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Thermally stimulated depolarization (TSD) current study of plasticized PVC

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Summary

Plasticized PVC samples of different plasticizer concentration were tested by the thermally stimulated discharge current (TSD) method. Processing conditions were also varied. It has been found that plasticized PVC consists of at least three structural units having different molecular mobility. Their amount and characteristics strongly depend on the processing conditions, i.e. the thermal- and shear history of the material.

TSD method because of its excellent resolving power proved to be a useful tool detecting these structural units.

Introduction

Polivinyl-chloride has unique supermolecular structure which is only partly destroyed during processing. PVC retains this structure even if it is plasticized. The existence of microdomains in plasticized PVC was first reported by Gezovich and Geil (1). Double T_g transitions were observed by DSC technique in plasticized PVC. In the study of Beirnes ans Burns (2) two adjacent T_g's were found over the complete range of concentrations. Bair and Warren (3) have postulated that the two T_g's which they observed by DSC in plasticized PVC are attributable to two distinct glassy processes. The higher T_g is assigned to non crystalline syndiotactic PVC segments, whereas the lower temperature transition is assigned to the more easily solvated atactic chain segments. Sony and Geil (4) used DSC and electron microscopy and supposed that the plasticized PVC contains about 15% unplasticized part whose quantity is independent of the milling time at 165°C. Microdomains are essentially unplasticized and do not fuse up to 165°C. Unplasticized aggregate phase was also discovered by Földes et al. (5) using thermomechanical, dielecrtric and TSD methods. delVal (6) resolved the TSD transitions of PVC and found a series of elementar processes. Activation energies were found 230...290 kJ/mole and 22...74 kJ/mole for the α and β processes respectively.

The DC electrical conductivity of plasticized PVC was investigated by Lupu (7) and 2 or 3 temperature regions of different activation energy were found. Calculated activation energy values were low 1.1...1.4 eV (106...133 kJ/mole)

Similar double peaks were found by Jelčić and Brajković (8) by the TSD method. Their published results show strong current inversion which must be the consequence of an air gap or other insulating media between the sample and electrodes. (During our experiments with plasticized PVC current inversion was observed only in case of broken circuit. Layered sample or rough phase structure may produce current inversion.)

These investigations revealed the complicated structure of PVC, in particular of plasticized PVC.

Experimental

Materials and apparatus

Plasticized PVC samples were prepared on roll-mill using the formulation below:

S-PVC resin K=70	100	phr
Plasticizer	x	“
CaZn stabilizer	1.5	“
Wax E lubricant	0.2	“

ONGROVIL S-5070, suspension type PVC resin, medical grade di (2 ethyl hexyl)-phtalate (DOP) and other ingredients were used as received. 50 phr DOP containing blend was mixed in a 10 1 MTI laboratory mixer, other blends were mixed by hand prior to the roll-milling. Roll-mill temperature was 160°C in general, other cases are indicated on the graphs and tables. Sheets of about 0.4 mm thickness were compression moulded and disks of 53 mm diameter were die-cut for TSD tests. In order to avoid the effect of solvents, water based graphite paint was used as electrodes.

Apparatus and test method has been described in a previous paper (9). Polarizing voltage, temperature and time were 1200 V, 110 °C and 15 min respectively. Cooling and heating rate was 1 K/min.

TSD current also depends on the polarizing field and the sample size. All recorded depolarization curves are converted to a 1 kV/mm field and 30 cm^2 electrode area in this paper.

Evaluation

The model described in Ref. 9 was used, however, a new evaluation software was developed for PC.

Assuming a process of single relaxation time the depolarization current density produces an asymmetrical peak in the function of the temperature and can be calculated by

$$j_{(T)} = -\left(\frac{P_0}{\tau_0}\right) \exp\left[-\frac{A}{RT} - \frac{1}{b\tau_0} \int_{T_0}^{T} \exp\left(-\frac{A}{RT}\right) dT \right] \qquad (1)$$

Let C = $\mathcal{A}P_0/\tau_0$, and B = $A/Rb\tau_0$. Replacing $A/RT \equiv s$ and integrating:

$$I_{(s)} = C \exp\left\{ -s - B\left[e^{-s}(s^{-2} - 2s^{-3} + 6s^{-4} \ldots \right]_{s_0}^{s} \right\} \qquad (2)$$

τ_0 can be calculated from the T_m temperature of peak maximum, A activation energy and *b* heating rate.

$$\tau_0 = \frac{RT_m^2}{bAe^{\frac{A}{RT_m}}} \qquad (3)$$

Activation energy can be obtained from the half width of the peak either from the lower

$$A = 1.443R\frac{1}{\frac{1}{T_l} - \frac{1}{T_m}} \quad \text{(4) or from the upper half} \quad A = 0.962R\frac{1}{\frac{1}{T_m} - \frac{1}{T_u}} \qquad (5)$$

The total charge of the transition is

$$Q = \int_{t_0}^{t} Idt = \frac{1}{b}\int_{T<<T_m}^{T>>T_m} IdT \qquad (6)$$

The relaxation strength

$$\Delta\varepsilon = \sigma/E\varepsilon_0 \qquad (7)$$

where $\sigma = Q/\mathcal{A}$ is the surface charge density.

Plasticized PVC samples are homogeneuos suitably, therefore the assumption

$$I_{d(T)} = \sum_{i=1}^{n} I_{d(T)_n} \qquad (8)$$

is realized and can be used for curve resolution.

Transitions were regarded as single relaxation time ones, temperature dependence was calculated accordingly.

Results and discussion

TSD spectrum of a plasticized PVC consists of three regions as shown in the Fig. 1, if the polarizing temperature (T_p) is well above the glass transition temperature. The glass transition is more or less discernible split one. The low temperature part of the curve may contain transitions of fine structure. High temperature part of the curve between the glass transition range and polarizing temperature increases exponentially in consequence of ionic currents or trapped

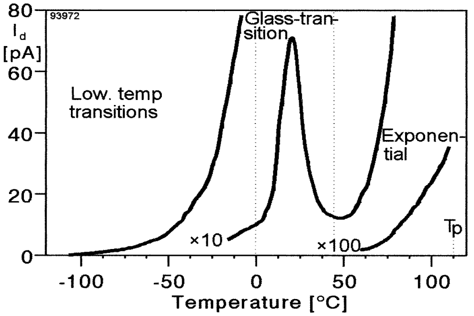

Fig. 1. Raw TSD curve of a plasticized PVC (50 phr DOP, processed at 170 °C) and the regions of the spectrum.

charges. Relaxation times at a peak are in the range of 100...400 seconds, 10 minutes polarization time and 1 K/min heating rate do not make possible the exact analysis over the T_p. A few centigrades above the T_p TSD thermogram has no information, it can not be evaluated. Relieving the TSD spectrum from high temperature currents, new transitions can be recognized. These transitions are more „noisy” as difference of great numbers.

Effect of plasticizer concentration

Blends were mixed with 0,10,20,30,50,70 and 90 phr DOP, roll-milled and compression moulded. Blends wihout plasticizer and with 10 phr DOP were roll-milled at 170°C, all of the others at 160°C. The higher is the plasticizer concentration the lower is the peak temperature of the glass transition. It is not surprising that this observation is in coincidence with results of other (dynamic mechanical, dielectric, DSC) methods. Fig. 2 shows the depolarization spectra of samples (with exception of 30 and 70 phr.), but high temperature exponential is already subtracted. All depolarization curves obtained are undoubtedly complex ones, the asymmetry of the main peaks are not consistent with the theoretical process. All spectra were resolved. Temperatures of peak maxima are plotted in Fig. 3.

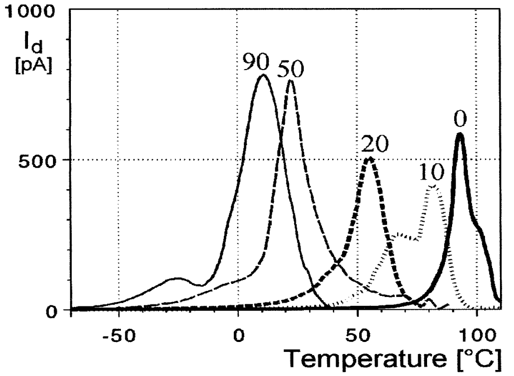

Fig. 2. TSD spectra of PVC samples of different plasticizer concentration. Numbers on the peaks represent the DOP content in phr. For processing temperature see text.

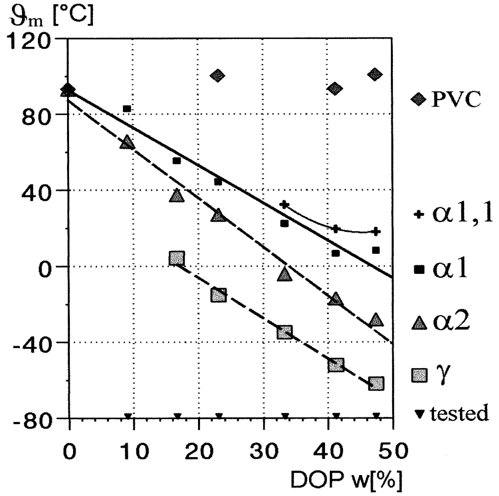

Fig. 3. Temperatures of peak maxima of resolved transitions v.s. DOP concentration.

Subtracting the exponential in case of 30, 70 and 90 phr DOP, a peak appears at about 100°C, in the range of rigid PVC. However, this peak is broader, it has lower activation energy than rigid PVC. Reproducibility of this peak is poor, its presence and intensity strongly depends on the history of the sample, i.e. on the processing conditions. This peak was also detected in the sample with 50 phr DOP, but prepared at different roll-milling temperatures. The main (glass) transition is double, independent of the plasticizer content. The two adjacent peaks are signed by α1

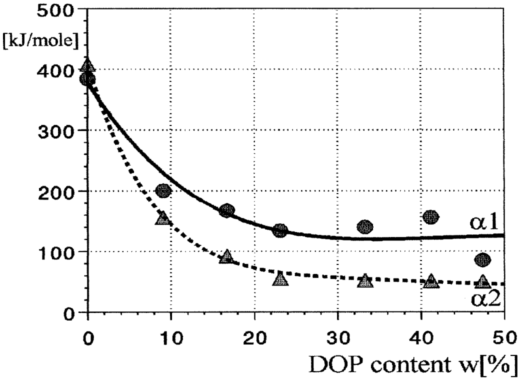

Fig. 4. Activation energy values of α1 and α2 transitions of plasticized PVC v.s. DOP concentration.

and α2. These peaks are very close in case of unplasticized PVC and difficult to separate. If the DOP content is higher than 50 phr, α1 has a high temperature shoulder of considerable intensity, signed by α1, 1.

A low temperature, low activation energy transition also appears over 10 phr DOP, signed by γ.

The peaks α1 and α2 are very similar, but α2 has lower activation energy in plasticized PVC as shown in the Fig.4. Rapid decreasing of A values can be explained by the fact that solvatation not only increases the mobility of segments but inhomogenities of solvatation produce broader relaxation time distribution, i.e. broader depolarization peak (10), in this way lower apparent activation energy.

Peak current (I_m) and the calculated relaxation strength ($\Delta\varepsilon$) values are fluctuating. It will be demostrated that peak intensities depend not only on the plasticizer concentration but also on the processing history of the sample, which is the consequence of supermolecular structure of PVC.

The presence of PVC α transition is dependent on the processing conditions, too. Increasing I_m with increasing plasticizer content suggests that I_m and $\Delta\varepsilon$ are not proportional to the amount of unplasticized PVC, polarizability of unplasticized PVC segments are governed by the surrounding media.

Effect of processing temperature

Plasticized PVC blend with 50 phr (33.3%) DOP was roll-milled at different temperatures and tested. Fig. 5. shows the depolarization spectrum (relieved from the high temperature exponential) of sample processed at 140°C and the calculated elementary processes. Fig. 6. shows the TSD spectra of samples in one graph. Despite the big differences of depolarization spectra all previously described transitions can be recognized in the curves, but the peak of unplasticized PVC was not evaluable in case of sample processed at 160 and 190°C. Data of resolved transitions are summarized in the Table 1. The α1,1 transition in the spectra of samples processed at 140 and 190°C is undoubtedly present, but resolving the other curves α1,1 can also be obtained. The intensity of transitions strongly increased using high processing temperature, only γ decreased in terms of I_m. However, in terms of $\Delta\varepsilon$ relaxation strength the intensity of γ transition is almost independent of processing temperature, it is in the range of 0.4...0.45. Calculating relaxation times using Eq. 1. α2 and γ processes give a narrow range, α1 are also near to each other, α1,1 seems to be confused. Activation energy values for this process strongly depend on the processing temperature and show a maximum in the range of 160...170°C range, as illustrated in the sub-plot of Fig. 7.

This fact explains the broad scattering of relaxation times of α1,1. However, the nature of this transition is not clear yet.

The effect of K-value of PVC and the plasticizer type were also investigated. It has been found that in case of suspension type PVC resin all transitions can be detected. Type of plasticizer has higher effect on the location of transitions, but using either phtalates or aliphatic ester plasticizers, these transitions appear in the TSD spectrum. Analysis of the effect of the plasticizer type is the subject of a forthcoming paper.

Table 1. Data of resolved transitions of 50 phr DOP containing plasticized PVC roll-milled at different temperatures

Milling temp. °C			140	160	170	190
exp.	k		28.44	39.78	28.21	40.82
	-B		8.09	11.82	7.68	11.63
PVC α	ϑ_m	°C	97.3		94.8	
	I_m	pA	212		457	
	A	kJ/mole	204		120	
α1	ϑ_m	°C	22.5	22.5	18.5	14.2
	I_m	pA	422	682	570	947
	A	kJ/mole	155	140	140	167
α2	ϑ_m	°C	-4.4	-3.9	-4.8	-5.6
	I_m	pA	70	79.6	77	58
	A	kJ/mole	51.7	52	52	44.5
γ	ϑ_m	°C	-40	-34.8	-37.6	-47
	I_m	pA	7.5	7.5	8	5.3
	A	kJ/mole	31.5	51	47	28
α1,1	ϑ_m	°C	36.4	32.4	25.5	24.2
	I_m	pA	285	315	371	762
	A	kJ/mole	68.5	160	210	96

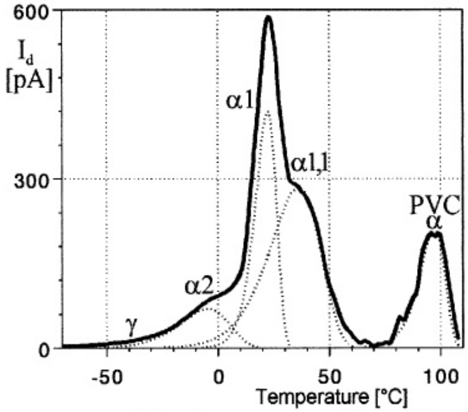

Fig. 5. Depolarization spectrum of plasticized PVC with 50 phr DOP, processed at 140°C. Dotted lines are the calculated elementary processes.

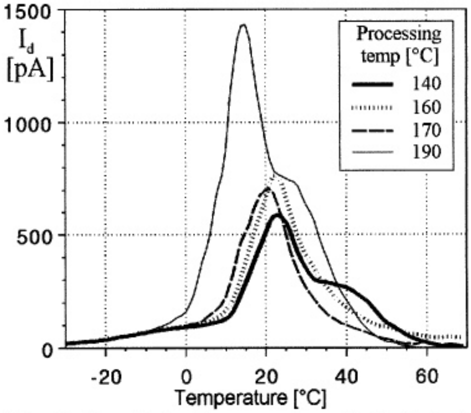

Fig. 6. Depolarization spectra of plasticized PVC processed at different temperatures, in the glass-transition range. DOP content is 50 phr.

Conclusions

Multiple transitions were found in plasticized PVC using the TSD technique. Two distinct glassy transitions were observed by other methods as well, as reported by Bair and Warren (3) and signed by α1 and α2 in the present paper.

Over 50 phr (33.3%) plasticizer concentration α1 is also a split transition, a new peak appears, signed by α1,1.

The α1 and α2 transitions must be attributable to structural units existing inherently in PVC. These peaks are hardly separable in unplasticized PVC. The distance of these

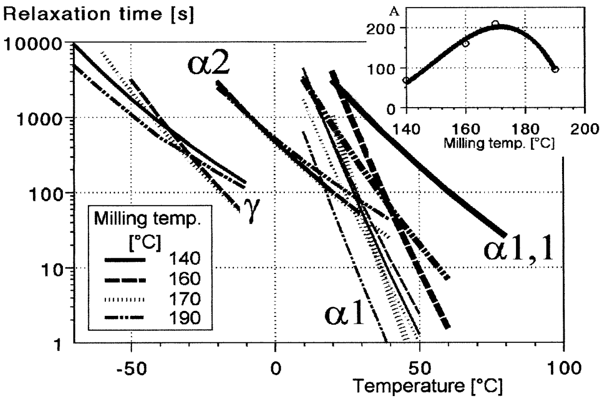

Fig 7. Relaxation time map of plasticized PVC containing 50 phr DOP processed at different temperatures. **Sub-plot:** Activation energy of α1,1 process v.s. roll-milling temperature

transitions increase by increasing plasticizer content (s. Fig. 3) while apparent activation energy decreases (s. Fig. 4).

At 50 phr DOP concentration, peak temperatures of α1, α2 and α1,1 are decreasing by increasing processing temperature, however, relaxation times show different picture (s. Fig. 7). The α2 is almost independent of processing both in τ relaxation time and Δε relaxation strength intensity. The α1 of samples processed at 140...170°C also produce a narrow range of relaxation times, but the sample, processed at 190°C shifts to lower values. These observations do not support the idea of Bair and Warren (3) whereas the transition of higher temperature can be assigned to non-crystalline syndiotactic PVC sequences, whose amount is low and constant. In order to settle this problem we intend to produce and test PVC's of different syndiotactic content.

Characteristics of α1,1 transition strongly depend on processing temperature and shows a confused relaxation time picture. It is most probable that the plasticizer concentration differs in aggregate and inter-aggregate regions, α1 of higher mobility corresponds with the less ordered plasticized regions and α1,1 to the internal particle ones.

Dramatic change in the 160...170°C processing temperature range supports that the decomposition of aggregare structure is controlled by the temperature in the same manner as in unplasticized or impact modified PVC (10).

The nature of the low intensity γ transition is not clear. At high DOP concentration its ϑ_m peak maximum temperature approximates the melting point of DOP (-78°C) measured by TSD. However, γ is also independent of processing, therefore it is unlikely that it origins from a DOP rich phase.

No regularity was found in the presence of unplasticized PVC peak, but it was undoubtedly detected in some cases, even at high plasticizer content. High sensitivity for shear is supposed, which is less controlled during processing.

Aknowledgement

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List of symbols

$\mathcal{A}$	area	cm^2, m^2
A	apparent activation energy	kJ $mole^{-1}$
B	constant, -A/RT	-
b	heating rate	K min^{-1}
E	electric field	Vm^{-1}, kV mm^{-1}
I	current	A, pA
I_d	depolarization current	pA
I_m	current at peak maximum	pA
j	current density	A m^{-2}
k	constant, preexponential factor	-
P, P_0	polarization, initial polarization	As m^{-2}
Q	charge	As, pAs
R	gas constant	8.314 J $mole^{-1}$ K^{-1}
t	time	s
T	temperature	K
ϑ	temperature	°C
σ	surface charge density	As m^{-2}, pAs cm^{-2}
τ	relaxation time	s
τ_0	relaxation time at 1/T=0	s
ε_0	permittivity of vacuum	$8.85 \cdot 10^{-12}$ F m^{-1}
$\Delta\varepsilon$	relaxation strength	-

Subscripts for T and ϑ

0	initial,
u and 1	at the upper/lower half
m	at current maximum
p	at the polarization