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DETECTION OF COMPATIBILITY OF SOME RUBBER BLENDS BY DSC*

A. A. Yehia[1], *A. A. Mansour*[2] *and B. Stoll*[3]

[1]Department of Polymers, National Research Centre, Cairo, Egypt
[2]Department of Chemistry, Cairo University, Giza, Egypt
[3]Department of Applied Physics, Ulm University, Ulm, Germany

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Abstract

The compatibility of some technically important polymer blends, namely BR/NR, NR/NBR and CR/NBR, has been investigated using the DSC method. In addition, dynamic mechanical measurements have been carried out for the NR/NBR blends over the frequency range of 10^{-4} Hz –200 Hz and temperatures ranging from –70 to +70°C.

The results obtained show that the three rubber blends are not compatible over the entire composition range as proven by the DSC and mechanical measurements. By analyzing the heat capacity increases at the glass transitions of the separate phases in the NR/BR blend, it was possible to suggest the presence of a limited compatibility at the boundaries of the two phases.

By comparing this work with prior measurements, it was possible to conclude that the calorimetric method is a more efficient tool for the study of compatibility of polymer blends when compared to ultrasonic and viscosity methods.

Furthermore, it was found that polymers that show compatibility when measured with an ultrasonic method could behave compatible, semicompatible or incompatible when analyzed by DSC. On the other hand, blends that show incompatibility by the ultrasonic method are always incompatible by the DSC method.

Keywords: compatibility, DSC, master curves, mechanical measurements, rubber blends

Introduction

Polymer blends represent an important class of engineering materials. They allow a wider spectrum of applications, because the physical properties of a blend can easily be tailored by varying the relative concentration of the components. As a consequence of the technical and commercial importance of polymer blends, characterization procedures of polymer blends are of growing importance. The most important parameter determining the quality of the blends is the degree of compatibility. It is still not clear whether the components in a blend are mixed on a segmental

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* Dedicated to Professor Wunderlich on the occasion of his 65th birthday

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level or on a scale somewhere between segmental and molecular [1, 2]. Furthermore, different methods used in the detection of phase separation could yield different results [3, 4]. For example, the calorimetric methods can discover the phase separation long before it is macroscopically evident through turbidity. Such contradictions between the results obtained by different methods could be attributed to the fact that each method is sensitive to another molecular level [3, 4].

Accordingly, it is of interest to investigate the compatibility by the DSC method for three technically important rubber blends and also to compare with the available literature data obtained by ultrasonic method [5, 6]. These blends are BR/NR, NR/NBR and CR/NBR. In addition, master curves obtained by dynamic mechanical spectroscopy are presented for NR/NBR blends with different compositions.

Materials and techniques

Materials

Natural rubber (NR): grade RSS 1 supplied from TRENCO, Alexandria, Egypt.

Polybutadiene rubber (BR): is of 1,4 *cis* form (97%).

Polybutadiene-co-acrylonitrile (NBR): It is a Bayer product perbunan N 3307 NS, the CN content is (34%). It is worth noting that this NBR exhibits only one glass transition temperature.

Table 1 Physical parameters of rubbers

Physical parameters	Rubber			
	NR	BR	NBR	CR
Sp. gravity	0.913	0.915	0.99	1.23
Mooney viscosity ML 4(100°C)	41±2	35±3	45±5	50±5
Cl_2 content/%	–	–	–	39±2
CN content/%	–	–	34±1	–
1,4 *cis*/%	–	97	–	–
Vis. aver. mol. wt.	174189	140326	163376	379711

Polychloroprene rubber (CR): It is a Bayer product Baypren 110. The physical parameters are given in Table 1.

Techniques

Blending

The binary rubber blends of different blend ratios were mixed for 10 min on a laboratory two roll mill (diameter: 470 mm, width: 300 mm, speed of slow roll: 24 rev/min, gear ratio: 1:1.4). The roll temperature was kept constant at about 70°C during mixing).

Thermal analyses

The thermal analysis was carried out using two instruments namely, a DSC2 of Perkin Elmer in the Section of Calorimetry, University of Ulm, Germany and a PL-DSC of Polymer Laboratories, in the Chemistry Department, University of Cairo, Egypt.

The calorimeters were calibrated according to the suggested procedures of the GEFTA, Germany [7–9] for temperature, heat and heat flow rate. The samples were measured at a heating and cooling rates of 10 K min^{-1}. The initial and final isotherms of the scanning cycle were carried out for 10 min. The samples were measured twice for both heating and cooling cycles. The values of T_g and Δc_p were reproducible within ±1 K and ±5%, respectively.

Table 2 DSC results obtained for NR/BR blends

NR/BR ratio	T_g/°C	Δc_p/J (g K)$^{-1}$		
		Cooling	Heating	Calculated
0/100	–103	0.52	0.51	
25/75	–103	0.33	0.35	0.39
	–66	0.07	0.06	0.11
50/50	–102	0.24	0.23	0.26
	–65	0.16	0.18	0.22
75/25	–102	0.11	0.13	0.13
	–64	0.28	0.30	0.32
100/0	–66	0.42	0.44	

Table 3 DSC results obtained for NR/NBR blends

NR/NBR ratio	T_g/°C	Δc_p/J (g K)$^{-1}$		
		Cooling	Heating	Calculated
0/100	–29	0.51	0.50	
25/75	–28	0.32	0.33	0.13
	–66	0.11	0.13	0.11
50/50	–28	0.22	0.22	0.25
	–64	0.19	0.20	0.22
75/25	–28	0.14	0.12	0.13
	–65	0.33	0.32	0.32
100/0	–66	0.42	0.44	

The results of the second heating and cooling measurements are presented in Table 2 and Table 3 for the NR/BR and NR/NBR blends respectively. The glass transition temperature, T_g, was determined at the half-vitrification point.

It is worth noting that the weight of all measured samples was almost constant, about 27 mg, (±2). The calculated Δc_p is based on the assumption of complete incompatibility.

The mechanical measurements were carried out for the NBR/NR blends using the mechanical spectrometer of the University of Ulm, Germany, using a double sandwich sample holder [10]. The spectrometer set-up contains a low noise generator, type HP203, which produces an alternating current in the range of 5×10^{-5} Hz to 60 Hz with an amplitude ranging from 0 and 15 V. The generator is controlled by 16-bit processor, type 21005, allowing measurements over 8 decades of frequency.

The sample is held by the shaker from one side, while the drift is measured on the other side using a displacement transducer type HBW 1 El 0–5. The sample thicknesses used in the present study were in the order of 1–1.5 mm, while the diameter was 5 mm.

The measurements were carried out in the frequency range of 10^{-4}–200 Hz at different temperatures [10].

Results and discussion

The temperature dependence of the change in heat capacity, Δc_p, of pure NR, pure BR and their blends with composition ratios 25, 50 and 75% wt. BR are shown in Fig. 1. It can be seen in this figure that the different blends exhibit two glass transitions at the same temperature as the pure components. This finding can be taken as an indication of the incompatibility of the two components.

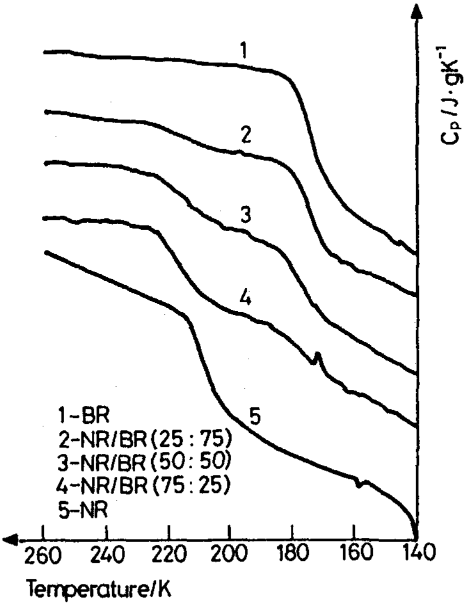

Fig. 1 Temperature dependence of the heat capacity, c_p of pure NR, pure BR and their blends with different compositions

The presence of two glass transition temperatures does not imply complete incompatibility of the two components. In some cases, the two phases could be present with some degree of compatibility and therefore a different composition ratio. The first phase may be rich in one component while the second, rich in the other. This scenario would, however, lead to a considerable change in the glass temperature (T_g) of each component in the blend. This is not the case for NR/BR as can be seen in Table 2. It is clear that neither of glass temperatures is changed by blending. On the other hand, the differences in the heat capacities at the glass transitions are not as expected for each phase of the blend when compared to the weight fractions. It is well known that the value of the difference in heat capacity Δc_p at the glass transition is proportional to the concentration of the polymer. Accordingly, one would expect that the increase in heat capacity at each transition would be proportional to the concentration of the corresponding polymer, if the two components were completely incompatible. The variation of Δc_p for the incompatible blends can be given by:

$$(\Delta c_p)_{bi} = \Delta C_{p_i} w_i \qquad (1)$$

Where $(\Delta c_p)_{bi}$) and Δc_{p_i} are the differences in heat capacities of the i-glass transition in the blend and in the pure states respectively; w_i is the weight fraction of the polymer i in the blend. Consequently, if the two polymers were completely incompatible, the two polymers should present a straight line which passes through the origin and follow Eq. (1). It can be seen in Fig. 2, that the experimental points (solid lines) are lower than the theoretical line (dashed lines) of 100% incompatibility.

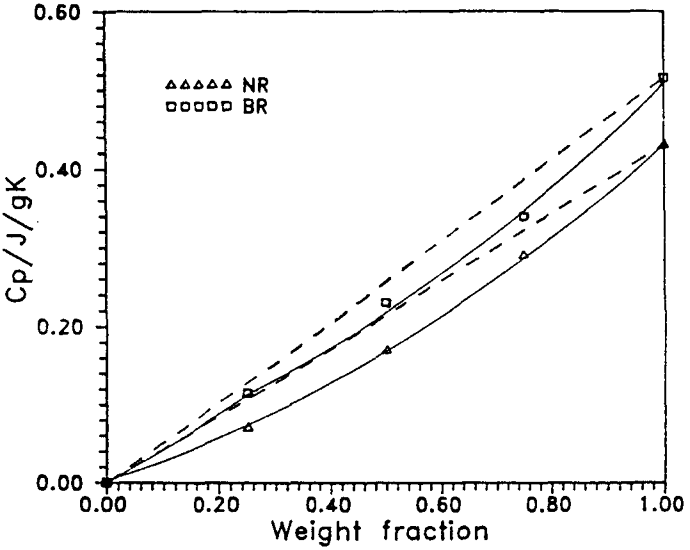

Fig. 2 Variation of the experimental Δc_p at the glass transition of NR and BR *vs.* NR/BR blend composition

The relative deviation for the NR component is somewhat greater than that observed for BR. It is worth noting that neither the Fox nor Gordon-Taylor equations can describe this deviation, since both glass temperatures of the components have not been changed by blending.

This deviation must be taken as an indication of the presence of a third phase of a limited degree of compatibility of the two components. The deviation observed for the BR component is of the order of 10% of the measured values, approaching the detection limit, while the deviation of NR varies from 9% to 40% of the measured values. The new phase of limited compatibility is must likely found at the interfaces between the two phases and has a greater concentration of NR than BR assuming an interfacial volume proportional to the deficit in Δc_p. The relative ratio of NR and BR can next be tentatively calculated from the experimental values of Δc_p by calculating the relative deviation from linearity of each component to the total deviation observed for each blend. This relative deviation represents the concentration of a certain polymeric component at these compatible regions. In such a way, the composition ratio is found to be 36, 30 and 28% BR for the blend 25, 50 and 75% wt. NR, respectively. Full justification of these estimates must await quantitative, absolute heat capacity measurements as done in the ATHAS laboratory that could identify the broad increase in heat capacity expected for the interfacial region [11].

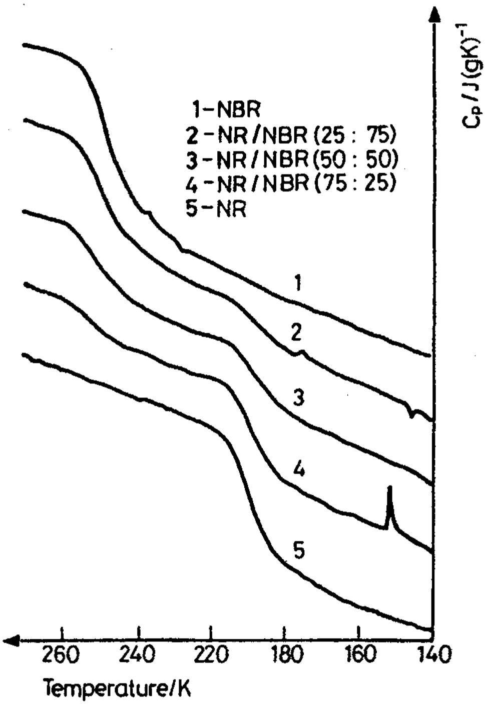

Fig. 3 Temperature dependence of the heat capacity c_p of pure NR, pure NBR and their blends with different compositions

The finding that NR and BR are not compatible blends stands in contrast to the ultrasonic and viscosity measurements which suggested that the two polymers are compatible [5, 6]. This contradiction may be attributed to the fact that the ultrasonic technique is sensitive to the presence of grain boundaries, whereas the DSC method detects all molecular and segmental dynamics. Therefore, one can conclude that the ultrasonic tool is not sensitive to incompatibilities that occur within the grain (i.e. it does not detect grains with a compatible surface layer). This conclusion could be understood if one assume that the propagation of the ultrasonic waves is mediated through the compatible surface regions, so that the difference in the surface boundaries of the different phases will not be detected.

The temperature dependence of the specific heat capacity Δc_p of a series of NR/NBR blends with different concentrations is presented in Fig. 3. It can be seen in this figure that, again, there are two glass transitions appearing at the same transition temperatures as the pure components. This finding together with the invariance of the glass temperature of the two components can be taken as indication of the incompatibility of the two polymers. In a similar way to that done for BR/NR blends; the variations of Δc_p of each transition is plotted *vs.* the concentrations and compared with the calculated line expected for completely incompatible blends. It can be observed in Fig. 4 that in this system there is a slight deviation, lower than 10%. This finding suggests that the two polymers are almost completely incompatible over the whole concentration range. The ultrasonic measurements showed in this case that these two polymers are incompatible [5]. For this reason it would be of interest to apply an additional, independent type of measurement which is known by its efficiency for identification of incompatible phases such as dynamic mechanical spectroscopy. The dynamic mechanical measurements were carried out in the frequency range of 10^{-4}–200 Hz using a double-sandwich sample holder over temperature range from –70°C to +70°C.

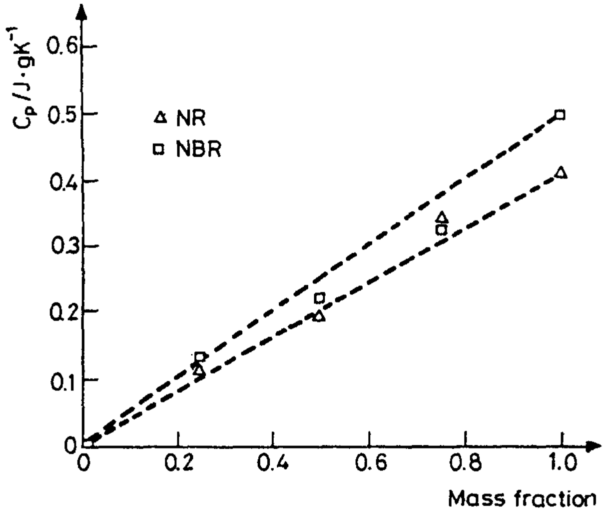

Fig. 4 Variation of the experimental Δc_p at the glass transition of each phase *vs.* NR/NBR blend composition

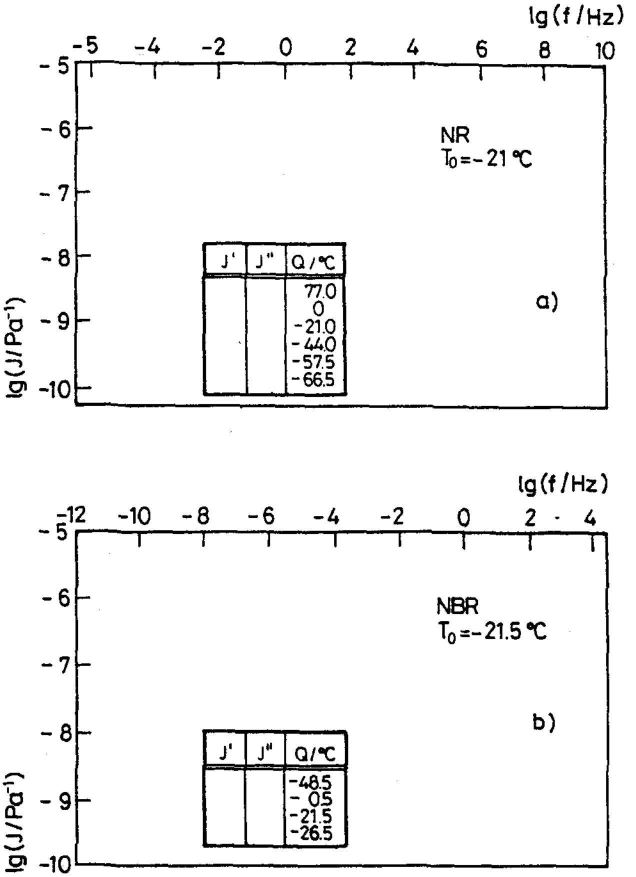

Fig. 5a–b Shear compliance master curves of pure NR (a) and NBR (b)

Figures 5a–b show the master curves for pure NR and NBR. Each master curve is composed of compliance J', J'' curves by shifting them along both logarithmic scales [10]. It can be seen in Fig. 5 that pure NBR and NR exhibit two relaxation processes namely, the glass process (that appears at 100 Hz and 10^{-4} Hz for NBR and NR, respectively, at –21°C) and a low frequency process is the shear-band process [10]. The glass relaxation process is associated with the microbrownian cooperative reorientation of the polymeric segments. On the other hand, the shear-band process which is very sensitive to the crosslinking density and could be attributed to unfolding of suitably arranged structural units, as suggested by the meander model [10]. Figures 6a–c show the master curves of the NR/NBR blends with compositions 25, 50 and 75% NR, respectively. The relaxation spectra of the blends show two glass processes appearing at the same relaxation frequencies as the pure components. It can be also seen in this figure that relative heights of the two processes are proportional to the admixed concentration of the corresponding components. It is of great interest to correlate the intensity of the relaxation processes with concentration. Therefore, analysis of the relaxation spectrum is done in a similar way as described before [10] to evaluate the variation of the relaxation strength of each process with composition. The relaxation spectra are resolved into three Cole-Cole processes [12], one for each glass process and only one for the shear band

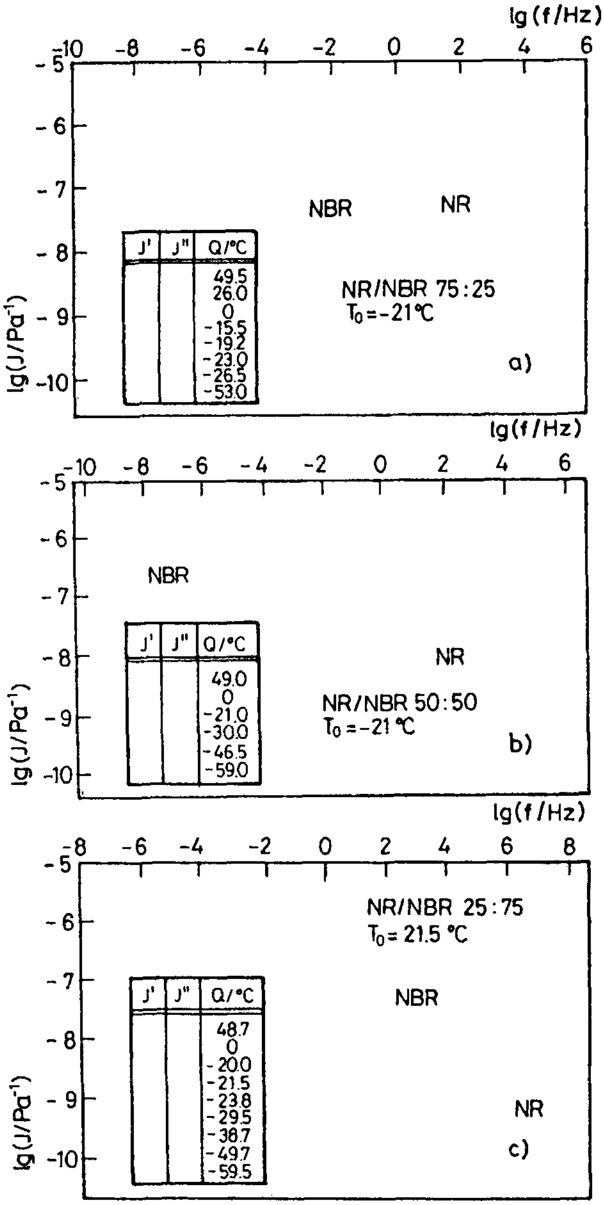

Fig. 6a–b Shear compliance master curves of NR/NBR blends with different compositions, namely, 75/25, 50/50, 25/75 NR/NBR, respectively

process, for simplicity. The relaxation strength obtained from the analysis are plotted against the weight fraction and are presented in Fig. 7. It can be seen in this figure that the relaxation strength of each process depends linearly on composition. This linearity means that the two polymers are completely incompatible and also, that there is no molecular interaction of the polymeric segments. This finding can be taken as a strong support for the results obtained from the DSC method.

It was also of interest to apply the DSC method to a third technically important rubber blend, NBR/CR. This blend represents a demanding test for the efficiency of this method because the glass transition temperatures of the two polymer components are only 11°C apart. Figure 8 represents the calorimetric measurements carried out for NBR/CR blends with the composition ratios: 0, 40, 60 and 100% NBR. It is surprising to observe that the blends shows two transition steps, although the

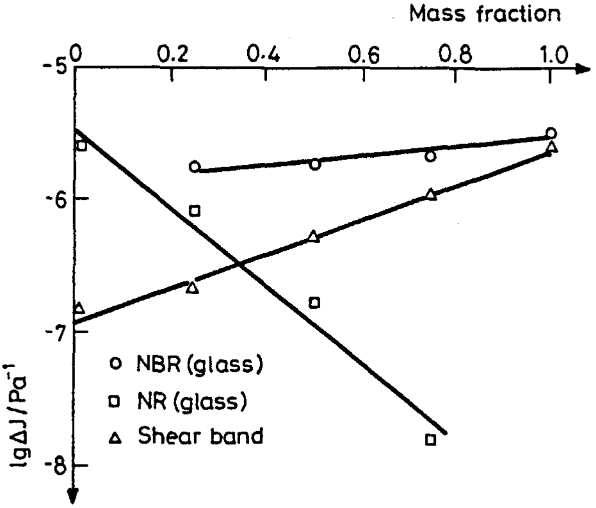

Fig. 7 Relaxation strengths obtained from the analysis of the master curves of NR/NBR blends with different compositions

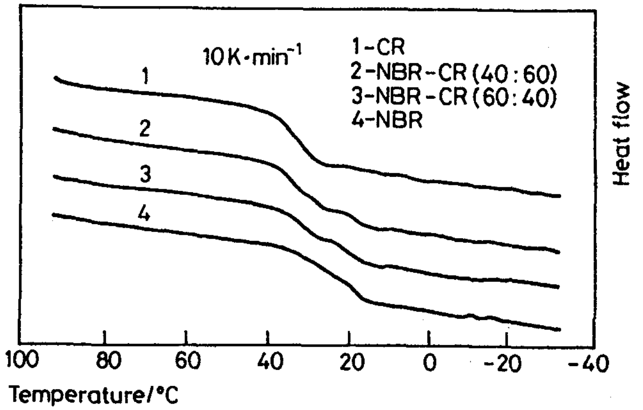

Fig. 8 Temperature dependence of the heat flow, of pure NBR, pure CR and their blends

glass transition temperature of the pure components differs only by 11°C. This finding can be taken as an indication of the incompatibility of the CR and NBR, and also as a proof for the efficiency of efficiency the DSC. Nevertheless, further analysis of the results obtained to determine the degree of compatibility is not possible. It must be stated that the dielectric measurements showed that CR and NBR are not compatible in the whole composition range [13].

Conclusion

It is clear that, as soon as the glass transition temperatures of the component polymers are sufficiently separated, the calorimetric method is an efficient tool for the study of the compatibility of polymer blends in comparison with other methods, such as viscosity and ultrasonic. This is attributed to the fact that the DSC is detecting a lower molecular level of mixing than could be detected by the ultrasonic method. For this reason, polymers that show compatibility by the ultrasonic measurements could be compatible, semi-compatible or incompatible. On the other hand, blends which show incompatibility by the ultrasonic were found also to be incompatible by the DSC method.

It has also been shown that the DSC method could offer a quantitative means for the detection of the presence of limited compatibility in blends. On the other hand, DSC measurements can supply qualitative indications of incompatibility, even in the critical cases were the glass temperatures of the two components are only different by about 10°C.

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