Polymer Bulletin 11, 429–431 (1984)

Polymer Bulletin

Analysis

Dielectric and TSC Study of Semicompatible PVDF/PMMA Blends

Wojciech Medycki, Bozena Hilczer

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19
PL-60179 Poznan, Poland

Jan K. Krüger and Alexander Marx

University of Saarbrücken, Dept. of Physics, D-6600 Saarbrücken, Federal Republic of Germany

Summary

Dielectric and TSC studies of charged (by stabilized electrical breakdown) and discharged PVDF/PMMA blends have been performed. The relative changes in ε'' are found to decrease with increasing PVDF content except for samples with 50 and 70 weight-% of PVDF. The temperature T_{max} of the TSC maximum is found to be shifted linearly towards lower temperatures with increasing PVDF content up to 30 weight-% of PVDF. For higher concentrations T_{max} is found to be independent on PVDF content except for samples of 70 weight-% of PVDF. These behaviours indicate that for PVDF concentrations higher than 30 weight-% the system starts to lose its compatibility.

Introduction

Compatibility of PVDF/PMMA mixtures has been found in the amorphous state, however, it is known that a part of PVDF can crystallize (1-7). A shift of the main glass transition temperature T_g towards lower temperatures has been observed with increasing PVDF content (1,4,5,7), however, there are certain discrepancies between the results reported. Wang (1) reported a linear shift of T_g vs. PVDF content, whereas Hirata et al (5) and Krüger et al (7) observed irregularities for blends of higher than 60 weight-% PVDF concentration.

In the present paper we discuss the charge storage (8,9) properties of PVDF/PMMA blends. We measured dielectric properties and thermally stimulated currents (TSC) of charged and discharged blends of various PVDF contents.

Experimental

PVDF (product of Deutsche Solvay, Solingen, PVDF Solef X8N) and PMMA (product of Röhm, Darmstadt, atactic PMMA 8N) were melted at about 200°C and mixed (7,10). The mixtures were pressed to 50 μm films and cooled as quickly as possible to room temperature. For dielectric and TSC measurements samples were polarized by stabilized breakdown (9) at T_p = 120°C; a voltage of V_p = -7 kV was applied for 1 h and a glass insert of 1 mm thickness was used. The temperature dependence of the real (ε') and imaginary part (ε'') of the permittivity ε^* at 10 kHz was determined for samples with painted silver electrodes using a HP 4210A bridge at a heating rate of 2 deg/min. $\varepsilon^*(T)$ was measured two times: 1.) the polarized sample during heating up to 120°C, 2.) the completely discharged sample after slow cooling down from 120°C. Short circuit TSC measurements (7) were carried out at the same heating rate. Refractive index measurements were performed on untreated samples using an Abbe refractometer (wave length of 589.3 nm).

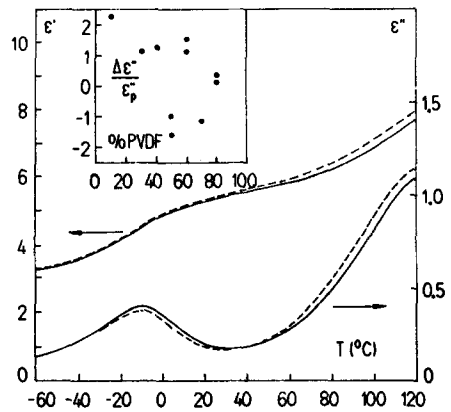

Fig. 1: ε'(T), ε"(T) for polarized (dashed) and discharged PVDF/PMMA 80/20 sample. Relative changes $(\varepsilon''_p - \varepsilon''_u)/\varepsilon''_p$ caused by polarization are plotted vs. PVDF content.

Results and discussion

Fig. 1 shows ε'(T) and ε"(T) for polarized (dashed) and discharged PVDF/PMMA 80/20. In all cases the values at temperatures higher than 40°C were greater for polarized samples than for unpolarized. In the same figure relative changes of ε" at -10°C caused by polarization are plotted vs. the PVDF content. It is rather hard to find a regular dependence. Irregularities were observed for 50 weight-% and 70 weight-% of PVDF. It seems however, that the relative changes of ε" decrease with increasing PVDF content. Fig. 2 shows an example of a current thermogram for a PVDF/PMMA 80/20 sample charged negatively by electrical breakdown. The TSC peak was found to consist of two overlapping maxima and it is difficult to distinguish the contribution of the PVDF molecule orientation since both PVDF and PMMA exhibit TSC maxima in the same temperature region (8,11). Therefore we plotted the temperature T_{max} of the greater TSC maximum vs. the PVDF content (Fig. 3). T_{max} was found to be shifted linearly towards lower temperatures with increasing PVDF concentration up to 30 weight-%. For higher concentrations T_{max} was found to be nearly independent on the PVDF content. For PVDF/PMMA 70/30 sample we observe deviations in the TSC and the dielectric measurements. The results obtained are similar to re-

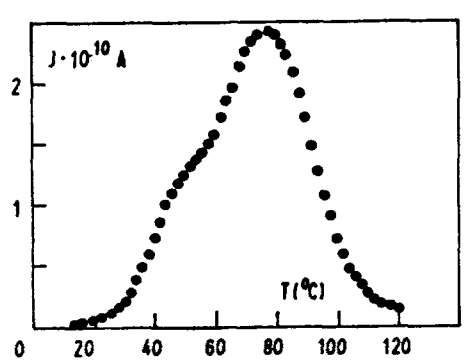

Fig. 2: TSC spectrum of a negatively charged PVDF/PMMA 80/20 sample.

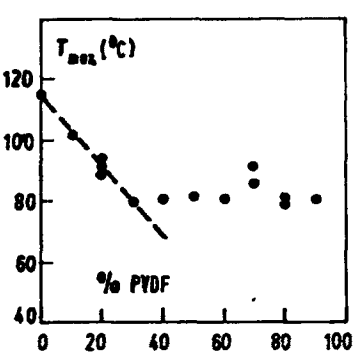

Fig. 3: Temperature T_{max} of TSC maximum vs. PVDF content.

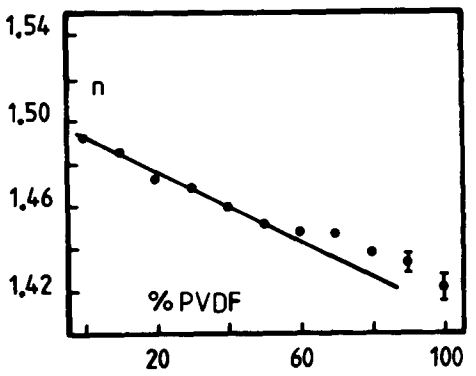

Fig. 4: Refractive index n^{589} vs. PVDF content

sults of mechanical and DTA measurements of Hirata and Kotaka (5) who found deviations in the concentration dependence of T_g for samples of higher than 60 weight-% PVDF concentrations. The fact that we observe deviations for blends of lower PVDF contents we relate to increasing crystallization caused by heating above 120°C. Deviations from the additivity are also observed in the refractive index measurements. Fig. 4 shows the refractive index of PVDF/PMMA blends as dependent on PVDF concentration.

Conclusions

Dielectric and TSC studies of charged and discharged PVDF/PMMA blends show deviations from the additive behaviour for PVDF concentrations higher than 30 weight-%. Similar deviations were found from refractive index measurements to start at ~60 weight-% of PVDF for untreated samples of lower crystallinity. Samples of 70 weight-% of PVDF exhibit an exceptional behaviour both in dielectric and TSC measurements. Deviations for PVDF/PMMA 70/30 blends have been observed also in IR studies by Leonard et al. (12) and are related to the existence of the β crystal form.

References

1. T. Nishi, T.T. Wang, Macromolecules, 8, 909(1975)
2. D.R. Paul et al., Polym. Eng. Sci. 18, 1225(1978)
3. E. Roerdink, G. Challa, Polymer 19, 173(1978)
4. J.S. Noland et al., Adv. Chem. Ser. 15, 99(1971)
5. Y. Hirata, T. Kotaka, Polymer J. 13, 273(1981)
6. B.S. Morra, R.S. Stein, J. Polymer Sci., Polymer Phys. Ed. 20, 2243 (1982)
7. J.K. Krüger, Ferroelectrics, in print, 55, xx(1984)
8. J. van Turnhout, Thermally Stimulated Discharge of Polymer Electrets, Elsevier, Amsterdam 1975
9. G.M. Sessler et al., Electrets, Springer-Verlag, Berlin 1980
10. J.H. Wendorff, J. Polym. Sci., Polym. Phys. Ed., 18, 439(1980)
11. P.C. Hehendru et al., Indian J. Pure Appl. Phys. 18, 183(1980)
12. C. Leonard et al., Polymer Commun. 24, 110(1983)

Accepted March 18, 1984