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Thermal study on binary blends of ethylene-propylene elastomers and acrylonitrile-butadiene rubber

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Summary

The thermal behavior of several formulations consisting of ethylene-propylene elastomers and acrylonitrile-butadiene rubber was investigated by differential scanning calorimetry. The sample compositions cover the whole concentration range of ((EPDM, EPR)/NBR = 100/0, 20/80, 40/60, 60/40, 80/20 and 0/100). The evaluation of molar enthalpies for studied polymer blends allowed to calculate molar capacities at various temperatures from 335 K up to 450 K. Due to the lack of additivity in the molar capacities of studied blends, the contributions of each component to the overall values of C_p are calculated. The dependency of component contributions on their concentrations follows a first order function, which explains the existence of a certain interaction between components.

Introduction

Elastomers blends have become technologically important materials for their diverse applications [1-10]. Their physical and chemical properties recommend them as engineering materials for electric insulators, chemical industry, automotive and aircraft production, packaging, and many other areas. Several studies on thermal behavior of polymer blend define high performances over large temperature ranges.

The polymeric materials used for wire and cable insulation and jacketing or sealant manufacture are subjected to an accelerated degradation under the action of environmental factors and/or electrical field. The oxidation of such materials has been reported by DSC investigations. Mason and Reynolds [11] characterized the resistance to the attack of oxygen by the determination of oxidation induction time as a proper parameter of long life warranty. Sun et al. [12] have discussed the behavior of some cable materials under thermal and radiation ageing emphasizing the effects of crystallinity on the delaying the thermal oxidation by the decrease in the diffusion of oxygen. The processing parameters that are required in various thermal transformations have been analyzed [13-17] for many polymers by identifying the transitions occurred during thermodynamic investigations (DSC measurements).

The miscibility of various categories of polymers has received a special attention for the assaying of component compatibility and for the thermal characterization of multicomponent formulations. The effects of component content and of substrate morphology changes in the T_g values, on the material resistance to oxidation were assessed [18-22]. Radiochemical investigations for the evaluation of the modification in physical properties due to the action of high energy radiation have also been carried out. The measurement of enthalpy on large temperature ranges has pointed out structural alterations that are caused by the energetic transfer on macromolecules [23-27]. The DSC technique allows the calculation of heat capacity for modified materials providing information on the thermal consequences of degradation hard condition along service time (simultaneous action of heat, mechanical overcharge, oxidative environment, electric field, radiation). The deviation of heat capacity from the additivity law [18] is a proof for the interaction between components, when they are subjected to the degradative stressors.

This paper is an attempt on the evaluation of thermal characterization properties for several blends consisting of ethylene-propylene rubbers and acrylonitrile-butadiene rubber, which would be successfully used in the manufacture of various sorts of seals, anticorrosive sheets and membranes, industrial packaging for rain protection, sound absorber composites. This study reports basic knowledge on the heat transfer process that accompanies all industrial activities.

Experimental

The raw materials, ethylene-propylene copolymer (EPR) and its similar terpolymer (EPDM) were provided by ARPECHIM Piteşti (Romania). Acrylonitrile-butadiene rubber (NBR, CAROM®) was supplied by CAROM Săvineşti (Romania). EPDM had contained 3.5 % (w/w) ethylidene norbornene (ENB) as added diene. Both ethylene-propylene polymers presented the same ratios of ethylene/propylene units (3:2). The samples consisting of various ratios of physically blended components (100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 w/w) were prepared by solvent ($CHCl_3$) removal from polymer solutions. The drying of polymer films was performed on stainless steel trays in air at room temperature. The molecular structures of tested materials are presented in Figure 1. The difference that exists between these two ethylene-propylene elastomers consists of their unlike unsaturation contents (0.063 C=C units / 1000 carbon atoms for EPR and 0.184 C=C units / 1000 carbon atoms for EPDM).

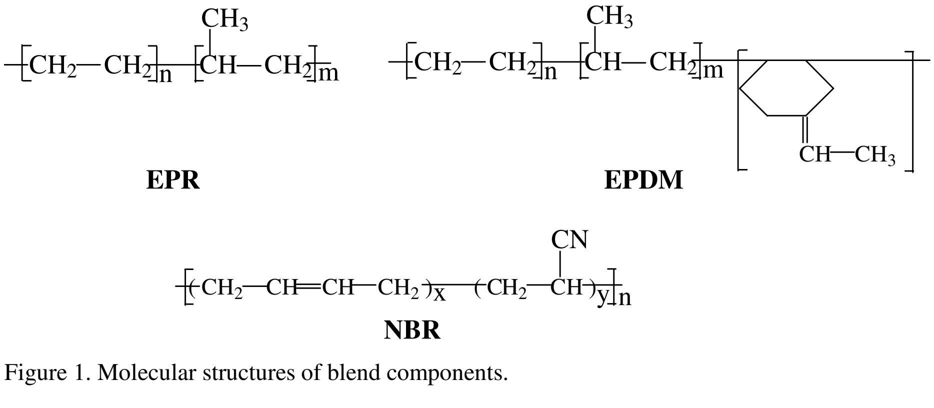

Figure 1. Molecular structures of blend components.

Differential scanning calorimetric measurements between 335 and 450 K with a step of 5 K using DSC-2 (Perkin Elmer) equipment were performed in air. Heating rate was 10 $K.min^{-1}$. Molar enthalpies were evaluated by means of O'Neill method [28] with alumina as standard.

Results and discussion

The modifications in the heat capacity of polymers are caused by the changes in the configuration of materials. [29, 30] In polymer blends, the molecular neighborhood plays an important role; the bond nature determines the vibration amplitude at increasing temperature. The energetic transfer on polymer matrix would provide resonance effects between adjacent macromolecules. The interaction established between the molecules of different constituents justifies the absence of colligative property for heat capacity.

In Figure 2 the dependencies of heat capacities on temperature for the three investigated polymers are presented. It may be noticed that the thermal behavior of EPDM is an intermediate one between EPR (saturated polymer) over the lower temperature range, and NBR, which contains double bonds, on higher temperature region. This feature would be explained by the differences in molecular structures and by the discontinuous interaction along molecular chains. It would be expected that their blend will confirm this assumption.

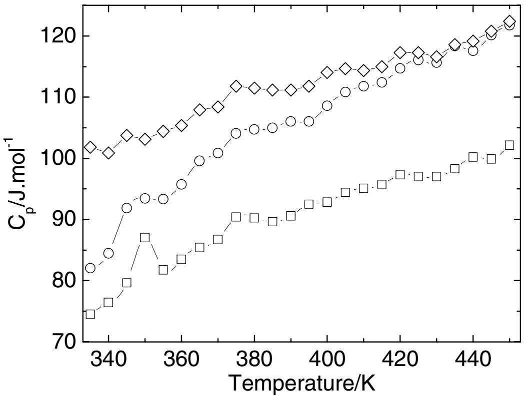

Figure 2. The temperature dependencies of heat capacity for EPR (□), EPDM (○) and NBR (◊).

The increase in heat capacity at higher temperatures indicates the activation of vibrations that requires superior energy values. It means that the alteration in the thermal stability of material on higher temperature domain is caused by the successive excitation of stronger bonds. Double bonds bring an important contribution of 72.4 $J.mol^{-1}$ to the overall value of heat capacity [31]. EPDM and NBR display greater C_p values, in contrast with EPR, which presents a saturated structure. The higher content of double bonds in NBR confirms its upper position relative to the curves for ethylene-propylene elastomers (Figure 2). As temperature rises, the oxidation of polymer samples takes place and new products participate with higher contribution at molecular heat capacity ($C_{p(C=O)}$ = 96,1 $J.mol^{-1}$ and $C_{p(COOH)}$ = 209 $J.mol^{-1}$).

The blending process modifies the surrounding of pristine components. The sample formulations show different shapes of heat capacity dependency on temperature. In figures 3 (a and b) and 4 (a and b) the changes in thermal properties of the two types of blends are presented. The relative positions of experimental dependencies in these figures are predictably correct, because the content of components varies monotonically.

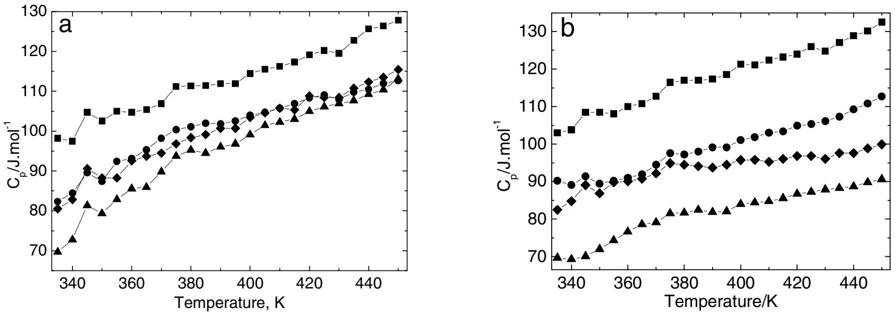

Figure 3. Experimental dependencies of heat capacity on temperature for EPR/NBR (a) and EPDM/NBR (b) blends at various mixing proportions (%)
(■) 20:80; (●) 40:60; (♦) 60/40; (▲) 80:20.

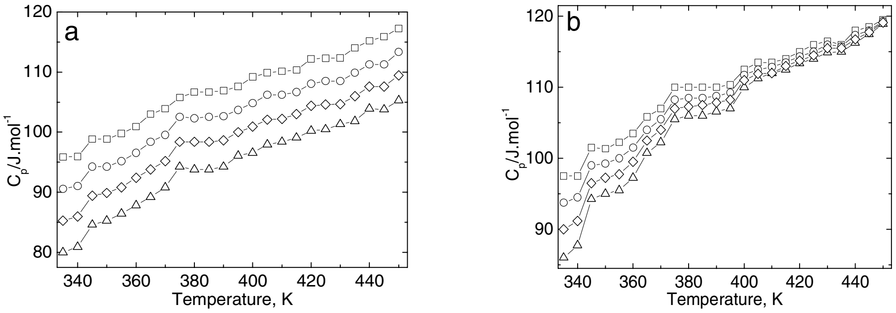

Figure 4. Theoretical dependencies of heat capacity on temperature for EPR/ NBR (a) and EPDM/ NBR (b) blends at various mixing proportions (% w/w)
(□) 20:80; (○) 40:60; (◊) 60/40; (Δ) 80:20.

For EPR/NBR blends, the $C_p(T)$ functions for the specimens with higher content of one component (20:80 and 80:20) look similar (figures 3a and 3b). It may be considered that the two constituents are diluted on each into other. For the other two formulations (40:60 and 60:40), the curves are closer to each other; the interaction between constituents becomes evident at higher temperatures.

The calculated heat capacities from the contribution of structural units are presented in Figure 4. It may be remarked that the dependencies $C_p(T)$ for EPR/ NBR blends are somewhat parallel, in contrast with similar drawing for EPDM/NBR mixtures. The convergence of $C_p(T)$ functions on the higher temperature range indicates the stronger interaction between the macromolecules of constituents (ethylene-propylene terpolymer and acrylonitrile-butadiene rubber), especially because of their double bonds.

Due to the "screening" effect of saturated moieties on double bond units, particularly of carbonyl functions, and the existing differences between the oxidation strength of studied materials, the rates of oxidation, which is characterized by the differences in C_p values seems to be similar for each group of binary blends.

The deviation in the heat capacities of blends from the law of additivity is demonstrated in Figure 5. For EPR/NBR = 20:80 and 80:20, where the main component is acrylonitrile-butadiene rubber, the change in ΔC_p are small (sparse-lined light grey and white columns, Figure 5a) as measurement temperature rises. The other group of samples (EPR/NBR = 60:40 and 40:60, black and white columns from Figure 5a) presents larger change in ΔC_p for increasing temperature. The difference in heat capacities is mitigated at higher temperatures. By contrary, for EPDM/NBR blends, the variation in ΔC_p is predominantly negative indicating that the interaction between constituents is more prominent. The formulation EPDM/ NBR = 20:80 (sparse-lined and light grey column, Figure 5b) displays the smallest values of differences between experimental and theoretical C_p.

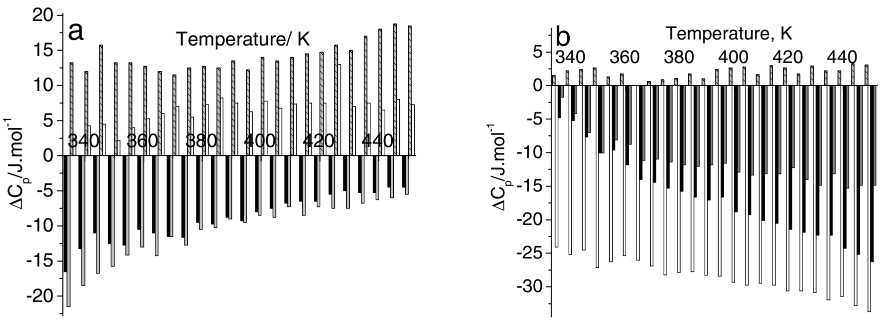

Figure 5. The deviation of C_p experimental values from theoretical evaluation for EPR/NBR (a) and EPDM/NBR (b) blends
(sparse-lined and light grey) 20:80; (light grey) 40:60; (black) 60:40; (white) 80:20.

The confirmation of the interaction between blended components is found in figure 6, where the contribution of each polymer to the C_p values follows a linear dependency. The difference between the structures of the two ethylene-propylene elastomers determines different slopes of these lines (table). The higher slope of EPDM/NBR system indicates the stronger interaction between components in comparison with EPR/NBR blends. The contribution of each polymer to the global C_p values is really lower than the figures obtained for separate materials.

The key of this feature is the formation of coalescent structure around acrylonitrile-butadiene rubber phase [32]. However, the values of heat capacities for nitryl and carbonyl units are similar and the accumulation of oxygen-containing moieties and their resonant interaction with CN groups do not modify substantially their contributions to the overall values of molecular C_p.

The dissimilarity in the thermal behavior of studied unsaturated compounds (EPDM and NBR) is caused by the unlike contribution of the norbornene and nitryl structures to the C_p values.

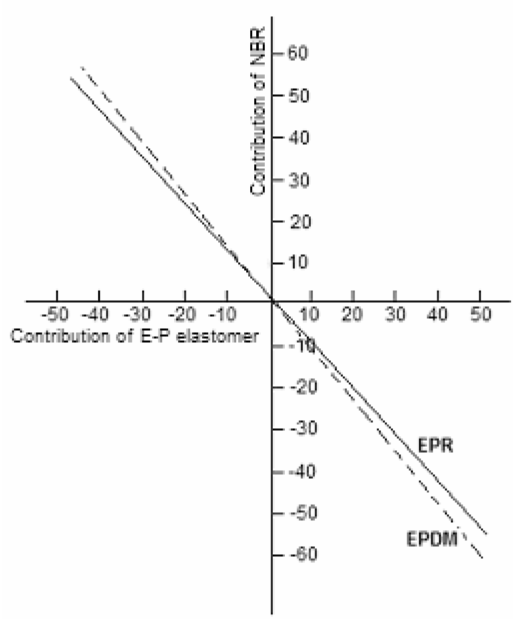

Figure 6. The contribution of the two components of elastomers blends to the C_p values of mixtures.

Table. Analytical expressions of component contributions to the C_p values of blends

Blend	Expression*	Correlation factor
EPDM/NBR	Y = -1.08X ± 0.65	0.979
EPR/NBR	Y = -1.23X ± 0.52	0.988

* Y denotes the contribution of acrylonitrile-butadiene rubber and X ethylene-propylene signifies the contribution of each ethylene-propylene elastomer [18]

Conclusion

This investigation on the heat capacity of (EPR, EPDM)/NBR blends by differential scanning calorimetry provides information regarding the effect of heating on the participation of each component to the C_p values of materials. The composition of samples influences the extent of modification in the thermal properties of studied systems, the material formulation being an important parameter for the characterization of thermal exchange. The difference in molecular structures reveals the specific contributions of blending components that are related to the interaction between neighbor molecules. The linear dependency of real component contributions, which were calculated from experimental data, was established for all selected formulations and temperatures. It is the evidence for the effective influence of constitutive units on overall C_p values. Thus, it was demonstrated that the molecular fragments of tested polymers participate differently to the calculated Cp due to their characteristic energies of thermal vibrations. The reciprocal influence of neighboring structures belonging to the closest polymer chains may be pointed out for polymer blends by DSC investigation.

References

[1] M. Pracella, F. Pazzagli, A. Galeski (2002) Polym. Bull. 48:67

[2] Y. Aoshuang, G, Zhengtao, L. Li, Z. Ying, Z. Peng (2002) Radiat. Phys. Chem. 63:497

[3] G. Burillo, P. Herrera-Franco, M. Vazquez, E. Adem (2002) Radiat. Phys. Chem. 63:241

[4] E. M. Araúho, E. Hage-jr, A. J. F. Carvahlo(2003) J. Mater. Sci. 38:3515

[5] Hr. Yordanov, L. Minkova (2003) *Eur. Polym. J.*, 39:951

[6] El Yilgör, I. Yilgör, S. Süzer (2003) *Polymer* 44:7271

[7] Q-H. Zhang, D-J. Chen (2004) J. Mater. Sci. 39:1751

[8] M. Ichazo, M Fernández, J. González, C. Albano, N. Domínguez (2004) Polym. Bull. 51:419

[9] S. Al-Malaika,W. Kong (2005) Polymer 46:209

[10] F. Fraïsse, V. Verney, S. Commereuc, M. Obadal (2005) Polym. Degrad. Stabil. 90:250

[11] L. R. Mason, A. B. Raynolds (1997) J. Appl. Polym. Sci. 66:1691

[12] Y. Sun, L. Fan, K. Watkins, J. Peak, C. P. Wong (2004) J. Appl. Polym. Sci. 93: 513

[13] T. Zaharescu, V. Meltzer, R. Vîlcu (1999) Polym. Degrad. Stabil. 61:383

[14] M. Brebu, C. Vasile, S. R. Antonie, M. Chiriac, M. Precup, J. Yang, C. Roy (2000) Polym. Degrad. Stabil. 67:209

[15] J. Pospíšil, Z. Horák, J. Pilař, N. C. Billingham, H. Zweifel, S. Nešpůrek, Polym. Degrad. Stabil, 82:145

[16] G. Amarasinghe, F. Chen, A. Genovese, R. A. Shank (2003) J. Appl. Polym. Sci. 90:681

[17] Z. Dobrowski (2006) Polym. Degrad. Stabil. 91:488

[18] T. Zaharescu, V. Meltzer, R. Vîlcu, D. Oprea (1998) J. Thermal Anal. 53:255

[19] M. Krištofič, A. Marcinčin, A. Ujheryiová (2000) J. Thermal Anal. 60:357

[20] H. Y. Chen, Y. W. Cheung, A. Hiltner, E. Baer (2001) Polymer 42:7919

[21] M. Song (2001) J. Thermal Anal. 63:699

[22] G. Burillo, P. Herrera-Franco, M. Vazquez, E. Adem (2002) Radiat. Phys. Chem. 63:241

[23] J. Suwanprateeb, P. Trontong (2003) Mater. Sci., Mater. Med. 14:851

[24] J. J. Suñol, J. Saurina (2002) J. Thermal Anal. 70:57

[25] A. R. Tripathy, P. K. Patra, J. K. Sinha, M. S. Banerji (2002) J. Appl. Polym. Sci. 83:937

[26] S. H. El-Sabbagh (2003) J. Appl. Polym. Sci. 90:1

[27] P. Perera, C. Albano, J. Gonzáles, P. Silva, M. Ichazo (2004) Polym. Degrad. Stabil. 85:741

[28] M. G. O'Neill (1964) Anal. Chem. 36:1238

[29] S. F. Lau, B. Wunderlich (1983) J. Thermal Anal. 28:50

[30] U. Gaur, M-Z. Cao, R. Pan, R. Wunderlich (1986) J. Thermal Anal. 31:421

[31] T. Zaharescu, V. Meltzer, R. Vîlcu (1966) J. Mater. Sci. Lett, 15:1212

[32] M. Giurginca, T. Zaharescu (2002) Polymer 41:7583