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Thermally stimulated discharge current (TSD) study on PVC-CPE blends

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SUMMARY

Chlorinated polyethylene is a commonly used impact modifier for PVC. Because the PVC and CPE are not compatible, the structure, and therefore the properties of their blends strongly depend on processing conditions.

It has been found that the TSD spectra show the structural changes in the PVC-CPE blend well and allow the processes at the phase boundaries to be ascertained. The impact strength values of tested samples can be related to TSD results.

INTRODUCTION

The theory of thermally stimulated discharge currents has been summarized by vanTurnhout (1), Aoki and Brittain (2), and Hedvig (3). The individual transitions are described well by a convergent series (2,4).

In case of the short circuit method the assumption

$$I_{d(T)} = \sum_{i=1}^{n} I_{d(T)_n} \qquad (1)$$

is generally fulfilled, i.e. at temperature T the observed current is the sum of currents of individual transitions. (This assumption may not be used for layered samples!)

Many methods of calculating activation energy of transitions exist (1,2,3,4). In our laboratory a simple method has been worked out to assess the activation energy from the half width of TSD peaks (7).

The mechanical properties, especially the impact strength of PVC-CPE blends depend strongly on processing conditions. This fact has been attributed to the changes in phase structure and investigated comprehensively by mechanical methods (8,9,10,12) and the use of electron microscopy (8,10,11) to observe the phase structure. The processing conditions of PVC modified by CPE have a narrow optimum, therefore the processing of PVC-CPE blends is difficult.

Low effective frequency methods, such as thermally stimulated creep (16) and TSD (15) have also been used successfully to investigate PVC-CPE blends regardless of the influence of processing. Toughened PVC prepared by rolling was tested by Hedvig (17); in this work a peak was found, named α'_2 and assigned to structural defects.

EXPERIMENTAL

Sample preparation

A simple formulation was mixed in a 25 l Trusioma high-speed mixer:

PVC ONGROVIL S-5070	90 w.parts
CPE ONGROVIL 36HI02 (36% Cl)	10 "
Tin stabilizer (maleate type)	1.5 "
Wax 2411 (paraffin type)	0.2 "

One batch of blend was mixed and this was used for all processing experiments. The processing was carried out on a roll-mill at 150, 160, 170, 180, and 200 °C for 4, 8 and 16 minutes. One sample was prepared at 175 °C for 8 minutes.
Sheets of 0.4 and 4 mm thickness were compression moulded for TSD and Charpy tests respectively.

Apparatus

For TSD investigations a home made apparatus was used described in a previous paper (7). Polarizing voltage was 1210V, the samples were polarized at 115 °C for 30 minutes. Cooling and heating rates were 1 K/min.
For impact strength measurements a simple Charpy pendulum was used. The tests were carried out at 0 °C according to DIN 53453 using 6 x 4 x 50 mm notched specimens.

TSD calculations

The recorded currents were transformed to 30 cm^2 electrode area and 1 kV/mm field. This representation is more descriptive than the dipolar conductivity. Activation energies were determined by eq.12 in Ref.7. The approximation of transitions were performed by eq.7 in Ref.7. Relaxation strength (δ) was calculated by

$$\delta = \sigma / E\varepsilon_0 \qquad (2)$$

where $\sigma = Q/\mathcal{A}$. Q values were obtained by numerical integration of measured currents between suitable limits.

RESULTS AND DISCUSSION

The typical shape of a TSD curve of PVC-CPE blend is shown in Fig.1. below, compared with the curve of unmodified PVC.

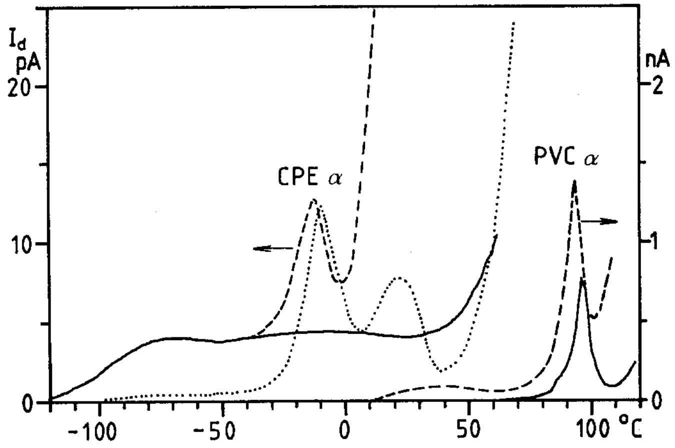

Figure 1.

TSD curves of unmodified PVC (solid line) and a PVC-CPE blend (dashed line) processed at 170 °C for 8 minutes using the same additives.

The dotted line shows the TSD curve of pure CPE used in this experiment divided by 10

At low temperatures the curves are very similar. The α transition of CPE is superposed on the β transition of PVC which is followed by a broad peak. It consists of a set of transitions. The intensity of the PVC α transition became higher by blending with CPE, however, the peak position is only ~2 °C lower. The CPE has no significant plasticizing effect. It was shown by a former experiment that the α peak of CPE is only detectable at CPE contents over 1% and the intensities are always lower than is calculated from the additivity. The loss in the measured charge is partially attributed to the internal currents, because the electric field in the CPE particles differs from zero. Fig.2. shows the relaxation strength values of CPE α peaks using the relaxation strength of the α peak of pure CPE as reference. It seems that the PVC "dissolves" about 1% CPE in melt. Over 1% concentration the PVC-CPE blends always form multiphase systems. Because the PVC α peak position does not depend on CPE concentrations at above 1% CPE, it does not appear to be compatible at these higher concentrations. It is to be noted that the CPE is never a homogenous polymer, its structure depends on the conditions of chlorination, mainly on the temperature. The structural changes can be detected sensitively by TSD, this subject has also been investigated by us. The structure must influence the compatibility of CPE with PVC. By changing the processing temperatures of the PVC-CPE blend the TSD curves obtained do not differ much below 0 °C, howewer, there are differences in the intensities of the PVC α peak and a broad, multiple transition in the range of 0 – 90 °C appears, as shown in Fig.3. below.

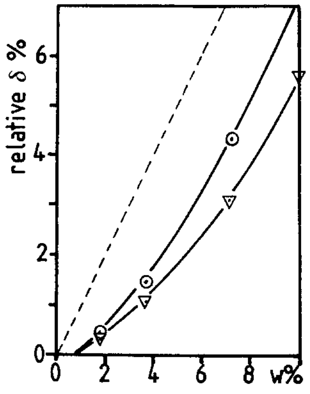

Figure 2.

Relative relaxation strength values vs. CPE content of CPE peaks in PVC–CPE blend calculated from the whole –Δ——Δ– and from the simulated —⊙——⊙— transition of pure CPE.

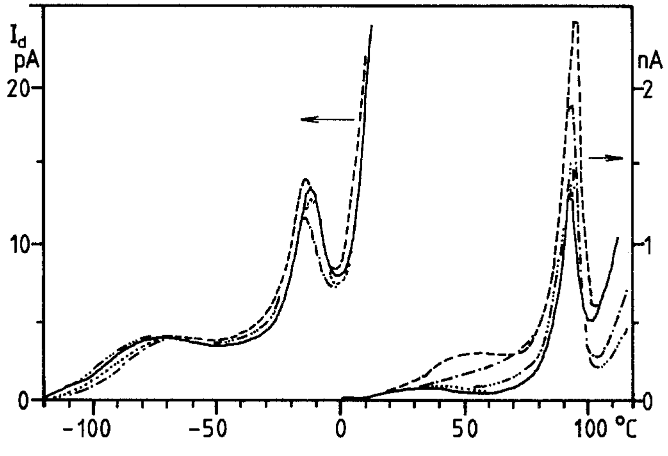

Figure 3.

TSD curves of PVC–CPE blends processed for 8 minutes at

160°C ————

170°C ....

180°C – – – – – –

190°C –·–·–·– and

200°C –··–··–··

Unfortunately, the plots like Fig.3. seem to be confused, therefore the TSD spectra of samples processed for 4 and 8 minutes are not represented in this paper. The spectra of samples processed at 150 °C are also not plotted, because those are practically equal to the curves of samples processed at 160 °C.
Parameters of PVC α transitions were determined for all experiments. Substracting these simulated transitions from the respective spectra, it becomes possible to separate the currents of transitions taking place between the CPE α (-12 °C) and PVC α (+92 °C) peaks. Fig.4. represents the TSD curves of blends without the PVC α currents.

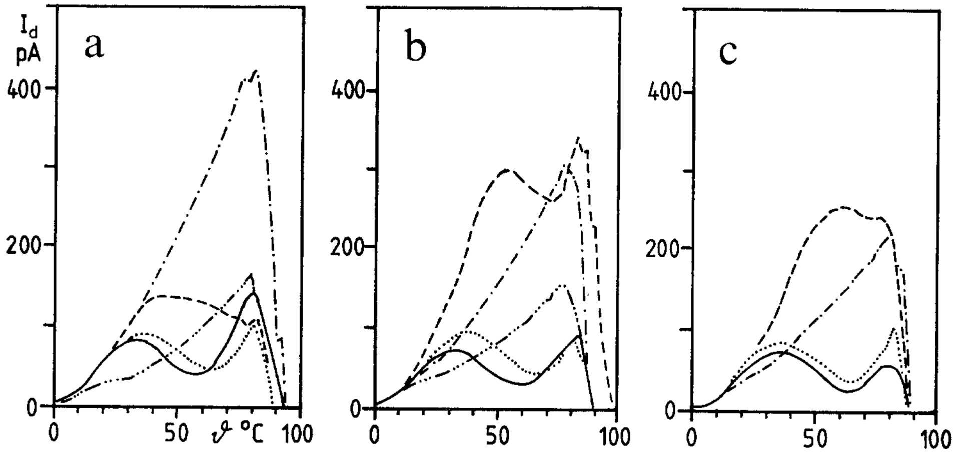

Figure 4.

TSD curves of PVC-CPE blends after substracting of PVC main transition processed for 4 min (a); 8 min (b); and 16 min (c); at 160°C ———— ; 170°C ·········· ; 180°C – – – – – ; 190°C —·—·—·— ; and 200°C —··—··—

The curves obtained are complex and consist of two transitions at least. The individual transitions are difficult to resolve especially in case of samples processed at 180 °C or over. These form a broad transition. The intensities strongly depend on the processing temperature, but weakly on the processing time. It is assumed that a multiphase structure develops in the melt. One of the phases is always the CPE having a main transition under 0 °C (see Fig.1.). A small part of CPE is dissolved in the PVC martix causing stuctural defects. At low processing temperatures the phases are well separated, the ψ relaxation (19) of PVC (60...90 °C) and the charges stored on the PVC-CPE phase boundaries (10...50 °C) are distinguishable. By increasing the processing temperature the CPE particles become smaller (10),this process leads to the increase of interfacial polarisation. Over 170 °C the chains of PVC and CPE partially penetrate into one another instead of maintaining distinct phase boundaries new structure is formed, moreover, there is a contribution from the decomposition of supermolecular structure of PVC.(11). The final structure is similar to the unmodified PVC with very small CPE inclusions and enhanced ψ processes. The curves of Fig.4. were integrated between 0 and 92 °C. Relaxation strength values were calculated from the Q charges and plotted in Fig.5.

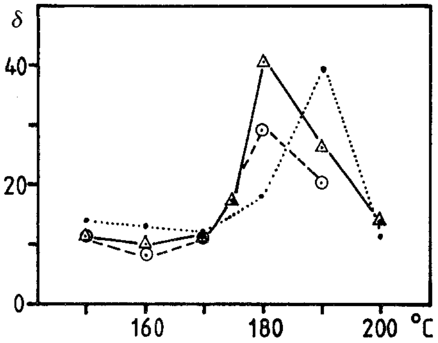

Figure 5.

Relaxation strength values of PVC-CPE blends processed at various temperatures for 4 min ·······•······· ;8 min ——△—— ; and 16 min – – -⊙– – –
Data were calculated from the curves of Fig.4. between 0 and 92 °C.

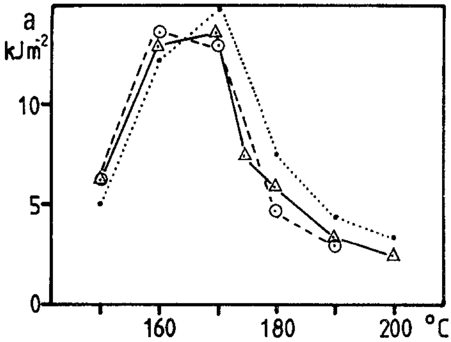

Figure 6.

Impact strength values of PVC-CPE blends processed at various temperatures for 4 min ·······•······· ;8 min ——△—— ; and 16 min – – -⊙– – – ; tested by Charpy method at 0 °C.

This representation also shows the effect of processing time. Increasing the processing time the maxima are shifted to lower temperatures. Nevertheless, it is supposed that below 170 °C and over 200 °C the processing time has no considerable influence.

The Charpy-impact strength values measured at 0 °C are shown in Fig.6. The maximum values are obtained between 160 and 170 °C processing temperature, above this the impact strength decreases dramatically. In order to obtain good impact behavior the CPE must form an optimum phase structure. Both coarse phase structure and the strong interactions i.e. the interpenetrating of chains cause poor impact properties.

The presence of CPE in the blend also enlarges the relaxation strength of PVC the α transition. On increasing the processing temperature or time a decreasing activation energy is obtained, as shown by the Table 1.

Table 1. Activation energies (A, kJ/mol) and relaxation strength (δ) values of PVC α transitions of PVC-CPE blends

Processing time ▷	4 min		8 min		16 min	
Processing temp ▽	A	δ	A	δ	A	δ
150	330	24.0	358	20.5	358	23.8
160	375	23.4	342	21.1	333	25.5
170	343	23.1	332	23.0	333	23.2
180	300	32.6	324	45.6	293	46.0
190	300	49.9	292	44.9	286	39.7
200	343	25.9	270	36.6	–	–

The decrease of apparent activation energy can be explained by the complex character of the α transition. By the effect produced by shear and heat CPE segments are mixed with PVC. This is the reason for the transitions becoming broader. It is supposed that because of the multiphase structure an MWS (Maxwell-Wagner-Sillars) polarisation appears, partly governed by the PVC α processes, causing the increase of the PVC α peak. Other less compatible impact modifiers do not cause the increase of PVC α peak.

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REFERENCES

1. vanTurnhout,J. (1975) Thermally stimulated discharge of polymer electrets, Elsevier, Amsterdam
2. Aoki,Y.-Brittain,J.O. (1976) J.Appl.Polym.Sci. **20** : 2780
3. Hedvig,P. (1977) Dielectric spectroscopy of polymers, Hilger, Bristol
4. Cowell,T.A.T.-Woods,J. (1967) Brit.J.Appl.Phys. **18** : 1045
5. Kamm,A. (1985) Kunststoffe 75 : 900
6. Gancheva,T.S.-Dinev,P.D (1981) Int.J.Polym.Mater. **9** : 51
7. Marossy,K. (1989) Polym.Bull. **22** : 213
8. Kiss,L.-Sztankai,G.-Nagy,P.-Karger-Kocsis,J. (1984) J. Vinyl Techn. **6** (3) : 125
9. Kiss,L.-Nagy,P.-Karger-Kocsis,J.-Sztankai,G.(1983) Műanyag és Gumi **20** : 201
10. Fleischer,D.-Fischer,E.-Brandrup,J.(1977) J.Macromol.Sci.-Phys. **B14** : 17
11. Fleischer,D.-Brandrup,J.-Heinzmann,O. (1977) Kunststoffe **67** : 312
12. Borotai,S.-Köves,L.-Mariska,Gy.-Marossy,K. (1980) Műanyag és Gumi **17** : 235
13. Kakutani,H.-Asahina,M. (1969) J.Polym.Sci. part A-2. **7** : 1473
14. Schwenke,H.F. (1989) J.Vinyl.Techn. **11** : 28
15. delVal,J.J.-Alegría,A.-Colmenero,J.(1986) J.Appl.Phys. **59**: 3829
16. delVal,J.J.-Lacabanne,C.-Hiltner,A.(1988) J.Appl.Phys. **63**: 5312
17. Hedvig,P.-Földes,E. (1974) Angew.Macromol.Chem. **35** : 147
18. Marossy,K. (1988) 31st Microsymp. on Macromolecules, Poly(vinyl chloride), Prague
19. Harrell,E.R.-Chartoff,R.P. (1977) J.Macromol.Sci.-Phys. **B-14** :277

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