

Permanently Electrostatic Dissipative (ESD) Property Via Polymer Blending: Rheology and ESD Property of Blends of PETG/ESD Polymer

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SYNOPSIS

Rheological and electrical properties were studied on blends of a PETG polyester (cyclohexanedimethanol-modified polyethylene terephthalate) and an inherently static dissipative high molecular weight polyether based copolymer, hereafter referred to as ESD polymer. Several important electrical properties and flow phenomena have been observed. First of all, the PETG blends could result in ESD protected material with excellent performance and a minimal effect on physical properties and melt processability. The rheological characterization reveals that the ESD polymer has a high melt viscosity even at a temperature more than 150 degrees above its melting temperature and that it exhibits pseudoplastic behavior. The PETG melt shows a near constant dynamic viscosity at a low frequency region. The viscosity of the ESD polymer and PETG melt exhibits a cross over at the temperature range from 200–220°C; the PETG melt is the lower viscosity component at low shear rate and the ESD polymer is the lower viscosity component at high shear rate. This appears to result in the existence of a small composition difference in the thickness direction of an injection-molded ESD polymer/PETG part, with a greater fraction of the ESD polymer component in the skin section. This, in turn, could enhance the surface conductivity of the skin region of an injection-molded part. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

As a rule, polymers act as electrical insulators. This ability is the basis for many applications in electrical and electronic devices, etc. But there are many cases when electrical conductivity in the polymeric materials is required. The inherent insulating properties of the plastics have introduced problems with electrostatic discharge (ESD). The plastics allow static charge to build up until an electrostatic discharge occurs, often resulting in damage to adjacent microelectronic components.

Until recently, there have been basically three major material approaches used to alleviate the ESD problems of plastics: external chemical treatments,^{1,2} internal chemical additives,² and conductive fillers.³ Each approach, while effective in certain

specific applications, suffers from significant deficiencies.

The external treatments suffer from reliance on high humidity for effectiveness. Permanence is also an issue since the treatment can be rubbed, wiped, or washed off resulting in a loss of ESD protection.^{1,2}

The internal chemical additives rely on additive migration to the surface of the plastics to provide ESD protection. While this approach provides more permanence than the external treatments, it is also prone to being temporarily wiped, rubbed, or washed away. This lack of permanence results in periods of ESD susceptibility until additional additives can bloom to the surface.³ The internal chemical additives also depend on high humidity to be effective.

The use of conductive fillers can alter the ESD properties of plastics. These materials can include conductive carbon black and metallic fillers or fibers. Although not humidity dependent and not susceptible to being wiped, washed, or rubbed away, they

Table I Some Pertinent Data of an Experimental ESD Polymer

Molecular weight	$M_w > 150,000$
Chemistry	Polyether based copolymer
Physical form	Free flowing, nondusting granules

do have certain disadvantages. They have a tendency to increase the melt viscosity for processing and to decrease physical properties such as impact resistance.³

Recently, a novel approach for permanently static dissipative thermoplastics has been introduced.^{4,5} An ESD polymer based on polyether copolymer with a bulk resistivity in the order of 10^{10} ohm-cm is blended with thermoplastics to make the plastics static dissipative. The polymeric blending approach resulted in ESD protected plastics that were non-contaminating and had excellent permanence, humidity independence, and good processability.⁴ In this paper, we report our study on blends of an experimental ESD polymer with a PETG thermoplastic polyester (cyclohexanedimethanol-modified polyethylene terephthalate). In particular, we emphasize the melt rheological behavior of the blend components and its effect on the electrical properties of these blends.

EXPERIMENTAL

Materials

The materials discussed were based on a PETG polyester and an experimental grade of an inherently static dissipative high-molecular-weight polyether based copolymer, hereafter referred to as ESD polymer. Some pertinent data of this ESD polymer are shown in Table I.

Blends of PETG and ESD polymer were prepared using an electrically heated two-roll mill. For this evaluation, we restricted our efforts to examine the pure effects of the addition of the ESD polymer. The blend ratios (PETG/ESD polymer) studied were A = 100/0, B = 0/100, C = 90/10, D = 80/20, and E = 70/30.

Rheological Measurements

The rheological properties of these blends were measured using a Rheometrics Dynamic Spectrometer. The measurements were carried out using frequency sweep mode at 200°C, 210°C, and 220°C. The dynamic results are reported in the form of complex viscosity η^* , storage modulus G' , and loss modulus G'' .

Injection Molding

Impact-strength test specimens of blend D (i.e., PETG/ESD polymer = 80/20) were further prepared using an Arburg-220-90-350 injection molding machine. The mold temperature was set at 55°C. The melt temperature was varied from 200–220°C.

Thermal Analysis

Specimens from each injection-molding condition were further analyzed using a Perkin-Elmer DSC-7 differential scanning calorimeter. In particular, we studied the size of the melting endotherm of the ESD polymer phase in the skin and core regions of an injection-molded part.

The experimental conditions for the DSC analysis were:

Sample size	~10 mg
Reference standard	empty aluminum pan

Table II Some Properties of the Blends of PETG/ESD Polymer

	A	B	C	D	E
Composition					
PETG	100	0	90	80	70
ESD Polymer	0	100	10	20	30
Surface resistivity (ohm/square)	$> 10^{14}$	10^9	10^{14}	10^{12}	10^{11}
Static decay (s) @ 15% relative humidity					
90% Decay	Insulator	No test	6.35	0.47	0.36
99% Decay	Insulator	No test	Insulator	1.32	1.02
Notched Izod impact (ft-lb/in) @ room temperature	0.5	—	0.6	1.3	5.8

Table III Surface Resistivity of Blend of PETG/ESD Polymer (80/20) (Blend D) as a Function of Injection-Molding Melt Temperature

	D-1	D-2	D-3
Melt temperature (°C)	200	210	220
Surface resistivity (ohm/square) skin region	10 ¹²	10 ¹²	10 ¹¹
Number of melting peaks of the ESD polymer phase			
Skin	3	3	3
Core	1	1	1
Heat of fusion of the ESD polymer crystallite (J/g)			
Skin	5.95	5.90	7.60
Core	4.60	5.01	4.26
Izod impact (ft-lb/in)			
Notched	2.0	3.1	3.2
Unnotched	30.0	26.1	32.1

Heating rate 40°C/min starting at -100°C following a first heat up to 150°C and a quench to 0°C and annealing at 0°C for 10 min

Atmosphere nitrogen.

Electrical Properties

Static decay testing of compression-molded samples (blends C, D, and E) were done in accordance with FTMS 101C method 4046.⁶ The surface resistivity of injection-molded impact-strength test specimens (blend D) was measured using a Surface Resistivity Meter (Monroe Electronics, Inc., Lyndonville, New York).

RESULTS AND DISCUSSION

Electrical Properties

Many electrostatic dissipating materials generally have a 90% decay time of greater than 3 s and a

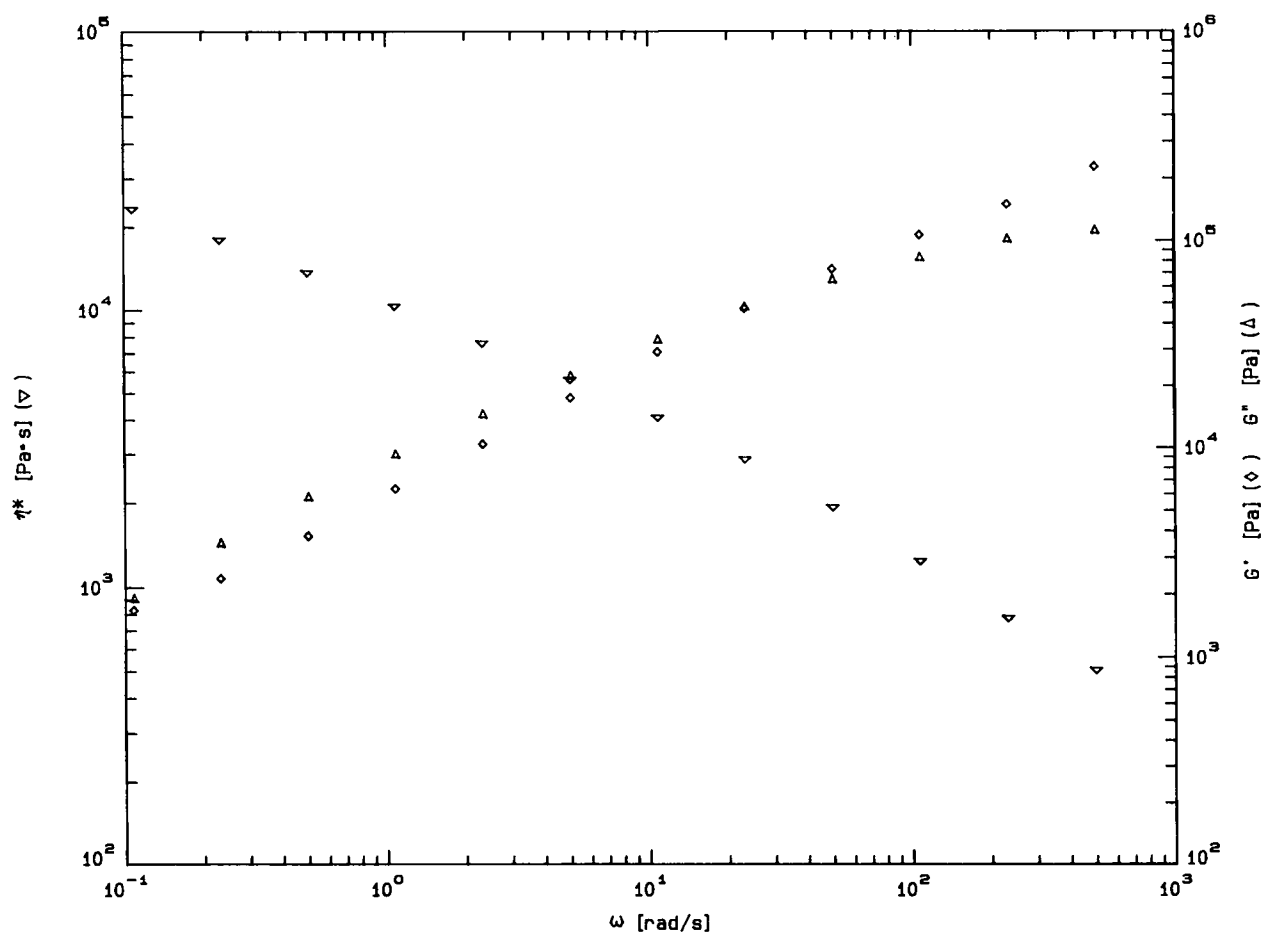


Figure 1 Dynamic mechanical properties of the ESD polymer melt at 200°C.

99% static decay time of greater than 5 s. The U.S. Military Standard (MIL-81705B) requires 2 s as an upper limit for a 99% static decay time. The results of the static decay testing versus the ESD polymer loading level are shown in Table II. The ESD polymer is indeed an effective static dissipater for PETG. The blends containing at least 20 wt % of the ESD polymer have a 99% decay time of less than 2 s. Mass and coworkers⁴ have reported that the ESD polymer is also effective in other plastic resins such as polystyrene, high impact polystyrene, styrene-maleic anhydride, and polypropylene.

The results of the surface resistivity are also shown in Table II. These indicate that there is an enhancement in surface conductivity occurring with the addition of the ESD polymer.

We further studied the effect of the injection-molding conditions on the electrical property of blend D (PETG/ESD polymer = 80/20). Specimens ($5'' \times \frac{1}{2}'' \times \frac{1}{8}''$) were injection molded at 200°C, 210°C, and 220°C. Table III lists the surface resistivity of this particular blend composition as a func-

tion of the injection melt temperature. The surface resistivity enhancement was observed when the injection melt temperature was 220°C. This could be explained in terms of phase distribution as discussed in the next section.

Melt Rheology of ESD Polymer and PETG

Figures 1–4 shows the frequency dependence of dynamic viscosity (η^*), storage modulus (G'), and loss modulus (G'') of the ESD polymer at 200°C, 210°C, 220°C and 230°C, respectively. It appears that the ESD polymer has a high melt viscosity even at temperatures more than 150°C above its melting point. The melt behavior of this ESD polymer is pseudo-plastic in character: that is, the dynamic viscosity decreases with frequency, and G' and G'' increases with frequency. The data also suggest that the chain entanglements of this ESD polymer are very tight in nature.

Figure 5 shows the frequency-dependent dynamic viscosity of PETG melt as a function of temperature.

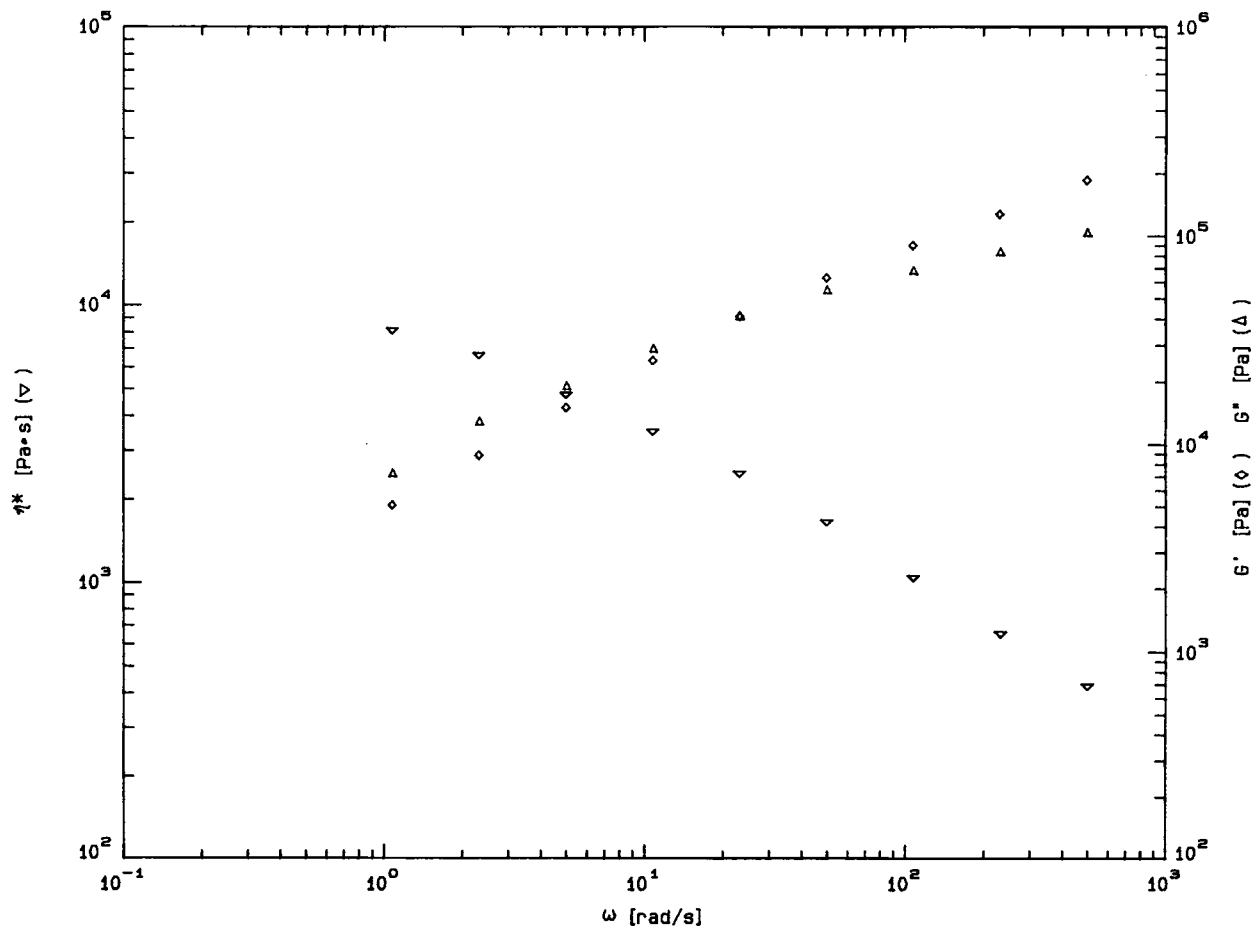


Figure 2 Dynamic mechanical properties of the ESD polymer melt at 210°C.

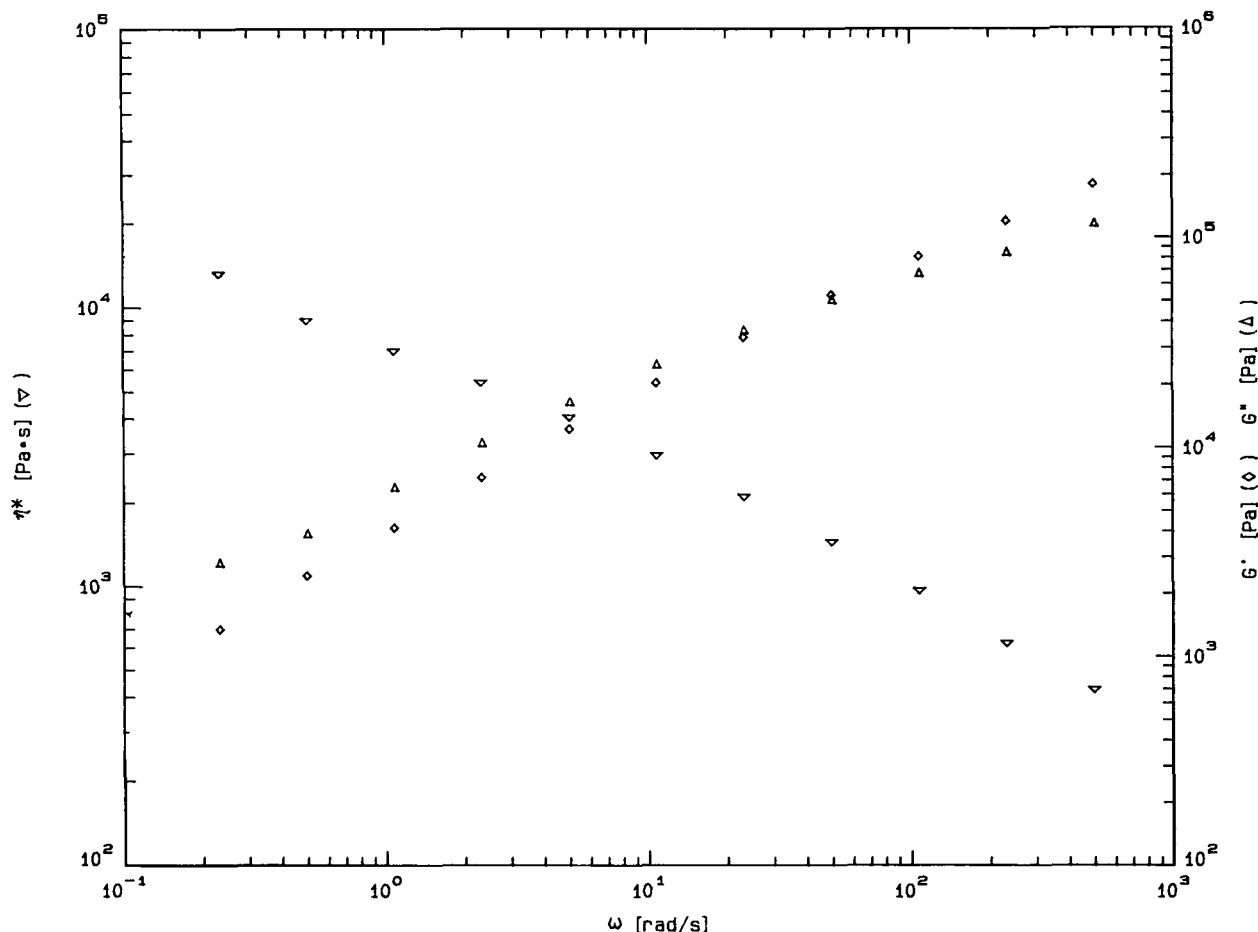


Figure 3 Dynamic mechanical properties of the ESD polymer melt at 220°C.

The PETG melts show a near-constant dynamic viscosity at low frequency region.

When comparing the dynamic viscosity of PETG and the ESD polymer melts at the same temperatures, we notice that there is a crossover. The PETG is the lower viscosity component in the low frequency region, and the ESD polymer is the lower viscosity component in the high frequency region.

Phase Distribution

Various research groups⁷⁻¹² have studied the possible phase migration or separation of flow of two-phase polymer systems. For incompatible polymer melts, there is a tendency for the skin or high shear rate region to be rich in low viscous melts. The possible phase separation of the incompatible blends of PETG/ESD polymer is the creation of composition heterogeneity over the cross section of an injection-molded part. Composition D (PETG/ESD polymer = 80/20) was used to study whether such a fractionation occurred. Accordingly, the injection-

molded impact-strength test specimens were sectioned into skin and core portions by a razor blade. The surface section represents approximately the outer 10% of the original thickness. DSC, in particular, the melting endotherm of the ESD polymer phase, was used to evaluate the composition heterogeneity.

Figure 6 shows the DSC trace of the ESD polymer. The glass transition temperature is about -52°C . The melting temperature of the crystallites is broad and not sharp. The heat of fusion is about 33 J/g.

The DSC traces of the skin and core regions of an injection-molded specimen are shown in Figure 7. Two points are important to mention:

1. There is a difference in the number of melting peaks of the ESD polymer phase in the skin and core sections. Three pronounced melting peaks, probably due to low molecular-weight ESD polymer crystallites, for the skin section are always observed.

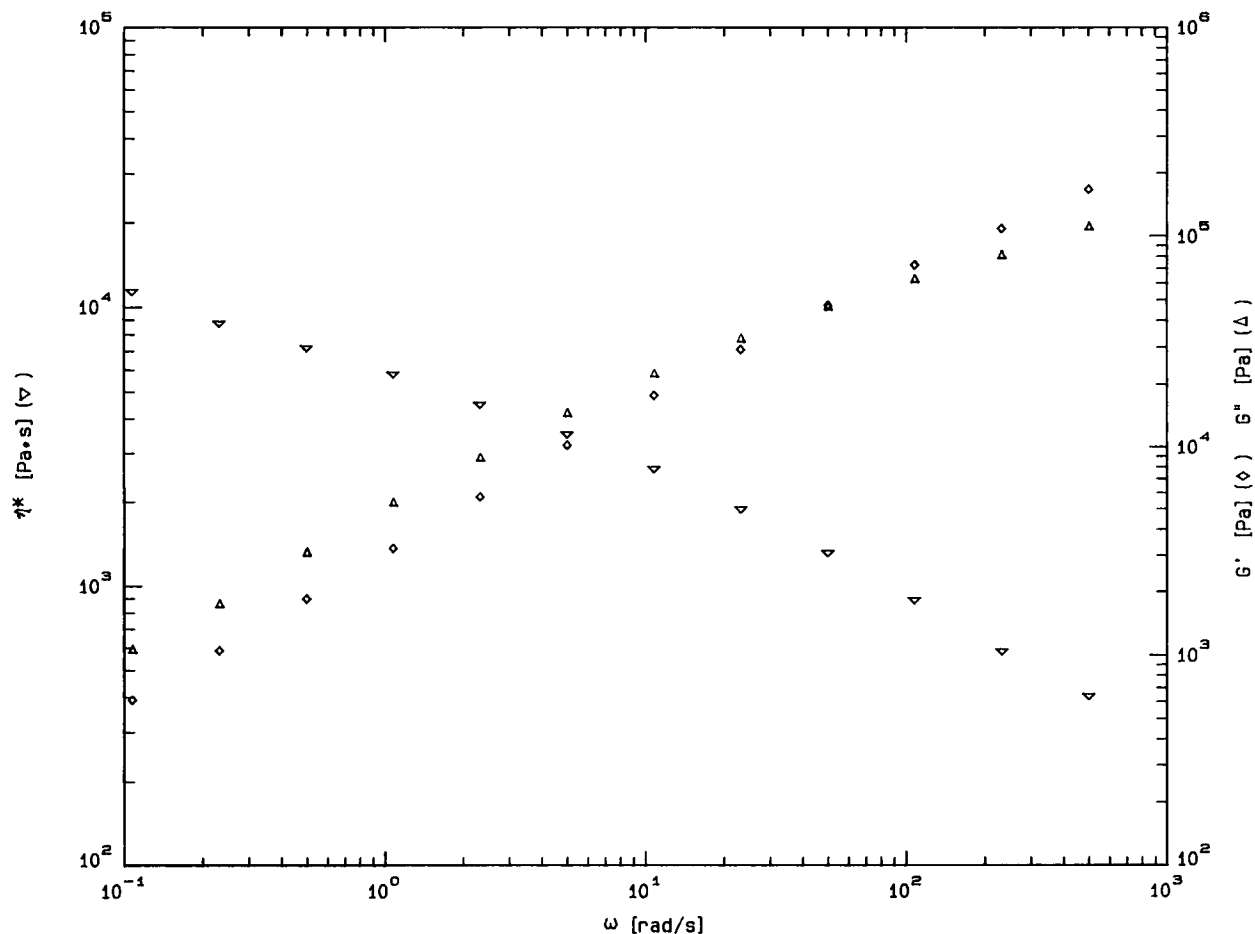


Figure 4 Dynamic mechanical properties of the ESD polymer melt at 230°C.

2. The heat of fusion of the ESD polymer crystallites of the skin section is always higher than that of the core section. These results are summarized in Table III.

Compared to the viscosity function as shown in Figures 1–5, the DSC results reveal that for blends of PETG/ESD polymer there exists a small composition difference in the thickness direction of an injection-molded part, with a greater fraction of ESD polymer component in the skin section. This appears to be consistent with the result on the enhancement of the surface resistivity of the skin region of sample D-3 cited in Table III.

Impact Strength

After giving consideration to the static dissipative properties and the rheological properties of this blend system, the next obvious question is whether the ESD polymer affects the physical properties of the PETG blend. In this paper, we restrict our dis-

cussion to the impact strength just for the purpose of illustration. Tables II and III also list the results of the impact strength of the blends. As shown in Table II, some improvement in impact strength with increasing ESD polymer level is observed. Furthermore (Table 3), there is a minimal effect on the impact strength due to the change in the injection-molding conditions.

CONCLUSIONS

PETG blends using a high molecular-weight ESD polymer based on polyether copolymer appear to offer a viable alternative for making PETG static dissipative. In addition to improving the electrical property of PETG for ESD application, polyether copolymer also improved the impact strength with a minimal effect on melt processability. The viscosity of the ESD polymer and PETG melt exhibits a crossover at the temperature range from 200°C–220°C; the PETG melt is the lower viscous com-

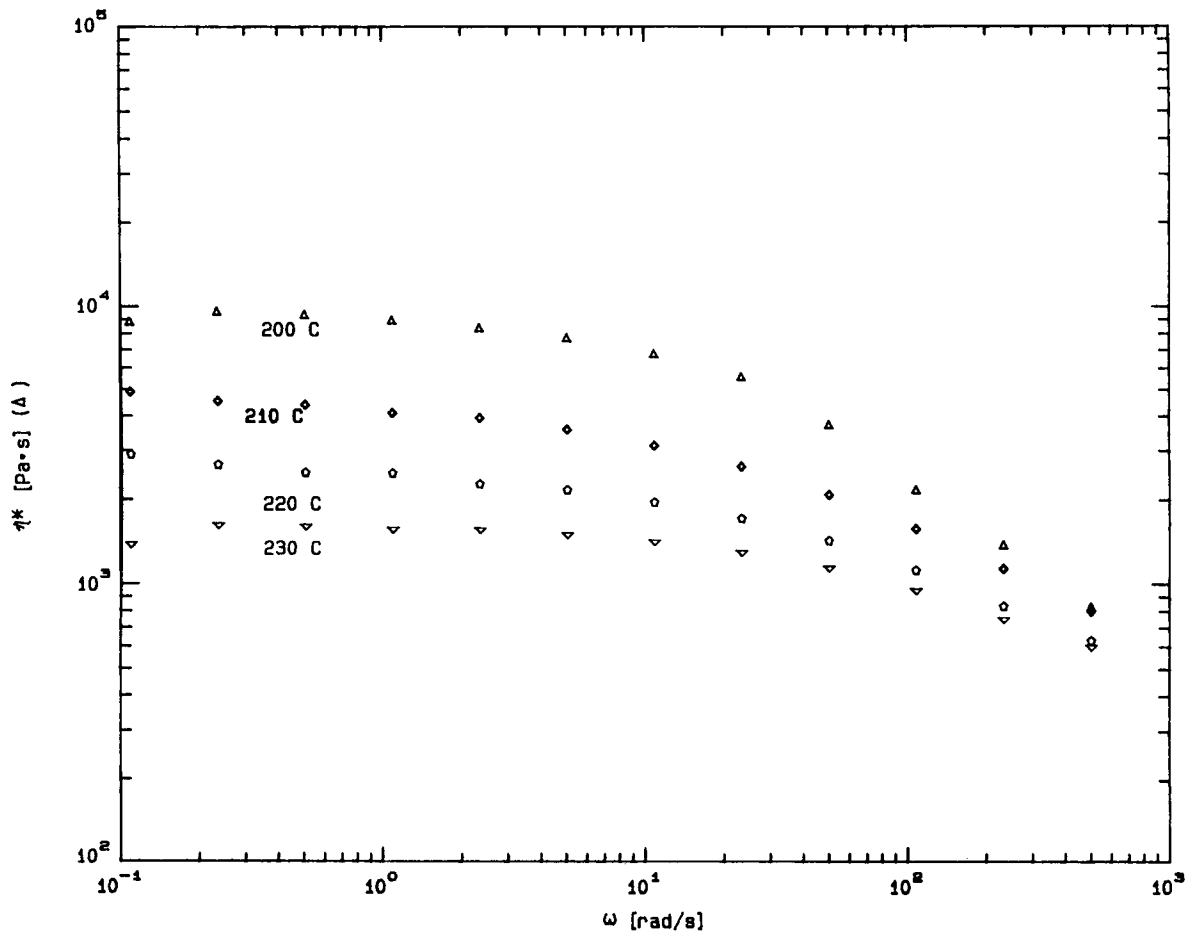


Figure 5 Dynamic viscosity of PETG melt at different temperatures.

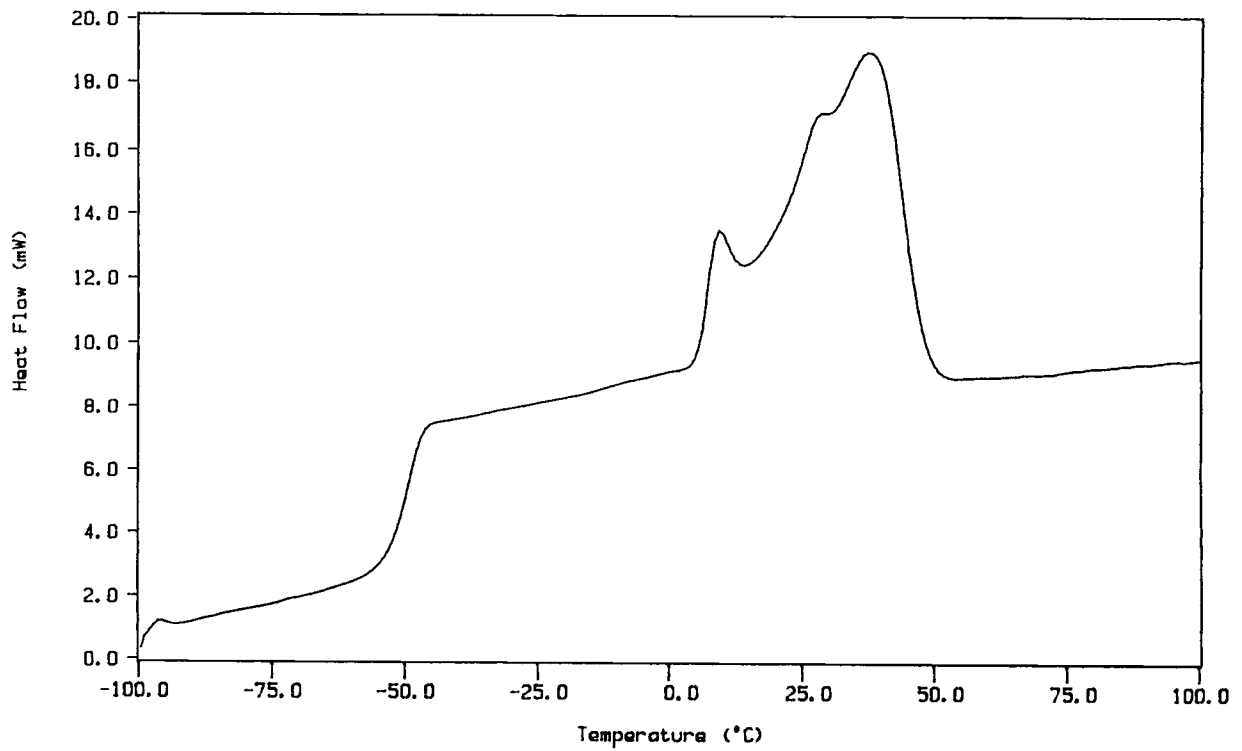


Figure 6 DSC scan of the ESD polymer.

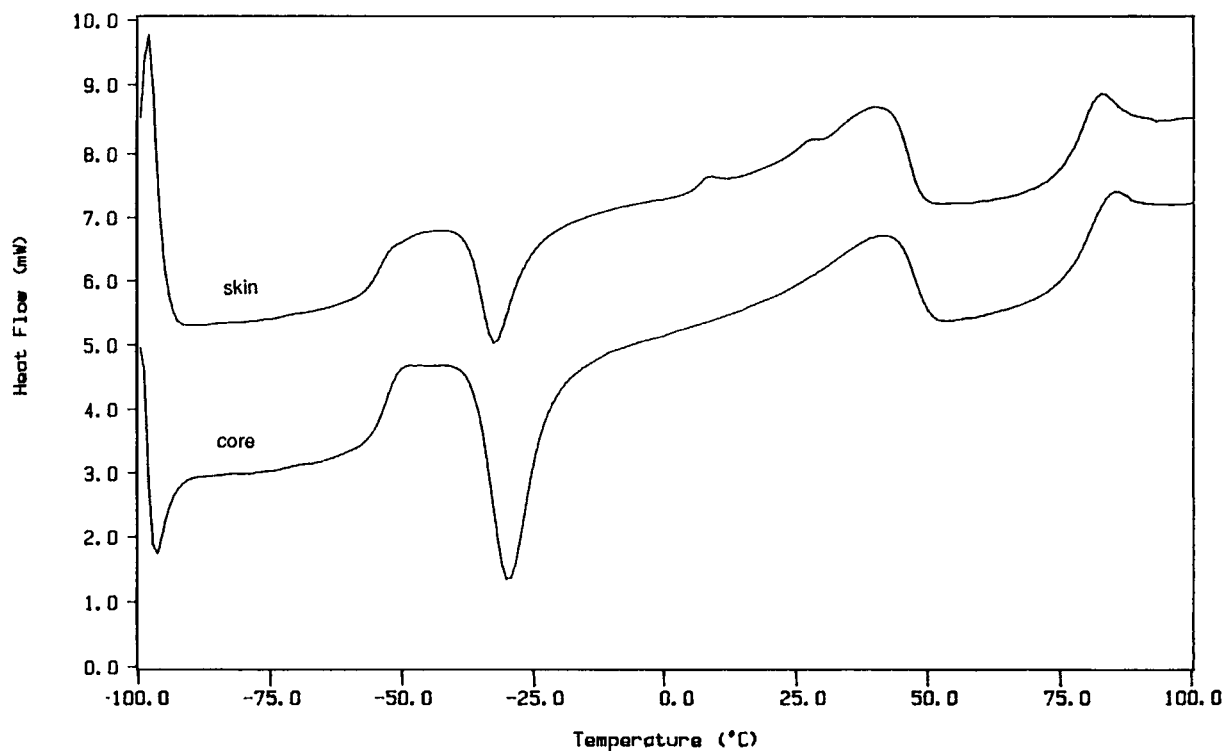


Figure 7 DSC scan of an injection-molded blend of 80/20 PETG/ESD polymer (blend D-2) as a function of the thickness location.

ponent at the low shear rate and the ESD polymer is the lower viscous component at the high shear rate region. This appears to result in the existence of a small composition difference in the thickness direction of an injection-molded ESD PETG part, with a greater fraction of the ESD polymer component in the skin section. This, in turn, could enhance the surface conductivity of the skin region of an injection-molded part.

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