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Compensation effect in styrene–acrylonitrile copolymer and acrylonitrile–butadiene–styrene terpolymer as explored by thermally stimulated depolarization measurements

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Thermally stimulated depolarization currents of styrene–acrylonitrile and acrylonitrile–butadiene–styrene copolymers have been investigated in the high-temperature range. A peak associated with the glass transition temperature was observed which has the characteristic of a dipolar relaxation process. Parameters such as activation energy and relaxation time associated with the dipolar relaxation process have been calculated. The compensation effect is observed to be valid and the value of the compensation temperature differs slightly from one compound to other. The linear relationship between the activation energy and the logarithm of the pre-exponential factor of the relaxation time is discussed in terms of the compensation temperature and the chain environment.

1. Introduction

The compensation effect, a linear relationship between $\ln \tau_0$ and ΔH, where τ_0 is the pre-exponential factor and ΔH the activation energy in a process which is temperature-activated, may reveal real physical behaviour. The physical meaning of the compensation temperature is still a subject of investigation and controversy [1–3]. The physical origin of the compensation law has received several explanations [4–6]. Thermally stimulated depolarization (TSD) coupled with the thermal sampling technique give further sufficient and reliable evidence for the existence of the compensation law [7–9]. The explanation of this effect needs further study. In order to gather information about the compensation temperature and its relation to the molecule, we have carried out investigations relating to a compensation law in styrene–acrylonitrile (SAN) and acrylonitrile–butadiene–styrene (ABS) copolymers. The results of our studies are given below.

2. Background theory

The interpretation of the spectra obtained by the particular TSD method known as thermal sampling (TS) is based on a Debye model of dipole relaxation [10] in which the relaxation time τ depends on temperature T according to

$$\tau = \tau_0 \exp(\Delta H/kT) \tag{1}$$

where k is the Boltzmann constant. In the case of a relaxation time, the compensation law can be written as

$$\ln \tau_0 = \ln \tau - \frac{\Delta H}{kT_c} \tag{2}$$

where T_c is the compensation temperature at which all values of τ are equal to $\tau(T_c)$ which is the common relaxation time taken on by all the sub-processes providing the distribution of ΔH values. Equation 1 thus takes the form

$$\tau(T) = \tau(T_c)\exp\frac{\Delta H}{k}\left(\frac{1}{T} - \frac{1}{T_c}\right) \tag{3}$$

Therefore, for a physically significant compensation effect, it is expected from Equation 3 that depending upon whether $T > T_c$ or $T < T_c$, $\tau(T)$ will increase with concomitant increase or decrease in ΔH.

3. Experimental details

The ABS copolymers were, Novador ABS-I-PK and ABS-II-PH-AT (Bayer, W. Germany). Each consists of polyacrylonitrile (A)-styrene (S) grafted on polybutadiene (B). The relative compositions of copolymers ABS I and ABS II were A: 20 and 24%, B: 29 and 14%, S: 51 and 62%, respectively. 75% styrene–25% acrylonitrile copolymer was obtained from Polyscience (USA).

Films were prepared under compression using a hot press (Carver Laboratory Press, Model M2114, Freds and Carver Fountain, USA). Film thicknesses ranging from 40 to 80 μm were obtained. Some samples were heated at atmospheric pressure for several hours while being short-circuited. In all our thermal stimulation experiments the samples were first polarized by heating to a specific poling temperature T_p. Once the desired temperature was obtained, an electric field was applied and the sample then kept at that polarizing temperature for a specific time. In most cases the cooling and heating rates were kept the same. The experimental set-up and film thickness measuring technique used here have been published elsewhere

[11]. The sample holder was designed to avoid thermal gradients throughout the sample. The temperature T was varied in the range from room temperature up to 530 K. Most of the measurements were carried out with conducting carbon paste (Neubauer Chemikalien, W. Germany) electrodes except for some limited observations which were made with gold, silver and aluminium evaporated electrodes. Thermal currents were measured using a Keithly electrometer type 610 C. The sample temperature was measured by a Beckman Industrial temperature–voltage converter thermocouple TP 850.

The reproducibility of the spectra obtained with identically prepared samples was very satisfactory and the position of the peaks was reproducible (with $\Delta T_m = \pm 1$ K). SAN and ABS do not have a well-defined glass transition temperature T_g. Differential scanning calorimetry (DSC) was carried out on a Setaram (Lyon, France) DSC111. Weak transition temperatures were observed around 393 K in the case of SAN, ABS I and ABS II. Infrared studies of the fresh and preheated films reveal the existence of (-C≡N) groups using a Perkin Elmer 1430 ratio recording infrared spectrometer.

4. Results and discussion

Fig. 1 represents the TSD current (TSDC) spectra for SAN and ABS thermoelectrets heated at the rates indicated from well below the glass transition T_g. In both materials, a prominent and intense peak is associated with the temperature T_g. A linear variation of the peak amplitude with field intensity is observed. The position and height of the peak are independent of the electrode material. Also a symmetry between the thermally stimulated polarization and thermally stimulated depolarization currents occurs. All these facts confirm the respective attribution of this peak to a dipolar relaxation process [12]. These results are comparable with those reported on an SAN air-gap charged electret [13] and an ABS thermoelectret [14]. Hence this process will be termed hereafter an α-relaxation process.

The effect of the polarizing temperature on the TSDC spectra revealed that the temperature maximum of the peak is a function of the poling temperature. Further, the activation energy calculated using the initial rise method [15] reveals that it too is a function of the poling temperature. Because of the complexity of the α-peak, the TS technique [16, 17] was utilized to investigate the relaxation process in SAN and ABS. A typical response of SAN and ABS to the TS procedure in the α-relaxation region is shown in Fig. 2. It is clear that the peak occurs by a process that slowly rises exponentially as the temperature continues to increase, reaches a maximum and then drops sharply as the randomization of preferentially oriented dipoles become complete. The TS technique showed that the relaxation is distributed as the activation energy is a continuous function of the poling temperature T_p.

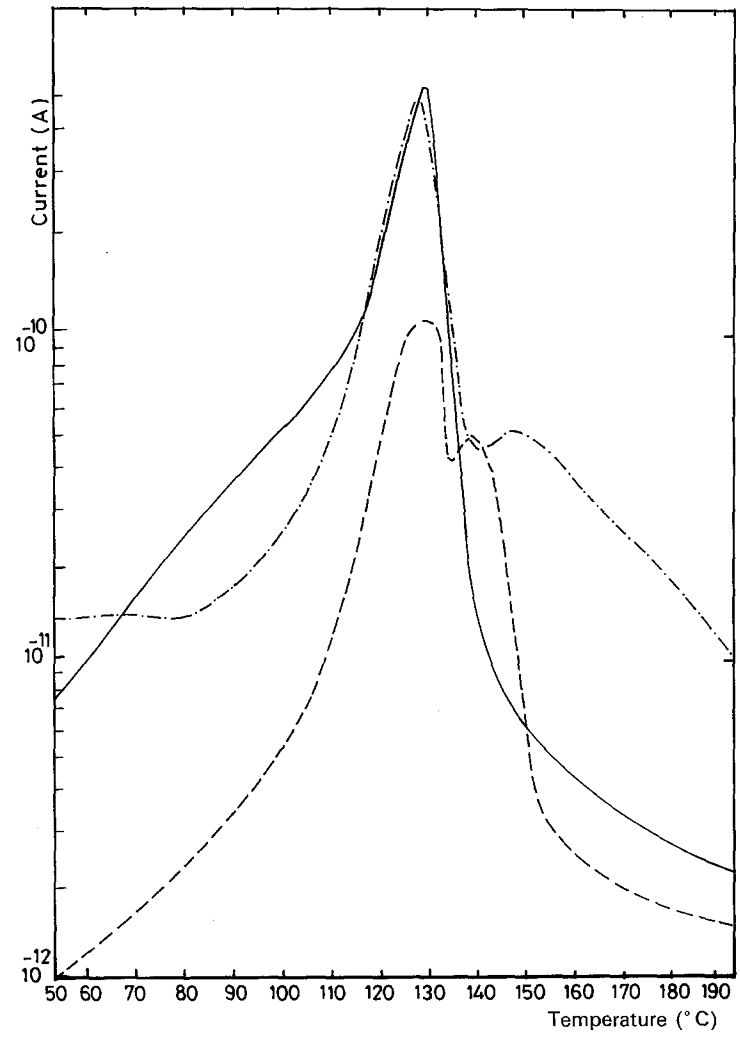


Figure 1 TSDC spectra of (- - -) SAN, (——) ABS I and (-·-·-·-) ABS II thermoelectrets. Polarizing temperature T_p = 393 K, polarizing time t_p = 3 h, heating rate β = 3 k min^{-1}, electric field E_p = 6 × 10^6 V m^{-1}.

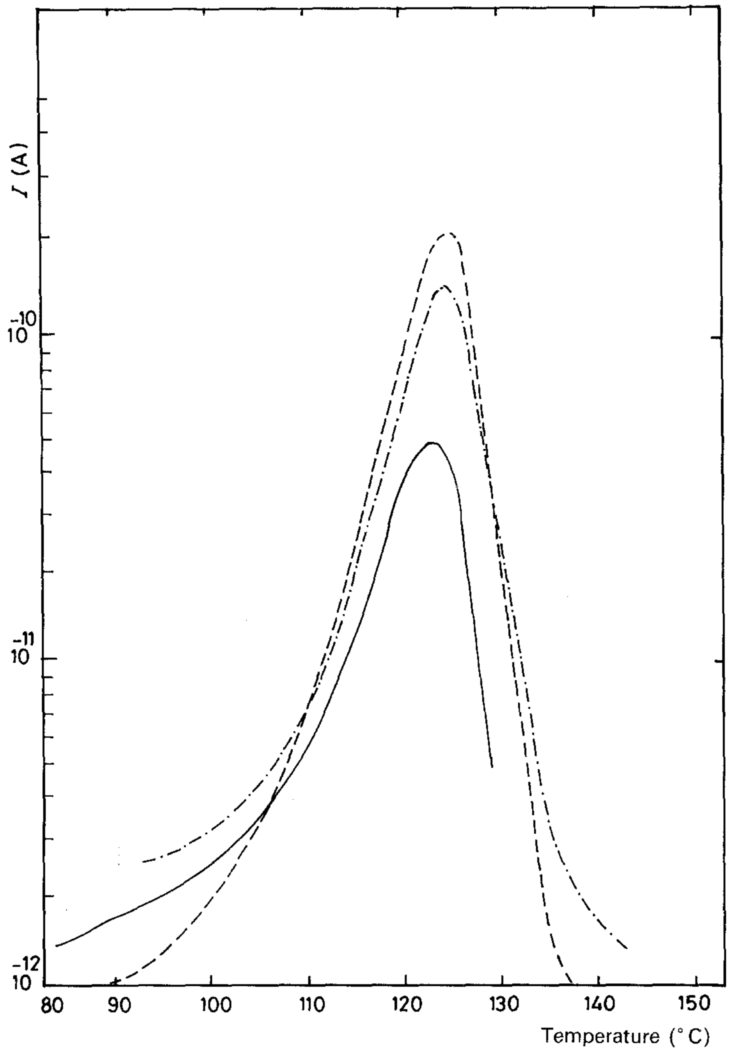


Figure 2 Typical thermal sampling response of (- - -) SAN, (——) ABS I and (-·-·-·-) ABS II in the α-relaxation region; polarizing temperature $T_p = 373$, 378 and 378 K, respectively. Polarizing time $t_p = 15$ min, depolarizing time $t_d = 15$ min, heating rate $\beta = 2\,\mathrm{K\,min^{-1}}$, electric field $E_p = 5 \times 10^6\,\mathrm{V\,m^{-1}}$.

The TSDC method of thermal sampling was used in order that the different effects in the TSDC spectra could be resolved. In this way the values of the activation energy and relaxation time at different temperatures were obtained. As the depolarization of the sample is thermostimulated, time and temperature are related by a linear relationship in the case of our materials, so the relaxation time is temperature-dependent. A plot of ln $\tau(T)$ against $10^3/T$ can thus be obtained.

Figs 3a, b and c show the least-squares fitting of plots from the TS responses isolated in the α-relaxation of SAN, ABS I and ABS II, respectively. It is clear that in the diagrams showing ln τ_0 against $1/T$ most Arrhenius plots pass through a common point located at $T = T_c$, suggesting a compensation law in the case of our samples. Table I gives calculated values of τ_0 from the equation [18]

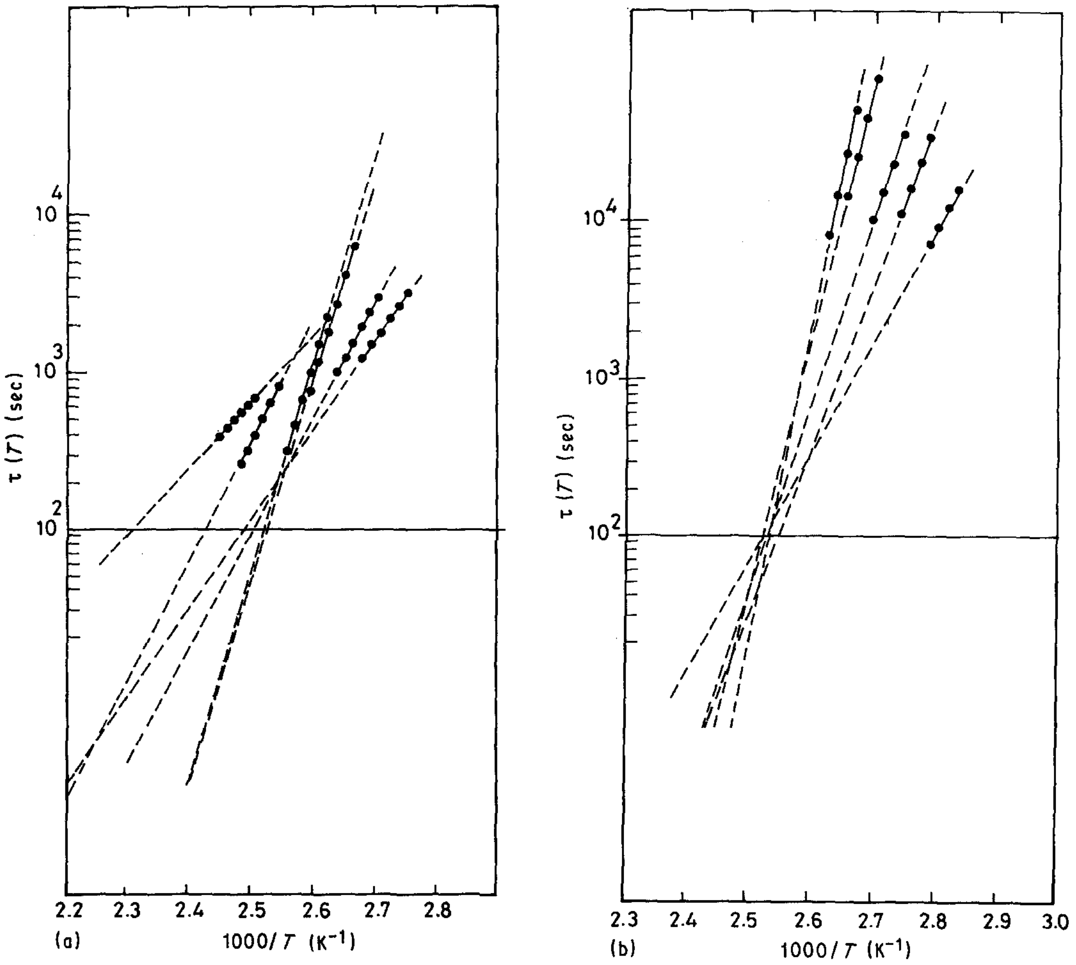
$$\tau_0 = \frac{kT_m^2}{\beta \Delta H} \exp\left(-\frac{\Delta H}{kT_m^2}\right) \tag{4}$$

where T_m is the temperature at which the peak is maximum (obtained by thermal sampling) and β is the heating rate. ΔH is obtained from a semilog plot of the current against $1/T$ according to the initial rise method [14].

It may be seen from Table I that τ_0 is not constant in the range of the polarizing temperature T_p. It generally decreases with increasing T_p. Hence the α-process may be considered to be a continuous distribution for both the activation energy ΔH and the pre-exponential factor τ_0, i.e. both are distributed parameters. On representing ln τ_0 against ΔH for α-relaxation, we obtained the plots shown in Fig. 4. They show a linear

TABLE I Numerical results for ΔH and τ_0 of SAN, ABS I and ABS II α-relaxation

Polarizing window (° C)	SAN		ABS I		ABS II	
	ΔH (eV)	τ_0 (sec)	ΔH (eV)	τ_0 (sec)	ΔH (eV)	τ_0 (sec)
95–90	1.08	1.95×10^{-12}	1.43	3.13×10^{-17}	2.10	2.43×10^{-26}
100–95	1.32	1.58×10^{-15}	2.05	2.23×10^{-25}	2.10	3.42×10^{-26}
105–100	2.57	5.93×10^{-32}	2.30	2.15×10^{-28}	2.46	7.7×10^{-31}
110–105	2.43	5.5×10^{-30}	3.46	1.79×10^{-43}	3.54	1.39×10^{-44}
115–110	1.65	9.62×10^{-20}	3.66	6.54×10^{-46}	3.49	6.25×10^{-44}
120–115	1.47	6.14×10^{-17}	3.50	1.35×10^{-43}	6.60	4.24×10^{-84}



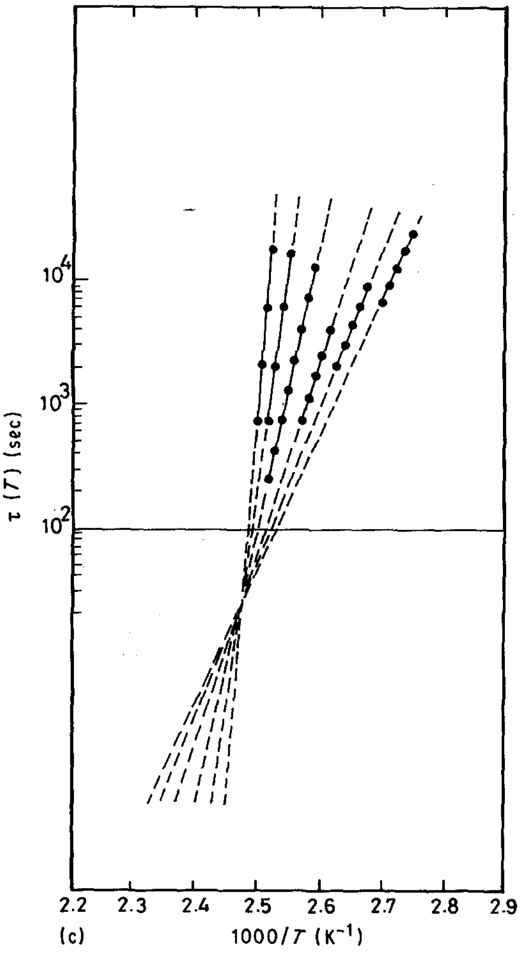


Figure 3 Least-squares fitting of linear part in (a) SAN, (b) ABS I and (c) ABS II α-relaxations; (●) experimental results, (- - -) least squares calculations. The polarizing temperatures were, from left to right, 120 to 90 K by steps of 5 K with a 5 K window.

relationship between the pre-exponential factor and the activation energy. The least-squares fitting procedure gives compensation temperatures T_c of 391, 397 and 400 K in the case of SAN, ABS I and ABS II, respectively, and their corresponding correlation coefficient is 0.999.

As is clear, the compensation temperature is shown to be slightly dependant on the nature of the polymers ABS I and ABS II. On the other hand a slight difference between the T_c values of SAN and ABS is to be seen that suggest a physical basis for the compensation effect which is expected to be related to the molecular structure of the materials.

A physical explanation can be offered for the present data. The compensation temperature is essentially comparable with the glass transition temperature. At this temperature all dipoles either go to having a zero moment or become energetically indistinguishable. The fact that there are distributions of ΔH and τ_0 associated with this process is in accord with the finding of Peacock-Lopez and Suhl [1] that a compensation law must exist in any system containing elements moving with different energy barriers and coupled to a thermal bath with the same coupling

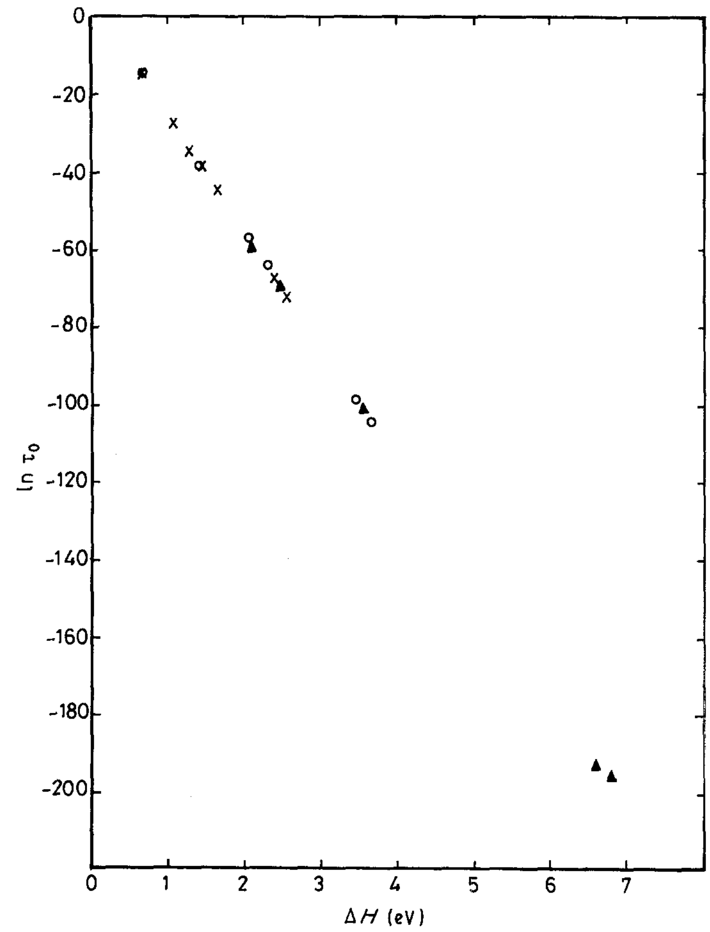


Figure 4 Compensation effect in (x) SAN, (O) ABS I and (▲) ABS II α-processes.

function. The compensation temperature would then be related to this transfer mechanism and T_c is characteristic of the heat transfer between the thermal bath and polymer chains.

5. Conclusion

The TSDC technique has been used to investigate the α-relaxation in SAN and ABS films. It could be shown by using the thermal sampling mode that the relaxation is due to a distributed process involving a distribution in activation energies and natural frequencies. The elementary processes that constitute the modes and the relaxation obey a compensation law with compensation temperature T_c comparable to the glass transition T_g. Hence T_c is characteristic of the heat transfer between the thermal bath and the polymer chains.

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