

Study on the Relaxation of Polystyrene, Ethylene–Propylene Diene Monomer, and the Blends of Polystyrene with Ethylene–Propylene Diene Monomer by Thermally Stimulated Current

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ABSTRACT: A thermally stimulated current (TSC) was used to study the relaxation of polystyrene (PS), the ethylene–propylene diene monomer (EPDM), and the grafted copolymer of EPDM with styrene (EPDM-*g*-St). The effect of the measuring conditions on the relaxation of PS is discussed. Some relaxation parameters of PS, EPDM, and EPDM-*g*-St were calculated in two different ways. In addition, the TSC spectra of PS/EPDM and PS/EPDM-*g*-St showed that PS/EPDM was an immiscible system, but there existed a special interaction between the plastic phase and the rubber one in PS/EPDM-*g*-St blends. The compatibility of PS blends was evaluated in terms of their compositions. The results of inverse gas chromatography (IGC) agreed well with those of the TSC measurements. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1199–1204, 1998

Key words: polystyrene; EPDM; EPDM-*g*-St; TSC; PS blend

INTRODUCTION

The thermally stimulated current (TSC) measurement was believed to be an important means with regard to the study and characterization of amorphous polymers.¹ The relaxations of polystyrene (PS) have been studied using TSC by many authors.^{2–8} However, their results did not agree well enough with each other. This may be attributed to the different samples that they used. Also, the experimental conditions played an important role in the TSC measurements. Furthermore, TSC studies on EPDM, styrene-grafted EPDM (EPDM-*g*-St), and their blends with PS have rarely been reported. It seems that PS/EPDM is

an immiscible system, while EPDM-*g*-St should have a certain compatible part with PS. Shaw and Singh⁹ studied the compatibility of PS/EPDM-*g*-St by the viscosity method.

In this work, we studied systematically the relaxations of PS, EPDM, EPDM-*g*-St, and their blends using the TSC measurement. The effects of the sample thickness and measuring conditions on the TSC spectra are discussed. The inverse gas chromatography (IGC) results confirmed the compatibility of the PS blends.

EXPERIMENTAL

Materials

Polystyrene (PS, density 1.05 g/cm³, $M_n = 1.6 \times 10^5$), the ethylene–propylene diene monomer (EPDM, propylene 35%, $M_n = 2.0 \times 10^5$, density 0.865 g/cm³), and EPDM-*g*-St (grafting yield [g]

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Table I Compositions of Polystyrene (PS) Blends (Wt %)

Polymer	Composition (Wt %)								
	100	95	90	85	80	70	60	50	0
PS	100	95	90	85	80	70	60	50	0
EPDM	0	5	10	15	20				100
EPDM- <i>g</i> -St (12.5%)	0	5	10	15	20				100
EPDM- <i>g</i> -St (32.6%)	0		10			30	40	50	100

12.5% and 32.6%) were synthesized in our laboratory (the grafted product was characterized by FTIR and H-NMR in Ref. 10). PS/EPDM and PS/EPDM-*g*-St were blended in a mixed apparatus (XXS-30, Mixer, China) at a temperature of 160°C and mixing time of 10 min. The compositions of the PS blends are listed in Table I.

Method

Thermally Stimulated Current (TSC)

The samples were melt-compressed into 0.2 × 25 mm circle films at 170°C, with thin aluminum evaporated at either side as electrodes. The TSC main instrument was made by the KEHAI Experimental Factory, Academia Sinica, China. The samples were placed in a shielded cell filled with dry nitrogen. The procedures of polarizing and depolarizing are as follows: (1) polarizing the sample in an electric field of $E_p = 30$ kV/cm at $T_p = 155^\circ\text{C}$ for 30 min; (2) cooling the sample to -100°C rapidly under the same electric field; (3) removing the electric field and keeping the sample at this temperature in a short-circuited state for 30 min; and (4) depolarizing the sample at a heating rate of 1.6°C/min and recording the TSC spec-

tra. The same experiment was carried out three times to confirm the validity. The experimental error was $T \pm 0.05^\circ\text{C}$.

The activation energy of the relaxation peak on the polymer was calculated by the TSC spectra.¹¹⁻¹³ The TSC from the theory of the dipole is given by

$$I(T) = \frac{P_0}{\tau_0} \exp \left[-\frac{E_a}{KT} - \frac{1}{b\tau_0} \int_0^\infty \exp \left(-\frac{E_a}{KT} \right) dT \right] \quad (1)$$

Here, $I(T)$ is the TSC and E_a is activation energy of relaxation. When the current value is the maximum for different heating rates, $dI(T)/dT = 0$, such as

$$\frac{b}{T_m^2} = \frac{K}{I_0 E_a} \exp \left(-\frac{E_a}{KT_m} \right) \quad (2)$$

where T_m is temperature at the maximum discharged current; b , heat rate ratio; τ_0 , and the preexponential factor of the relaxation time, a linear dependence of $\ln b/T_m^2$ on $1/T_m$ is found with the slope equal to E_a . In the initial rise method for the current rise, the equation is as follows:

$$\ln I(T) = C - \frac{E_a}{KT} \quad (3)$$

A plot of $\ln I(T)$ against $1/T$ should lead to a straight line having a slope of E_a .

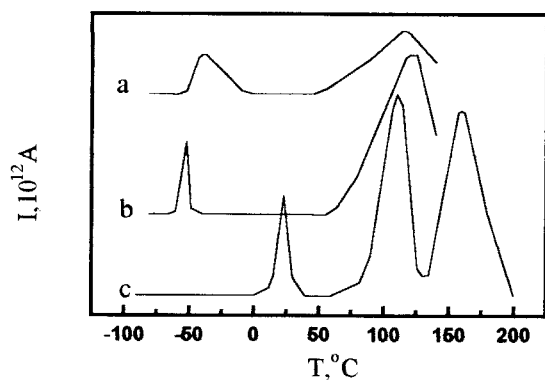


Figure 1 TSC spectra of PS, EPDM, and EPDM-*g*-St: (a) EPDM-*g*-St; (b) EPDM; (c) PS.

Table II The Dependence of TSC Peaks (°C) on Heating Rate

Heating Rate (°C/min)	0.97	1.61	1.95	2.55
T_g	100.5	111.2	114.4	119.0

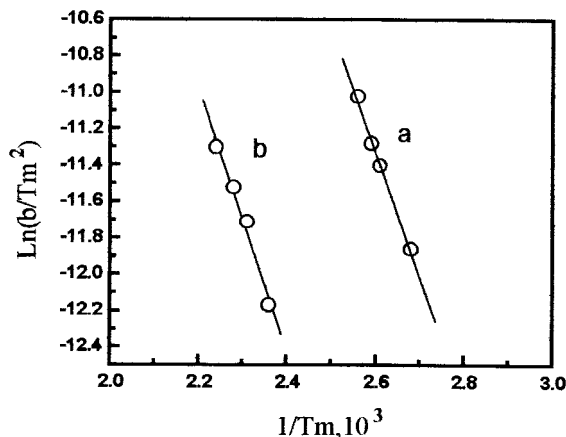


Figure 2 Plot of $\text{Ln}(b/T_m^2)$ against $1/T_m$ from Figure 1 on PS: (a) T_g ; (b) T_{11} .

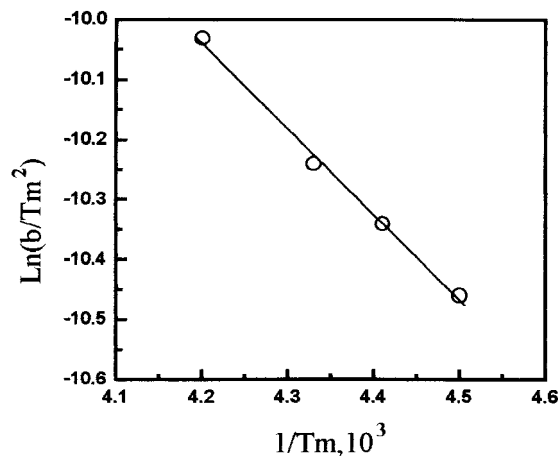


Figure 4 Plot of $\text{Ln} I(T_m^2)$ against $1/T_m$ from Figure 1 on EPDM.

Inverse Gas Chromatography (IGC)

The instrument was modified from the 102G GC by the Shanghai Analytical Instrument Factory. The columns were made of stainless steel with an inner diameter of 3 mm, an outer diameter of 5 mm, and 1 m of length. The carrier gas was high-purified nitrogen with a flowing velocity of 5–25 mL/min and the inspector was a thermal conductor. The probes were *n*-hexane, *n*-heptane, etc., each 0.1 mL. Sample preparations were as follows: (1) Polymers that were weighed accurately were completely dissolved into oxylene under stirring; (2) a solid support was put into the polymer solution; (3) the solvent was evaporated completely; and (4) the support coated with the polymer was dried in a vacuum for 72 h. The measure-

ment of the specific retention volume was as follows: The chromosorb support (80–100 mesh) was acid-washed and treated with dimethyldichlorosilane (DMCS) to eliminate the V_g^0 dependence on the sample itself. In our experiment, since this treatment did not eliminate the surface problem completely, the accurate V_g^0 was further determined by the extrapolation of the experimental V_g^0 data to infinite column loading.

RESULTS AND DISCUSSION

Relaxations of Polystyrene Blends by TSC

Figure 1 shows the TSC spectra of PS, EPDM, and EPDM-*g*-St. PS has three depolarizations at 23, 111.2, and 162.0°C, respectively. The characterization of pure PS by TSC has been carried out by many researchers. Bhargara and Srivastava² found two peaks at 77 and 112°C; Kulshrestha and Srivastava³ found three peaks at 65, 95, and 145°C; Goyand et al.⁴ discovered that for pure PS

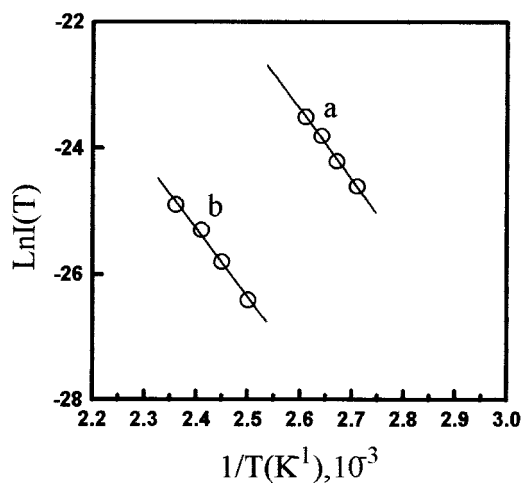


Figure 3 Plot of $\text{Ln} I(T)$ against $1/T$ from Figure 1 on PS: (a) T_g ; (b) T_{11} .

Table III Data of Activation Energies of T_g and T_{11} Transitions

Temperature	E_a (eV)1 ^a	E_a (eV)2 ^b	τ_0 (s) ^a
PS T_g	1.90	2.35	1.66×10^{-25}
PS T_{11}	1.42	2.23	4.38×10^{-25}
EPDM T_g	0.32	0.54	2.50×10^{-21}
EPDM- <i>g</i> -St T_g	—	0.77	—

^a Results from different heating rates.

^b Results from initial rise method.

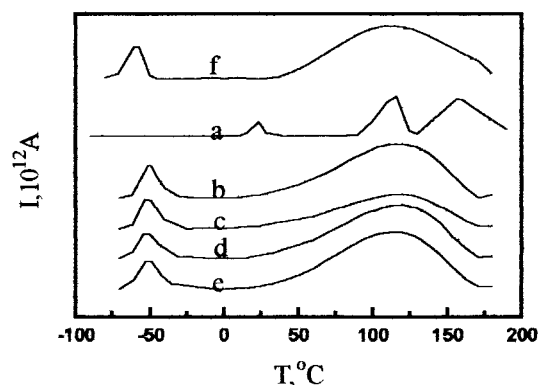


Figure 5 TSC spectra of PS/EPDM blends: (a) PS; (b) PS/EPDM (95/5); (c) PS/EPDM (90/10); (d) PS/EPDM (85/15); (e) PS/EPDM (80/20); (f) EPDM.

its T_{11} was equal to $T_g + 50^\circ\text{C}$ by TSC; and Pillai and Rashai⁵ reported two peaks above 80°C . The TSC spectra of PS by Shinichi⁸ also included three peaks at 32, 65, and 100°C ($T_p = 94^\circ\text{C}$, $E_p = 10^6$ V/cm). The glass transition temperature (T_g) of PS was reported to be 100°C by a dilatometer and it was 116°C for the T_g of PS by the TBA (Torsional Braid Analysis) measurement (0.9 c/s, $M = 1.2 \times 10^5$; if $M = 8 \times 10^4$, then $T_g = 100^\circ\text{C}$).¹⁴ It follows that the PS T_g should be 111.2°C in our experiment. The transition peak of 162.0°C is T_{11} , which is consistent with the information reported.⁴ The TSC peak at 23°C in our results is analogous to the 32°C peak of Shinichi. Yano and Wada¹⁵ reported that the β transition temperature of PS was 66°C by the dielectric method, which was different from 55°C by DMA. However, the β transition of pure PS could not always be measured by the TSC.²⁻⁸ There was no β transi-

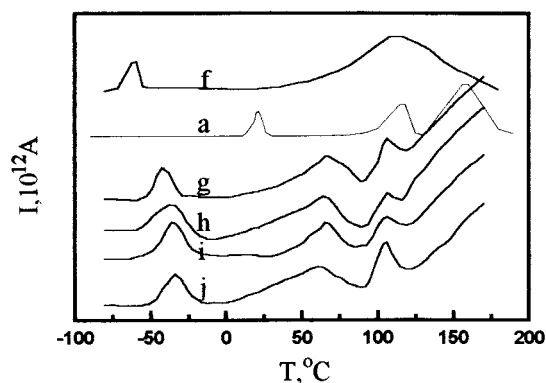


Figure 6 TSC spectra of PS/EPDM-*g*-St ($g = 12.5\%$) blends: (a) PS; (f) EPDM; (g) EPDM/EPDM-*g*-St (95/5); (h) EPDM/EPDM-*g*-St (90/10); (i) EPDM/EPDM-*g*-St (85/15); (j) EPDM/EPDM-*g*-St (80/20).

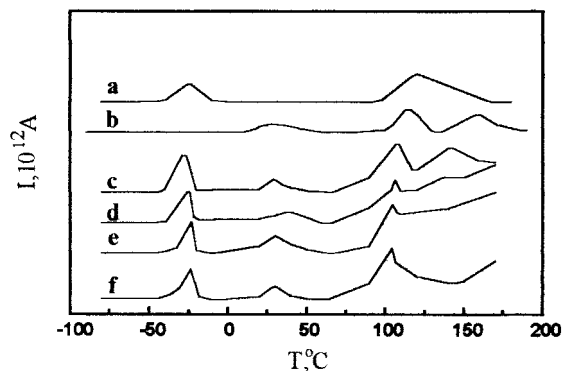


Figure 7 TSC spectra of PS/EPDM-*g*-St ($g = 32.6\%$) blends: (a) EPDM-*g*-St; (b) PS; (c) PS/EPDM-*g*-St (90/10); (d) PS/EPDM-*g*-St (70/30); (e) PS/EPDM-*g*-St (60/40); (f) PS/EPDM-*g*-St (50/50).

tion at about 60°C appearing in our TSC results of pure PS.

In Figure 1, EPDM has two TSC peaks: The -52°C peak represents the T_g of EPDM very near to the result by the dilatometer.¹⁶ The broad peak of 120°C is the T_{11} transition. Figure 1 also shows that the -38°C peak of EPDM-*g*-St ($g = 12.5\%$) and the -23°C peak of the EPDM-*g*-St ($g = 32.6\%$) TSC spectra are the T_g transition of the EPDM component. Due to the introduction of styrene segments, the T_g of the EPDM component was enhanced and the T_{11} of EPDM and some peaks of PS formed a very broad peak at the high-temperature area.

Because of the relaxation process, the TSC peak positions drifted to high temperature with increase of the heating rate except that the 23°C peak of pure PS is not sensitive to the heating rate. Table II lists the relationship between the peak positions and heating rates. According to the dipolar relaxation theory, the activation energies of the relaxation could be calculated by eqs. (2) and (3) (in Figs. 2-4). Table III lists the calculated data of the activation energies that were a little different from those using the initial rise method. The PS results were much bigger than those of Sharma and Sagar.⁶ This is partly due to the different experimental conditions. However, our results are very near to those of Broens (2.97 eV) by the dielectric method.¹⁴ The parameters of EPDM and EPDM-*g*-St have not been reported until recently.

The Relaxations of Polystyrene Blends by TSC

Figure 5 is the TSC spectra of the PS/EPDM system, in which *a* and *f* represent the TSC spectra

Table IV The T_g 's of Two Phases in PS/EDPM- g -St ($G = 12.5\%$) Blends

		PS/EDPM- g -St					
		100/0	95/5	90/10	85/15	80/20	0/100
Rubber phase	T_g		-35.6	-33.0	-33.6	-32.8	38.0
Plastic phase	T_g	111.2	108.5	106.0	106.6	108.0	
PS ^a	T_g	104.3		91.8		92.0	

^a IGC results.

of PS and EPDM, respectively. The -52°C peak of the PS/EPDM blends is the glass transition temperature (T_g) of EPDM independent of their compositions. The broad peak is not changed by the variation of the compositions. Clearly, we can deem that the two phases of the blends of PS/EPDM are incompatible. Figure 6 shows the TSC spectra of the PS/EPDM- g -St ($g = 12.5\%$) system, and Figure 7 depicts the TSC spectra of the PS/EPDM- g -St ($g = 32.6$) system. In the blends of PS/EPDM- g -St, the interactions have a close relation to their compositions, such that the T_g of the EPDM component rose and the T_g of the PS component was reduced in the blends (see Tables IV and V for the T_g 's of the rubber and plastic phases). It is obvious that with increase of the amount of graft EPDM the interactions between the two components become strong. This can be interpreted by the increase of interactive molecules in the blends because the amount of the styrene component is increased by the grafted EPDM amount. Thereby, the two phases are semicompatible in the blends of PS/EPDM- g -St. The peak of 60°C is believed to be the β transition of PS, which is not sensitive to the compositions (see Fig. 6). But the β peak of PS does not exist in the PS/EPDM- g -St ($g = 32.6\%$) blends, and we do not know the cause.

The IGC Measurements of Two Polystyrene Blends

From the dependence of V_g^0 on temperature, the plastic-phase T_g can be measured by the IGC in

PS blends. The results agree fairly well with those determined by the TSC (see Table IV). In addition, the V_g^0 values can also be used to evaluate the compatibility of the polymer blends. If it is an immiscible system, then $V_g^0 m = w_2 V_{g2}^0 + w_3 V_{g3}^0$. V_{gm}^0 , V_{g2}^0 , and V_{g3}^0 are specific retention volumes of the blend, polymer 2, and polymer 3, respectively. W_2 and W_3 is the weight fractions of the two polymers. Figure 8 shows the relationship between V_g^0 and the composition of the PS blends. It appears that the V_g^0 data of the PS/EPDM- g -St system are inconsistent with the calculated results of the immiscible blend. So, there must be a compatible part between the two components or the system is all-compatible between the two components.

CONCLUSION

In this article, the relation spectra of PS, EPDM, and EPDM- g -St were studied by TSC, and the β transition of PS was found. The activation energies of T_g on PS, EPDM, and EPDM- g -St were calculated by the measurement data of the TSC.

The relaxation spectra of the PS/EPDM and PS/EPDM- g -St blends have been discussed in terms of the TSC. The TSC spectra of the PS/EPDM blends are the simple overlap of the PS and EPDM spectra, irrespective of their compositions. The PS/EPDM system between the PS and EPDM phase is incompatible. In the blends of PS/EPDM- g -St, there are strong interactions be-

Table V The T_g 's of Two Phases in PS/EDPM- g -St ($g = 32.6\%$) Blends

		PS/EDPM- g -St (32.6%)					
		0	10	30	40	50	100
Rubber phase	T_g	0	-26.2	-24.1	-23.5	-23.3	-23
Plastic phase	T_g	111.2	108.5	106.2	104.8	104.2	

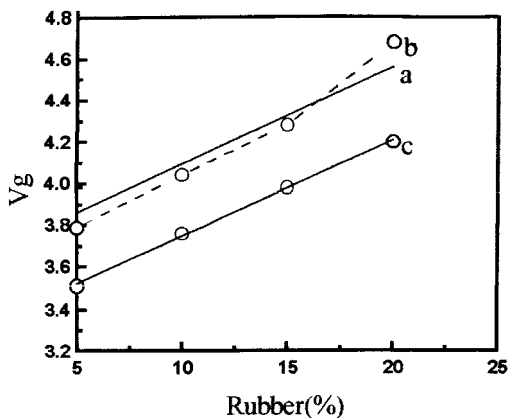


Figure 8 Relationship between V_g^0 and compositions of PS blends: (a) calculated result; (b) PS/EPDM system; (c) PS/EPDM-*g*-St system.

tween the PS main chains and the styrene grafting chains on EPDM-*g*-St, so the T_g of the EPDM component and the PS component was changed. Clearly, the PS component with the EPDM-*g*-St component on PS/EPDM-*g*-St is semicompatible. The β transition of PS has appeared in PS/EPDM-*g*-St ($g = 12.5\%$), but there is no β transition peak in the blends of PS/EPDM-*g*-St ($g = 32.6$) in the TSC spectra. We do not know its cause. The results of the IGC measurement on the blends prove that the PS phase with the EPDM phase is not incompatible and the PS component with the EPDM-*g*-St component is compatible or semicompatible.

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REFERENCES

1. J. R. Saffel, A. Matthiesen, R. McIntyre, and J. P. Ibar, *Thermochim. Acta*, **192**, 243 (1991).
2. B. Bhargara and A. P. Srivastava, *Indian J. Phys. A*, **53**, 47 (1979).
3. Y. K. Kulshrestha and A. P. Srivastava, *Polym. J.*, **11**, 515 (1979).
4. G. Goyand, C. Lacabanne, and J. P. Cotton, *Solid State Commun.*, **32**, 673 (1979).
5. P. K. C. Pillai and Rashmi, *Polymer*, **20**, 1245 (1979).
6. A. K. Sharma and D. S. Sagar, *Polym. Int.*, **25**, 43 (1991).
7. M. Topic and Z. Veksli, *Polymer*, **34**, 2118 (1993).
8. T. Shinichi, *J. Appl. Phys.*, **47**, 5480 (1976).
9. S. Shaw and R. P. Singh, *Eur. Polym. J.*, **24**, 1163 (1988).
10. J. Sheng and J. Hu, *J. Appl. Polym. Sci.*, **60**, 1499 (1996).
11. C. Bucci and R. Fieschi, *Phys. Rev. Lett.*, **12**, 16 (1964).
12. M. N. Perlman, *J. Appl. Phys.*, **42**, 2645 (1971).
13. Y. Aoki and J. O. Prittain, *J. Appl. Polym. Sci.*, **20**, 2879 (1976).
14. B. Qian, G.-P. Xu, and F.-S. Yu, *Transition and Relaxation on Polymers*, Beijing: Science Press, Beijing, 1986, p. 301.
15. O. Yano and Y. Wada, *J. Polym. Sci., A-2*, **9**, 669 (1971).
16. R. R. Garret, *Rubb. Plast. Age*, **46**, 915 (1966).