

EVALUATION OF THE COMPATIBILITY OF EPDM AND IIR

I. Specific heat capacity

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Abstract

The thermal effect of mixing of EPDM and IIR was studied by differential scanning calorimetry over the temperature range between 335 and 435 K. O'Neill's method was used for calculating the specific heat capacity with alumina as standard. The greater the butyl rubber content, the lower the heat capacity. The presence of butyl rubber induces a marked thermal instability because of isobutylene units. It is possible that a rearrangement occurs in the molecular sequence, accompanied by secondary reactions involving free radicals. The contribution of each component to the c_p of the tested polymeric systems is discussed. Differences between theoretical and experimental specific heat capacities increase as the operation temperature is raised. The relationship between the contributions of the two components to the specific heat capacity values of mixtures can be described by a first order equation, named the law of reciprocal thermal affinity. This aspect can be ascribed to the interaction of various reacting entities, which form certain units with low molar heat capacity.

Keywords: EPDM, IIR, polymer blends, specific heat capacity

Introduction

The thermal properties of materials are often invoked for durability evaluation [1]. Particular attention has been dedicated to polymeric blends [2-4], which are largely used under various hard operation conditions.

Modification in heat capacity can explain macroscopic effects as the result of structural changes. The characteristic behaviour of the studied materials indicates changes in the internal energy of specimens. In the case of polymers, the increase in oscillation amplitude is accompanied by production of free radicals

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which are afterwards involved in competitive processes, like recombination and oxidation. Exposure of polymers to the action of heat or any other damaging agent brings about new configuration of bond distribution along the molecular backbones. In fact, the distribution of absorbed energy among various bonds is non-uniform. The overall value of the specific heat capacity corresponds to certain concentrations of various structural units which can be modified by energy transfer onto the polymer.

Polymer blends would exhibit additive values for c_p , if no interaction occurred between reactive sites. But, the higher the affinity of radicals towards their neighbour, the larger the differences between theoretical and experimental values [5]. This behaviour has also been revealed by other procedures: physical and mechanical tests [6], SEM [7], ESR [8], chemiluminescence [9], IR spectroscopy [10], etc.

Previous studies performed in our laboratories concerning changes in specific heat capacity of ethylene-propylene elastomers [11, 12] proved that modifications occurred in molecular structures over the temperature range from 335 K up to 435 K and they were well described by DSC. Moreover, this method can be employed for the thermal characterization of aged materials [11, 13].

This paper presents the thermal effects of interaction on blending the components of EPDM/IIR systems, as determined by DSC measurements of the specific heat capacity.

Experimental

Ethylene-propylene terpolymer (EPDM) supplied by ARPECIIM, Pitesti (Romania) contains 29% propylene and 3.5% ethylene norbornene (ENB). It was intimately blended with polyisobutylene (IIR, 2045, Russia). This rubber incorporates 2% unsaturation. These polymers were not previously purified, in order to test commercial grade materials.

Sample mixtures were prepared from polymer solutions (1%) by evaporating the solvent (CHCl_3) on round aluminium trays. Component solutions were combined in such a manner as to obtain thin films with the following compositions: EPDM/IIR=75/25, 50/50 and 25/75 (w/w).

DSC measurements were performed in an inert atmosphere with a Perkin-Elmer DSC-2 equipment on individual polymers and on three mixtures with compositions given above. Molar enthalpies were evaluated by means of O'Neill's method [14] with alumina as standard over the temperature range from 335 to 430 K with a step of 5 K and in an inert atmosphere. The heating rate was 10 K min^{-1} .

Results and discussion

The large variety of possible polymer blends requires a suitable choice of materials for certain particular applications, especially where the operation runs un-

der special conditions. Energy transfer induces structural changes in polymers, namely cleavage of C–C and C–H bonds. Reactions (recombination and/or oxidation) of free radicals result in ‘new’ products, which will influence the behaviour of aged materials.

Thermal energy can be considered as a usual damage factor. The effect of heat treatment may be studied by evaluation of changes in specific heat capacity of polymers. Moreover, it may be supposed that binary blends of any pair of polymeric materials would reproduce the individual contribution of mixing components.

The dependences of specific heat capacity on the temperature for ethylene-propylene terpolymer (EPDM), polyisobutylene rubber (IIR) and three blends of them (3:1, 1:1 and 1:3) are presented in Fig. 1. It may be noticed that the lower c_p of IIR influences this property of the binary systems studied. Furthermore, the differences in values measured for these mixtures are not equally distributed for the curves of the 3:1 and 1:1 and 3:1 mixtures with the changes in composition. A higher IIR content shifts the curve corresponding to the 1:3 blend farther from that of the 1:1 blend than the 3:1 mixtures. This aspect can be explained by the higher stability of butyl rubber.

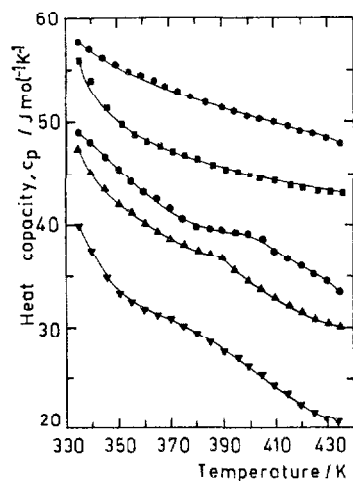


Fig. 1 Change in the specific heat capacity of EPDM, IIR and their mixtures. \blacklozenge – EPDM 100%; \bullet – EPDM/IIR=75/25; \blacktriangle – EPDM/IIR=50/50; \blacktriangledown – EPDM/IIR=25/75; \blacksquare – IIR 100%

On the other hand, large differences were observed between the theoretical and experimental values of c_p . Figure 2 demonstrates the strong influence of IIR on experimental specific heat capacities. The greater the rubber concentration, the larger the discrepancy between calculated and measured values. This means that the ethylene-propylene elastomer restores the initial structure of its hydrocarbon backbone more easily than the rubber component. This assumption is es-

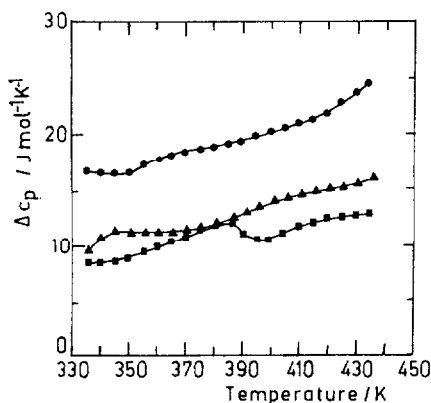


Fig. 2 Changes in the differences between theoretical and experimental c_p for three blends of EPDM and IIR. ■ – EPDM/IIR=75/25; ▲ – EPDM/IIR=50/50; ◆ – EPDM/IIR=25/75

pecially true for degrading polymers, because the free radicals formed by cleavage of C–C bonds belonging to tertiary and quaternary carbons require lower energy to abstract a detached hydrogen atom than to narrow the distance between the closest reactive sites on different macroradicals.

It is known [12] that the molar heat capacities of atom groups show different values. Their relative concentrations can be estimated by evaluation of changes in specific heat capacity of polymeric systems. Thus, the highest c_p values of $-\text{CH}_3$ and $-\text{CH}_2-$ (30.85 and $25.29 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively) are statistically averaged with the low values for $=\text{CH}-$ and $-\text{C}-$ units (15.55 and $21.53 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively). This means that in the tested samples (heated in an inert atmosphere) dehydrogenation and disproportionation take place simultaneously as the main reactions. Double bond formation is sure to occur but the small difference between the c_p values of methyl and methylene units and vinyl and vinylene structures (22.5 and $17.35 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively) cannot be detected.

For polymer blends it is difficult to evaluate separately the contribution of each component to the overall values of c_p because of the existence of competitive reactions in which radicals of various chemical nature are involved. Moreover, radicals which are progressively generated at rising temperature display certain affinity to their neighbours. It is followed by a certain reaction that requires very low activation energy. Polynomial expressions can be obtained for the dependences of specific heat capacities of polymeric systems on the temperature (Table 1). Similar relationships have been given by Mehta *et al.* [15].

Table 2 lists the contributions of EPDM and IIR to the c_p values for various blends. These values were obtained as solutions of linear systems of c_p equations for two close temperatures:

$$c_{pi} = X c_{p(a)} + Y c_{p(b)} \quad (1)$$

where X , Y are contributions of the blending components a and b to the overall c_p ;
 c_{pi} is the specific heat capacity for a certain temperature;
 $c_{p(a,b)i}$ are the corresponding heat capacities for the two components,
 a and b , respectively, measured at the same temperature as c_{pi} .

It can be noted that for most temperatures, $c_{p(a,b)}$ are close to the zero point of the (X, Y) axis. When the calculated figures are positive, it can be explained by lack of or only slight interaction between EPDM and IIR. The negative sign of some values can be attributed to the faster depletion of radicals belonging to one component and to the capability of the other component to restore its molecular structure. When one component is damaged to a large extent, its contribution to c_p is considerable and the other component is 'hindered' to react, so that the corresponding value of the specific heat capacity becomes very low. Negative signs of the solutions of type (1) equation systems indicate 'minimum' values. They can be explained by the 'saturation condition', when the amount of free radicals generated by one polymer reaches the greatest concentration under conditions of advanced degradation. A 5 K increase in temperature (from 370 to 375 K, or from 390 to 395 K or from 410 to 415 K, Table 2) produces a sign change, which can be ascribed to the fast reaction of the radicals of one kind to the detriment of the second component. These jumps describe an inversion in the concentration of the main component. The radicals provided by one constituent will stimulate advanced degradation of the other polymer. Thus, free radicals which can build up a new chemical structure might be produced either by thermal cleavage of weak bonds or by attack of radicals previously formed. These processes occur simultaneously, but one of them takes place at higher rate during a certain stage.

Table 1 Temperature dependence of specific heat capacity of EPDM/IIR systems

Material	Relationships	Correlation factor
EPDM 100	$-5.3 \cdot 10^{-5} T^3 + 3.4 \cdot 10^{-2} T^2 - 9.7 T + 1.1 \cdot 10^3$	0.990
EPDM/IIR = 75/25	$1.2 \cdot 10^{-4} T^3 - 5.6 \cdot 10^{-2} T^2 + 1.0 T - 4.7 \cdot 10^2$	0.993
EPDM/IIR = 50/50	$-8.4 \cdot 10^{-1} T^3 + 4.9 \cdot 10^{-1} T^2 - 1.3 \cdot 10^2 T + 1.2 \cdot 10^4$	0.989
EPDM/IIR = 25/75	$-5.2 \cdot 10^{-4} T^3 + 3.1 \cdot 10^{-1} T^2 - 84 T + 8509$	0.983
IIR 100%	$-1.4 \cdot 10^{-3} T^3 + 8.2 \cdot 10^{-1} T^2 - 216 T + 21220$	0.980

Table 3 and Fig. 3 present the analytical expressions and graph, respectively, for component dependence. From Table 3 it can be concluded that the coefficients which are obtained for the first order relationship between the contributions of the constituents to c_p (X for EPDM and Y for IIR) show quite similar values:

$$Y = aX + b \quad (2)$$

Table 2 Component contribution to c_p values of EPDM/IIR systems

Temperature/ K	EPDM/IIR = 25:75		EPDM/IIR = 50:50		EPDM/IIR = 72:25	
	EPDM	IIR	EPDM	IIR	EPDM	IIR
340	0.4236	0.4341	0.2189	0.6065	-0.1230	0.7444
345	0.3250	0.5441	0.0939	0.6550	-0.1278	0.8556
350	0.1761	0.7075	0.0930	0.7431	-0.2912	1.0351
355	-0.0627	0.9752	-0.0617	0.9165	-0.5760	1.3542
360	-0.5163	1.4907	-0.4907	1.3109	-1.1640	2.0226
365	-1.7118	2.8605	-1.4671	2.5235	-2.8443	3.9479
370	-12.3882	15.1362	-12.0393	14.6795	-18.8886	22.3958
375	5.9383	-5.9474	6.8007	-6.9950	9.3065	-10.0411
380	3.4105	-3.0426	4.8161	-4.7143	6.0089	-6.2517
385	3.1019	-2.6885	5.7266	-5.7588	6.7340	-7.0835
390	4.3921	-4.1664	11.4406	-12.3033	13.0643	-14.3340
395	-9.5140	11.7540	-38.2150	44.5245	-43.6691	50.5939
400	-1.1159	2.1349	-7.1319	8.9432	-8.4128	10.2356
405	-0.5790	1.5196	-4.4186	5.8332	-5.5508	6.9551
410	-0.8095	1.7844	-3.9775	5.3266	-5.4793	6.8730
415	-2.3121	3.5141	-5.6440	7.2450	-8.7411	10.6279
420	19.9826	-22.1917	25.3342	-28.4729	44.9521	-51.2805
425	3.1036	-2.7369	2.2453	-1.8606	4.6206	-4.7942
430	2.0476	-1.5246	0.9171	-0.3355	2.2023	-2.0176
435	1.6690	-1.0948	0.4929	0.1469	1.3833	-1.0859

Because the coefficients a and b representing the slope and the intercept of Eq. (2) are about the same, it may be possible to express this equation as the law of reciprocal thermal affinity. In the case of binary systems: ethylenic-propylene terpolymer/butyl rubber, this equation takes the following form:

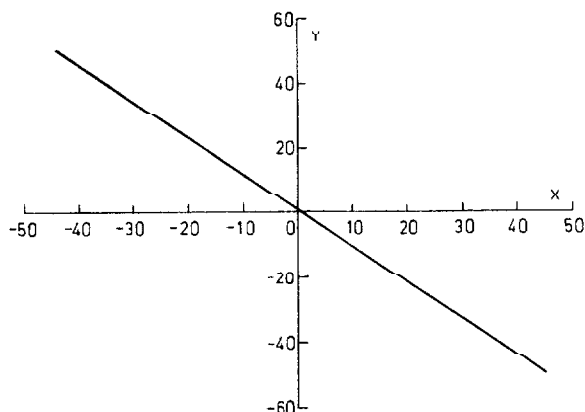
$$Y = -1.148X + 0.752 \quad (2')$$

The negative sign of the slope can be explained as a consequence of interdependence between the radical concentrations of both components; the higher the radical concentration of one component, the lower the involvement of the other one. It must be mentioned that this relationship (2') was obtained for virgin (unaged) materials. This state of sample supposes an isotropic behaviour, namely, that all macromolecules are surrounded by the same molecular configuration and concentration. This means that there is a competition between radicals and hydrocarbon molecules for all kinds of free radicals. A certain reaction path

Table 3 Relationships of reciprocal thermal affinity in binary systems (EPDM/IIR)

System	Relationship	Correlation factor
EPDM/IIR=75:25	$Y=-1.15X+0.87$	0.999
EPDM/IIR=50:50	$Y=-1.14X+0.78$	0.999
EPDM/IIR=25:75	$Y=-1.15X+0.61$	0.999
General	$Y=-1.148X+0.752$	0.999

is followed because of the affinity of reactive entities for the surrounding substrate. It is equivalent to a 'selection' of reactants.

**Fig. 3** Changes in c_p contribution of EPDM on c_p contribution of IIR

It is expected that this type of thermal affinity might be applicable to any other binary polymeric system. This statement will be checked in our laboratories for various other pairs of polymers. Moreover, it would be useful if this kind of assessment could be extended to multicomponent homogeneous mixtures.

Conclusions

It is possible to characterize the thermal compatibility of polymers by determination of specific heat capacities. This physical aspect of blending affinity can be correlated with the chemical behaviour of the tested mixtures. The capability of constituents to coexist under the same conditions can be evaluated from the overlap of the thermal affinity dependences determined for different mixing ratios.

References

- 1 C. Vasile and R. B. Seymour, 'Handbook of Polyolefins. Synthesis and Properties', Part II, Marcel Dekker, Inc., New York 1993.
- 2 V. Mentlik, J. Thermal Anal., 39 (1993) 1355.

- 3 H. J. Flynn, *Thermochim. Acta*, 217 (1993) 129.
- 4 Dong Il Kang, Chang Sik Ha and Won Jei Cho, *Eur. Polym. J.*, 28 (1992) 565.
- 5 A. Tager, 'Physical Chemistry of Polymers', ch. 6, Mir Publishers, Moscow 1978 (English version).
- 6 L. A. Utracki, D. J. Walsh and R. A. Weiss, ACS Symp. Series 395 'Multiphase Polymers: Blends and Ionomers', ch. 1, 1989.
- 7 J. van Gisbergen, 'Electron Beam Irradiation of Polymer Blends', PhD Thesis, Eindhoven 1991.
- 8 J. Sohma, *Prog. Polym. Sci.*, 14 (1989) 451.
- 9 S. Jipa et al., Proc. Bratislava Conf. on Polymer Degradation, Stara Lesna (Slovakia) 18–24 June 1996, p. 42.
- 10 M. Getlechermann, M. Trojan, A. Daro and C. David, *Polym. Degrad. Stab.*, 39 (1993) 55.
- 11 T. Zaharescu, V. Meltzer and R. Vilcu, *J. Mater. Sci. Lett.*, 15 (1996) 1212.
- 12 T. Zaharescu, V. Meltzer and R. Vilcu, *Polym. Degrad. Stab.*, 55 (1997) 135.
- 13 A. R. R. Zahran, A. Y. Kandcil, A. A. Higazy and M. E. Kassem, *J. Appl. Poly. Sci.*, 49 (1993) 1291.
- 14 M. G. O'Neill, *Anal. Chem.*, 36 (1964) 1238.
- 15 A. Mehta, R. C. Bopp, U. Gaur and B. Wunderlich, *J. Thermal Anal.*, 13 (1978) 197.