

Studies on phase morphology and thermo-physical properties of nitrile rubber blends

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Abstract The study deals with the morphological and thermal analysis of binary rubber blends of acrylonitrile-co-butadiene rubber (NBR) with another polymer. Either ethylene propylene diene terpolymer (EPDM), ethylene vinyl acetate (EVA), chlorosulphonated polyethylene (CSM), or polyvinyl chloride (PVC) has been selected for the second phase. Depending on the relative polarity and interaction parameter of the components, the binary blends showed development of a bi-phasic morphology through scanning electron microscopy (SEM). Use of different types of thermal analysis techniques revealed that these blends are generally incompatible excepting one of NBR and PVC. Derivative differential scanning calorimetry (DDSC), in place of conventional DSC, has been used to characterize the compatibility behavior of the blends. NBR–PVC shows appearance of only one glass transition temperature (T_g) averaging the individual T_g 's of the blend components. The partially miscible blend of NBR and CSM shows a broadening of T_g interval between the phase components, while the immiscible blends of either NBR–EPDM or NBR–EVA do not show any change in T_g values corresponding to the individual rubbers of their blend. The experimental T_g values were also compared with those calculated theoretically by Fox equation and observed to match closely with each other. Studies have also been made to evaluate the thermal

stability of these blends by thermo-gravimetric analysis (TG) and evaluation of activation energy of respective decomposition processes by Flynn and Wall method. Thermo-mechanical analysis (TMA) was found to be effective for comparison of creep recovery and dimensional stability of the blends both at sub-ambient as well as at elevated temperatures.

Keywords Nitrile rubber · EPDM rubber · Rubber blends · Scanning electron microscopy · Thermal analysis · Compatibility

Introduction

Nitrile rubber (NBR) is well known for its good oil resistance but has poor resistance to heat, oxygen and ozone. It is, therefore, blended with a saturated or low unsaturated rubber, e.g., ethylene propylene diene terpolymer (EPDM) to minimize its oxidative degradation during service. However, compatibility between the component phases is a necessity for these blends to show improved service performance [1]. In this context, Lohmar [2] also has reported on the studies on compatibility of NBR and EPDM blends by addition of poly-trans-octenylyne rubber (TOR). Compatibility of NBR and EPDM blends as evidenced by scanning electron microscopy (SEM), atomic force microscopy (AFM), flow visualization as well as by variety of other thermal techniques have earlier been reported by Setua et al. [3–8]. The effect of functionalization of EPDM on curing and mechanical properties of NBR/EPDM blends and the scope of reactive compatibilization of NBR/EPDM blends by combination of mercapto and oxazoline groups have been reported by Oliveira et al. [9–11]. Thermo-gravimetric analysis (TG), thermal aging, and dynamic

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mechanical behavior of NBR/ethylene vinyl acetate (EVA) blends have been reported by Varghese et al. [12, 13]. Jansen et al. [14] have reported on the effect of mercapto-modified EVA in rheological and dynamic mechanical properties of NBR/EVA blends. Elastomer blends based on NBR and chlorosulphonated polyethylene (CSM) are expected to be attractive due to heat, oil, and weather resistance of CSM which are to be combined with the oil resistance, abrasion resistance, and mechanical properties of NBR.

We report, in this article, the results of our studies on phase morphology, thermal degradation, and dimensional stability of binary elastomer blends based on NBR/EPDM, NBR/EVA, NBR/CSM, and NBR/PVC.

Experimental

Materials

All the raw rubbers, e.g., NBR, EVA, EPDM, CSM, and PVC, are virgin elastomers without any additives. The vulcanizates of binary blends use one common recipe in parts per hundred parts of rubber (phr) as follows: rubber 100.0, ZnO 3.5, sulfur 1.5, stearic acid 1.5, *N*-cyclohexyl-2 benzothiazole-2-sulphenamide (CBS) 1.5, pigment 0.5. Besides, the binary blends have blend ratio of 70 NBR:30 other polymers (EPDM, EVA, CSM, and PVC).

Preparation of blends

Mixing of rubber was carried out in a two-roll rubber mixing mill according to ASTM designation D 15-70 for 15 min at a friction ratio of 1:1.1. Vulcanization of the test slabs was done in a hydraulic press at 433.15 K, 4.5 MPa

pressure for 10 min. Samples for SEM and thermal analysis were obtained from these test slabs by razor cutting.

Scanning electron microscopy

A high-resolution scanning electron microscope (Carl Zeiss SEM EVO 50XVP) was used to investigate the phase morphology of the blends. The samples were vitrified in liquid nitrogen and cryosectioned in a Leica EM FC6 ultramicrotome. The ultrathin cut surfaces were carefully handled without touching the surface, sputter coated with gold, and were used for phase morphology studies at varied magnifications under the SEM.

Differential scanning calorimetry (DSC)

Samples of 5–10 mg in size, in hermetically sealed aluminum pans, were heated in a DSC 2910 (TA Instruments Inc., New Castle, NJ, USA) at 293.15 K/min from 123.15 to 323.15 K using liquid nitrogen cooling can.

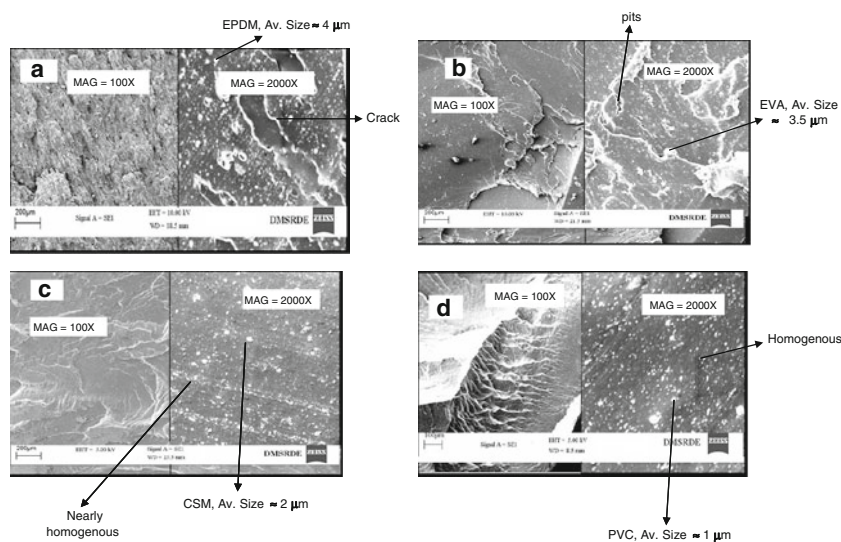
Thermogravimetric analysis (TG)

Samples of 5–10 mg in size were put in a platinum pan and heated from ambient to 1073.15 K at different heating rate of 278.15, 283.15, 288.15, and 293.15 K/min in nitrogen gas purge of 60 mL/min in a Hi-Resolution TG 2950 (TA Instruments Inc., USA).

Thermomechanical analysis (TMA)

The samples, of size 4×4 mm and thickness 4 ± 0.01 mm, were heated from 278.15 to 423.15 K at the heating rate of 278.15 K/min with expansion probe using mechanical cooling accessory. In addition, TMA isothermal creep

Fig. 1 SEM Photographs depicting the phase morphology of **a** NBR /EPDM; **b** NBR/EVA; **c** NBR/CSM; **d** NBR/PVC of the binary rubber blends



recovery experiments were also performed in a TMA 2940 (TA Instruments Inc., USA) at 303.15, 333.15, 363.15, and 393.15 K by applying a static load of 100 g over to the samples for 5 min and subsequently monitoring the penetration data. The load was then removed, and the recovery data were recorded for next 60 min.

Result and discussions

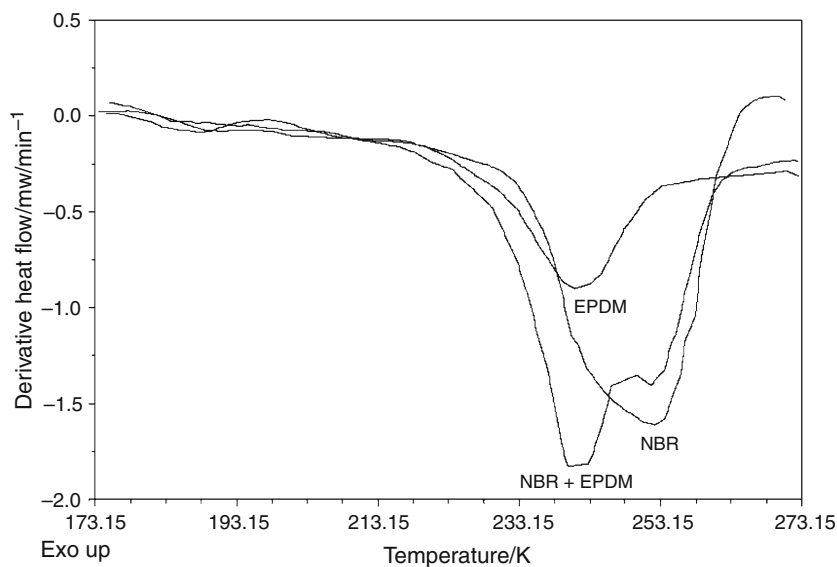
Scanning electron microscopy photomicrographs of the phase morphology of the four types of binary blends are depicted in Fig. 1. Blending of the two immiscible copolymers mostly leads to formation of a bi-phasic morphology, and the scale of the dispersed phase is strongly influenced by the relative polarity of the components and difference in solubility parameters. If the difference of solubility parameter is >1 , normally the blends show an immiscibility. Figure 1 is the SEM photomicrograph of the blends taken both at low ($100\times$) as well as at a higher magnification ($2000\times$). The domains of the dispersed polymeric phases and their location have been pointed out by arrows. The scale (average size) of the dispersed particles have been determined by quantitative statistical and spectral texture analysis using digital image processing method reported recently by Setua et al. [15]. It is quite evident that both NBR/EPDM and NBR/EVA blends are immiscible, while CSM in NBR/CSM blend forms fine domains of few micrometers in size, suggesting semi compatibility of components, and NBR/PVC has morphology similar to a miscible blend. There are, of course, other parameters which play important role in the generation of miscibility or compatibility viz., the blend ratio, mass and viscosity of the phase components, mixing

parameters and more importantly the use of a compatibilizer. Compatibilizers, which are either a block or graft copolymers, are added to a small proportion in a blend to cause major changes in the phase morphology and in mechanical properties. Thermo-physical properties of polymer blends are, however, characteristic of individual glass transition temperature (T_g) of the component phases. The changes in T_g of blend versus neat components, however, are dependent on the processing conditions and resulted morphology [16]. Single T_g of a blend is rather the measure of the state of dispersion. It is also an indirect method for determination of polymer/polymer miscibility. Conventional thermal techniques, therefore, need to be further improvised to conduct an in-depth study on the visco-elastic behavior and to accurately assess the thermodynamic and other long-term properties of polymer blends. Some novel methods have been evolved and are discussed in this article.

Derivative DSC (DDSC)

Glass transition temperature (T_g) of the component elastomers is generally difficult to measure accurately in elastomer blends. The DDSC curve exhibits a peak corresponding to the maximum slope of the endothermic shift accompanying T_g , and the DDSC peak temperature is close to the midpoint value of the T_g endotherm of DSC [17]. Figures 2 and 3 show the DDSC curves of representative NBR blends, and the values are given in Table 1. T_g of the component polymer in the NBR/EPDM and NBR/EVA blends remains unaltered indicating incompatibility in the blends. A negative shift of T_g of NBR by 283.15 K has been observed in the case of NBR/CSM blend, and the displacement of T_g of NBR toward lower temperature

Fig. 2 DDSC plots of NBR, EPDM, and NBR/EPDM



indicates an increase of the chain mobility of NBR caused by the presence of the CSM. The depression of T_g and the extent of broadening of the T_g interval between the two components as a measure of compatibility have also been reported earlier in several multi component systems [18–22]. The interval between the T_g of components NBR and CSM is increased from 280.11 to 287.46 K indicating partial miscibility in the blend.

The T_g interval between the components NBR and EPDM is 284.65 K which remains more or less unchanged in the blend. The same trend was followed in the NBR/EVA blend representing immiscibility.

For a blend that forms a single phase, T_g can be estimated from the Fox equation [23]:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}, \quad (1)$$

where W_1 and W_2 represent the mass fractions of the polymers 1 and 2, and T_g , T_{g1} , and T_{g2} are the T_g 's of the blend, polymer 1, and polymer 2, respectively. It may be

mentioned that the difference between the actual T_g and the one estimated by the Fox equation can be used as a measure of incompatibility in a rubber–rubber blend [24]. The deviation of T_g of the corresponding component from the T_g estimated by the Fox equation, given in Table 1, exhibits incompatibility in both NBR/EPDM and NBR/EVA blends. The maximum deviation in NBR/CSM further supports our conclusion of existence of semi-compatibility for the blend.

Thermogravimetry analysis (TG)

TG and derivative thermogravimetry (DTG) studies have been made at a heating rate of 293.15 K/min, and the curves are shown in Figs. 4 and 5, and results are summarized in Tables 2 and 3, respectively. The thermal degradation kinetics, based on the Flynn and Wall method, require three or more different heating rates [25]. The approach assumes the basic Arrhenius equation:

Fig. 3 DDSC plots of NBR, EVA, and NBR/EVA

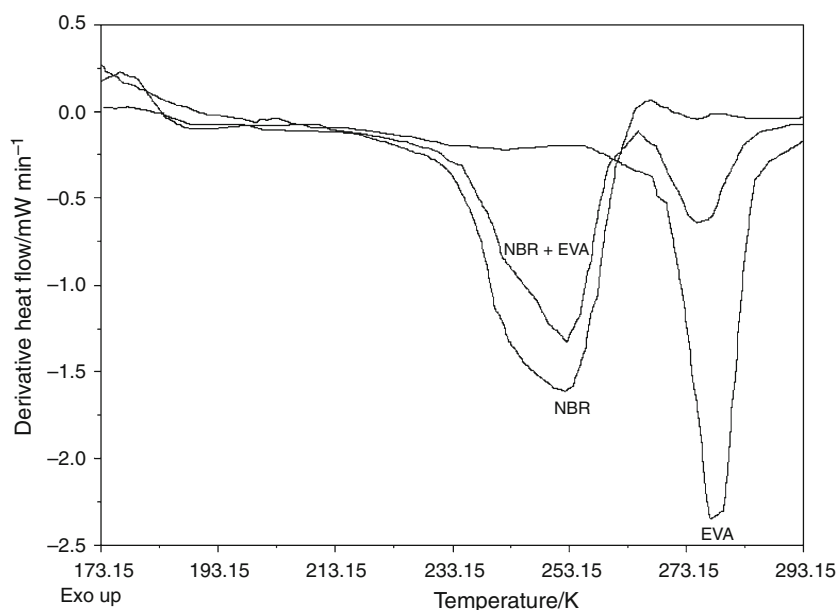


Table 1 DDSC values of raw rubbers and blends

Sample and blends	T_g of individual polymer and components of the blends/K	T_g estimated by Fox equation/K	Deviation of T_g of NBR (experimental and estimated by Fox eqn.)/K	Deviation of T_g of second component (experimental and estimated values)/K
NBR	252.46			
EPDM	270.96			
EVA	277.21			
CSM	-13.73			
NBR/EPDM	251.92/240.12	249.95	275.12	282.98
NBR/EVA	252.63/275.08	275.64	296.16	273.71
NBR/CSM	242.42/256.73	281.51	311.64	281.21

$$(d\alpha/dt) = A \exp(-E_a/RT)(1 - \alpha)^n, \tag{2}$$

where α is the fractional decomposition of the sample, t is the time (s), A is the pre-exponential factor (1/s), E_a is the activation energy (J/mol), R is the gas constant, and n is the reaction order.

The equation can also be rearranged to the form:

$$E_a = -(R/b) (d \ln \beta) / [d(1/T)], \tag{3}$$

where b is constant (0.457) when assuming the reaction order $n = 1$ and β is the heating rate ($^{\circ}\text{C}/\text{min}$).

Using the above formula, E_a for different conversion levels in a given process with extent from 10 to 50%

decomposition or conversion was calculated. The values of the activation energy are listed in Table 4 which clearly exhibits no improvement of thermal stability for either NBR or of any blend supporting the TG and DTG results given above.

Thermomechanical analysis (TMA)

Curves of TMA and derivative TMA of the blends are shown in Figs. 6 and 7, and the results are summarized in Table 5. These show no reduction either in the expansion or maximum rate of expansion in NBR after blending it

Fig. 4 TG curves of the blends

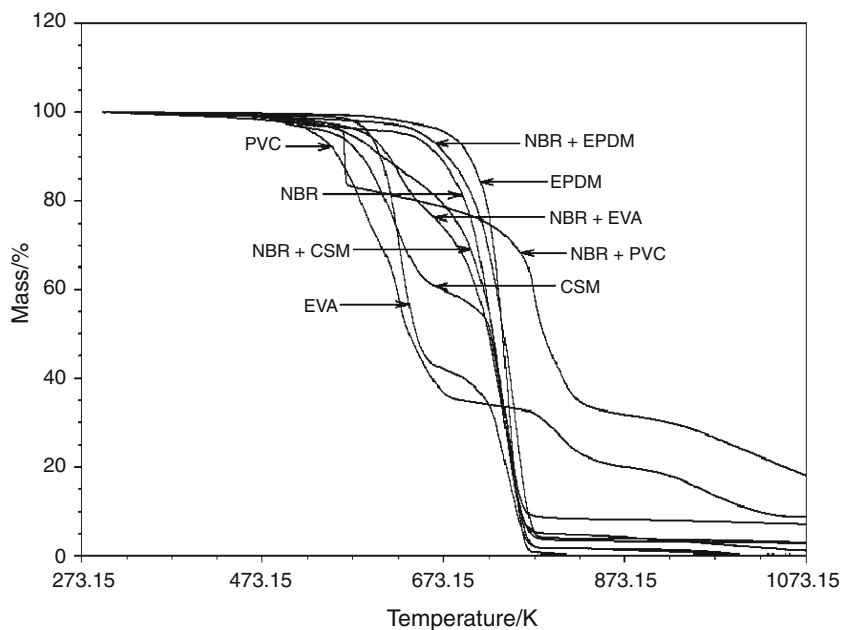


Fig. 5 DTG curves of raw rubbers and blends

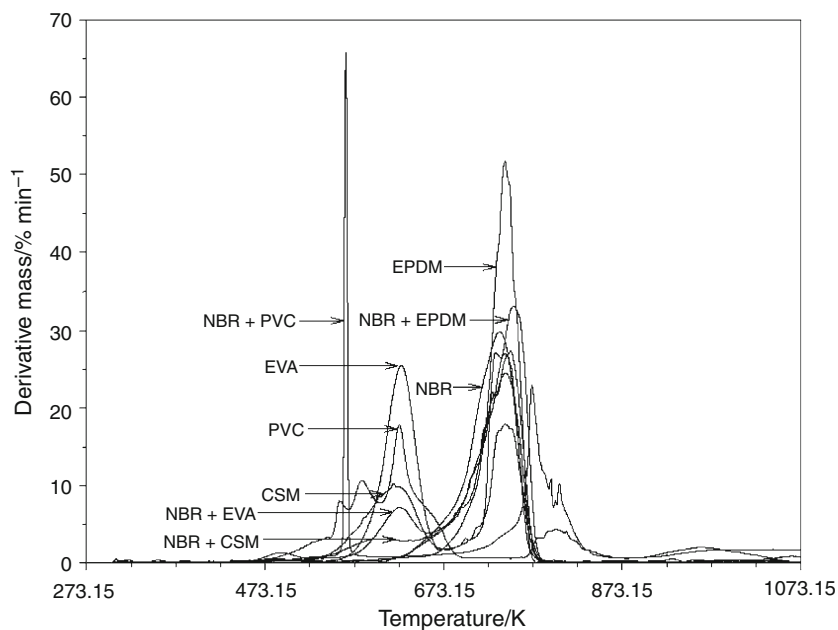


Table 2 TG results of raw rubbers and blends

Sample	Initial decomp. temp./K	First step of decomposition		Second step of decomposition		Third step of decomposition		Residue at 1073.15 K/%
		Onset temp./K	Mass loss/%	Onset temp./K	Mass loss/%	Onset temp./K	Mass loss/%	
NBR	618.65	698.30	88.69	–	–	–	–	1.044
EPDM	549.55	719.25	98.67	–	–	–	–	0.166
NBR/EPDM	597.85	712.11	92.48	–	–	–	–	2.963
EVA	498.05	601.70	57.47	723.44	40.39	–	–	0.021
NBR/EVA	452.45	589.72	21.59	711.92	73.83	–	–	2.756
CSM	436.20	468.69	3.020	580.26	36.79	724.20	57.22	0.025
NBR/CSM	422.45	455.55	1.653	562.38	11.71	709.72	77.77	7.062
PVC	412.08	504.37	65.96	776.69	14.17	924.71	11.25	8.660
NBR/PVC	404.05	562.47	14.38	760.36	45.82	936.61	13.79	18.020

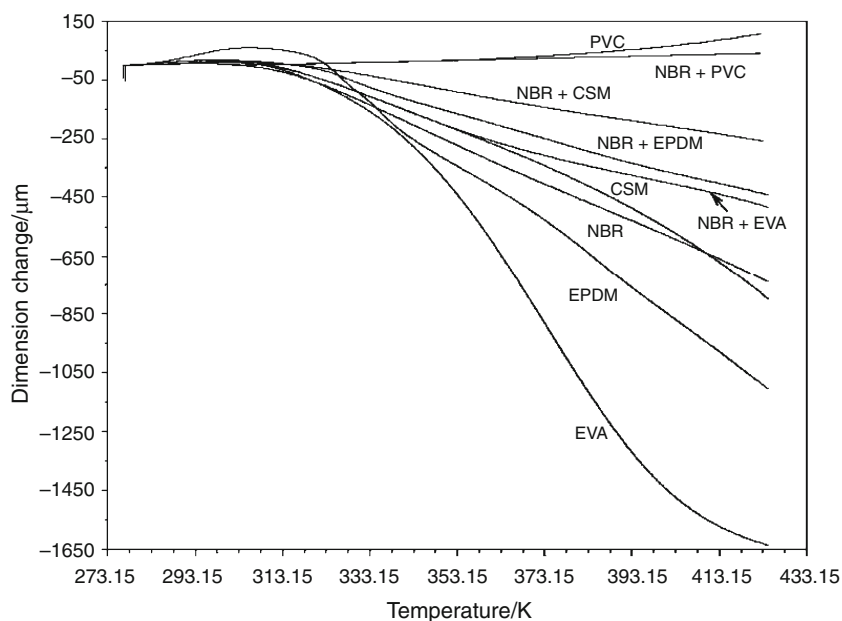
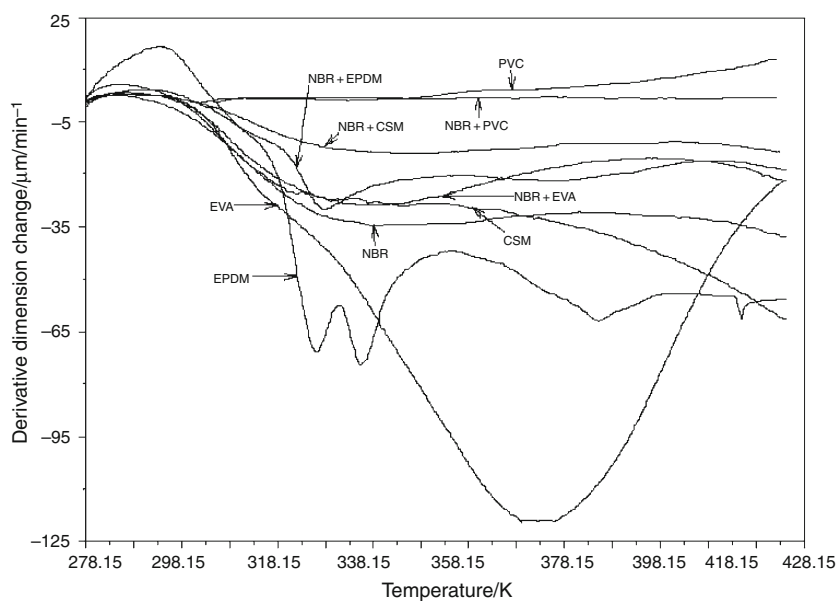
Table 3 DTG results of raw rubbers and blends

Sample	First step of decomposition		Second step of decomposition		Third step of decomposition		Complete decomposition		
	Peak temp./K	MRD ^a / % min ⁻¹	Peak temp./K	MRD/ % min ⁻¹	Peak temp./K	MRD/ % min ⁻¹	Reaction time/min	TML ^b / %	ARML ^c / % min ⁻¹
NBR	736.69	31.07	–	–	–	–	8.86	90.80	10.24
EPDM	742.95	51.40	–	–	–	–	6.78	96.58	14.24
NBR/EPDM	751.29	33.19	–	–	–	–	9.48	93.58	9.87
EVA	626.10	25.79	740.86	18.56	–	–	12.08	97.35	8.05
NBR/EVA	624.01	7.14	742.95	24.48	–	–	11.48	93.42	8.13
CSM	490.47	1.33	617.75	10.19	747.12	27.26	16.85	97.88	5.80
NBR/CSM	484.75	0.53	599.55	3.11	731.45	27.17	18.69	91.00	4.86
PVC	623.85	17.81	798.62	4.39	964.45	2.02	31.21	91.06	2.91
NBR/PVC	563.49	65.68	771.96	23.01	984.27	1.74	26.05	78.57	3.01

^a Maximum rate of decomposition, ^b total mass loss, ^c average rate of mass loss

Table 4 Values of activation energy of raw rubbers and blends for different conversion level

Activation energy/kJ mol ⁻¹	Conversion level/%	NBR	EPDM	NBR/EPDM	EVA	NBR/EVA 800	CSM	NBR/CSM	PVC	NBR/PVC
Ist step	10	241.4	78.0	109.9	104	75.3	61.2	78.6	60.5	62.3
IInd step	–	–	–	–	382.2	–	129.7	–	323.2	220.9
Ist step	20	175.5	82.5	143.2	104.1	110.5	76.1	125.2	61.3	79.8
IInd step	–	–	–	–	263.7	–	134.2	–	214.2	212.5
Ist step	30	161.3	84.8	166.8	105.0	113.4	78.5	119.2	66.8	106.1
IInd step	–	–	–	–	203.7	–	130.0	–	177.0	189.7
Ist step	40	148.5	86.6	155.9	106.8	115.4	78.0	133.8	71.8	105.8
IInd step	–	–	–	–	184.8	–	128.3	–	160.7	188.1
Ist step	50	141.7	87.8	153.0	108.6	118.6	77.8	125.1	74.5	104.7
IInd step	–	–	–	–	175.1	–	126.2	–	155.5	184.7

Fig. 6 TMA plots of raw rubbers and blends**Fig. 7** Derivative TMA plots of raw rubbers and blends

with EPDM, EVA, or CSM. However, the addition of PVC shows a decrease in the maximum rate of expansion. For contraction and maximum rate of contraction, the absolute values were reduced in NBR for all its blends with minimum in the case of NBR/CSM. The NBR/PVC blend, however, exhibited expansion only in entire temperature range affixed for the study. The results are significant in respective of dimensional stability of NBR which experiences a marked improvement when it is blended with PVC for ambient as well as for application

in higher temperature range of the blend for some component or devices.

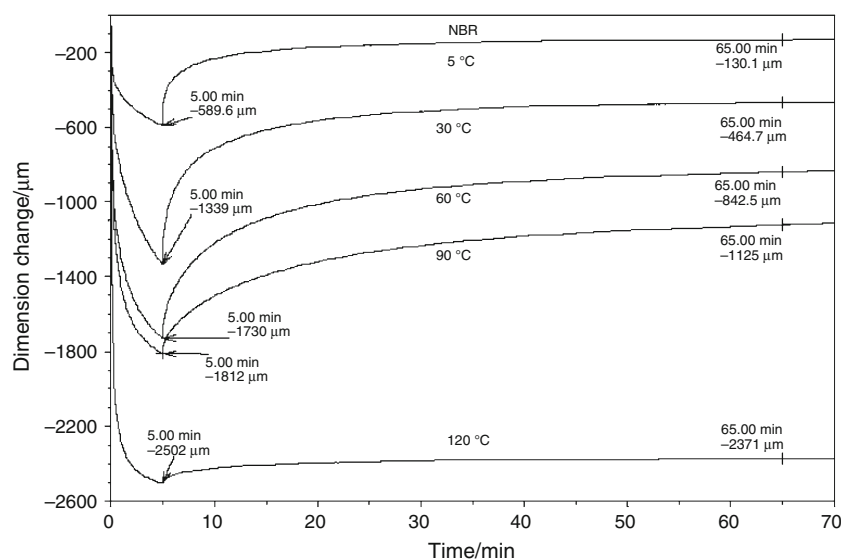
TMA also appears to offer a convenient method for qualitative comparison of viscoelastic characteristics of the elastomer and blends for scope of creep recovery analysis, and the experimental results are summarized in Table 6. A representative plot for NBR has been shown in Fig. 8. Being an indicator of the elastic modulus, elastic recovery results show that NBR displays the best mechanical property form ambient to higher temperature range when it is blended with PVC.

Table 5 TMA results of raw rubbers and blends

Sample	Expansion/%	Max. rate of expansion/ $\mu\text{m min}^{-1}$	Contraction/%	Max. rate of contraction/ $\mu\text{m min}^{-1}$
NBR	0.2173	2.482	29.09	34.69
EPDM	2.021	16.62	39.76	74.31
EVA	0.5579	3.055	91.27	119.7
CSM	0.4536	5.564	21.92	60.84
PVC	6.617	12.93	–	–
NBR/EPDM	0.5982	4.208	19.60	29.95
NBR/EVA	0.3203	3.393	15.84	28.96
NBR/CSM	0.4269	2.851	11.99	13.98
NBR/PVC	2.318	2.035	–	–

Table 6 Viscoelastic characteristics of elastomers and blends

Sample	NBR	EPDM	EVA	CSM	PVC	NBR/EPDM	NBR/EVA	NBR/CSM	NBR/PVC
Elastic recovery/% at 303.15 K	65.29	82.66	65.00	66.54	96.04	65.49	80.31	69.73	96.04
Elastic recovery/% at 333.15 K	51.30	77.61	12.26	60.22	92.76	54.73	73.79	64.47	93.80
Elastic recovery/% at 363.15 K	37.91	28.42	3.32	49.17	93.78	48.93	24.74	57.24	93.37
Elastic recovery/% at 393.15 K	5.23	19.46	0.68	27.73	97.11	8.61	2.51	28.08	93.21

Fig. 8 TMA curves on creep recovery experiments

Conclusions

- 1 Phase morphology of binary elastomer blends of NBR and their thermal analysis show good correlation when proper improvised methods of thermal analysis are adopted. In this respect, DDSC has been found to be more effective in the elucidation of compatibility of elastomer blends than conventional DSC.
- 2 Isothermal Creep recovery analysis by TMA for elastomers blends has been reported which proves to be a convenient tool to compare the elastic modulus qualitatively through creep recovery analysis and to

evaluate the dimensional stability of the elastomer blends.

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