2. Sircar, A.K. 1992. *Rubber Chem Technol* 65:508.
3. Maurer, J.J. 1974. *J Macromol Sci Chem A*8:73.
4. Maurer, J.J. 1981. Thermal characterization of polymeric materials; Turi, E.A., Eds.; Academic Press: New York.
5. Brazier, D.W.; Nickel, G.H. 1978. *Rubber Chem Technol* 48:661.
6. Rugo, G.; Urbani, M.; Barbattini, D.; Nastasi, C.; Orsi, M.; Poponessi, M. 1986. *Kautchuk Gummi-Kunststoffe* 39:216.
7. Tripathy, A.R.; Das, C.K. 1994. *Polym Plast Technol Eng* 33(2):195.
8. Tripathy, A.R.; Das, C.K. 1992. *Kautchuk Gummi-Kunststoffe* 45(8):626.
9. Maurer, J.J. 1969. *Rubber Chem Technol* 42:110.
10. Smith, D.A. 1966. *Kautchuk Gummi-Kunststoffe* 19:477.
11. Smith, D.A. *J Polym Sci, Part-B* 4 215.
12. Sircar, A.K.; Lamond, T.G. *Rubber Chem Technol* 48:653.