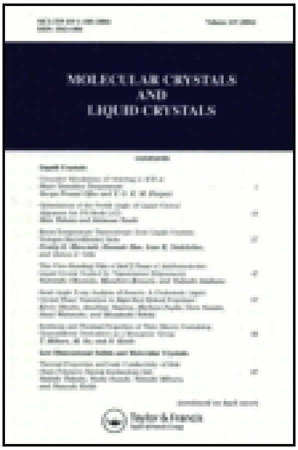

Molecular Crystals and Liquid Crystals

Electric Field Action on Annealing of Poly(Vinyl Chloride) and its Copolymer Composites

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Electric Field Action on Annealing of Poly(Vinyl Chloride) and its Copolymer Composites

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The difference in structures of a polymer and a polymeric composition on the annealing in the presence and the absence of the electric field has been determined. The ability of a polymer to transform its structure as a result of the electric field action and the annealing depends on more factors, among them it is a presence of other components in the system such as a plasticizer and a filler.

Keywords: electric field action; filler plasticizer; polarization

INTRODUCTION

A weak static electrical field causes a polarization of the polymer-dielectric. The effect is determined by the chemical nature of macromolecules, composition content, polarization characteristics: electrical field strength, temperature, and time.

In multicomponent systems, the electric field changes the intermolecular interaction, energy state of macromolecules, preferable conformation, and packing density in the presence of various additives. The initial structure of a sample becomes important, as it is changed under the influence of an additive and is determined by copolymer properties. Moreover, the efficiency of annealing with and without a static electric field depends on the concentration of a plasticizer in composites.

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EXPERIMENTAL

We studied the influence of an electrical field ($E = 100$ kV/cm) and the effect of annealing (60 min, $T = T_g + 10$ K, T_g is the glass transition temperature) on the structure and physical properties of films of polyvinyl chloride (PVC), copolymer of vinylchloride with vinylidene chloride (VCVD) and composites on the base of PVC and VCVD with a filler (20% $CaTiO_3$) and a plasticizer [0.5% and 10% dioctylphthalate (DOF)]. Samples for the annealing with and without electrical field were obtained under the same conditions: by pressing at a temperature by 30 K higher than a melting temperature of the polymer and with a cooling rate of 1 K/min (at a pressure of 15 MPa). The softening temperature of polymers and composites was determined from thermomechanical data under uniaxial deformation conditions at a constant tension stress of 0.85 MPa and a heating rate of 2 K/min. The dielectric characteristics (ε', tgδ) were measured over the frequency range $f = 0.7$–15 kHz. The temperature, at which the dielectric loss tangent is maximum ($T_{\mathrm{tg}\delta\max}$), was determined from dielectric data. Molar polarization ability of the substance (P), the dipole moment of a link caused by its chemical structure (μ_o), and the effective dipole moment (μ_{eff}) were calculated as in [1] with the use of the measurement data. The activation energy of an irreversible deformation of the substance at temperatures higher than T_p (E_a) was calculated using the Williams-Lendel-Ferry equations, and the activation energy of segmental movement ($E_{a,s}$) was determined from the frequency dependence $f_{\max} = A \cdot \exp(E_{a,s}/RT)$.

RESULTS AND DISCUSSION

In Table 1, we give the parameters for films of PVC, which contain the different quantities of a plasticizer (0.5% or 10% DOF) and a filler (20% $CaTiO_3$) in the initial state and annealed without electric field.

As one may see from Table 1, the introducion of the plasticizer into polyvinylchloride chains results in changes in $T_{\mathrm{tg}\delta\max}$, T_p, tg$\delta_{\max}$, and ε'. So, when 0.5% of the plasticizer added in the polymer, the flexibility of links decreases and the flexibility of side functional groups increases. But both the flexibilities of links and side functional groups increase at the annealing.

The analysis of the data in Table 1 indicates that the addition of 10% of the plasticizer increases the flexibility of macromolecules, but decreases the flexibility of side functional groups. At annealing, the flexibilities of links and side functional groups increase for this compound.

TABLE 1 Parameters of PVC with Plasticizer (DOF) and Filler ($CaTiO_3$) Initial and Annealed without Electric Field

	$Ttg\delta_{max}$		T_p		$tg\delta_{max}$		ε'	
Polymeric systems	init	ann	init	ann	init	ann	init	ann
PVC	381	375	348	342	13,7	14,3	2,97	3,00
PVC + 0,5% DOF	389	383	355	351	14,4	14,9	3,04	3,16
PVC + 10% DOF	359	354	322	317	13,3	13,6	2,30	2,33
PVC + 0,5% DOF + 20% $CaTiO_3$	391	388	356	352	15,1	15,5	3,2	3,25
PVC + 10% DOF + 20% $CaTiO_3$	359	355	323	320	13,5	13,8	2,62	2,64

In Table 1, we also see that the presence of 20% $CaTiO_3$ in composites which contain 0.5% or 10% DOF doesn't influence the character of changing the parameters which is identical at annealing and without annealing. However, a filler somewhat change the reconstruction structure at annealing.

In Table 2, we present the values of parameters for films of VCVD which contain the different amounts of the plasticizer (0.5% and 10% DOF) and 20% $CaTiO_3$ in the initial state and annealed without electric field.

The comparision of Tables 1 and 2 shows that the characters of changing the parameters for the compositions on the base of PVC and VCVD are similar.

The effect of annealing is identical for both PVC and VCVD. But the effect of the plasticizer is greater for the composition on the base of PVC than that for the composition on the base of VCVD which has more flexible chains.

TABLE 2 Parameters of VCVD with Plasticizer (DOF) and Filler ($CaTiO_3$) Initial and Annealed without Electric Field

	$Ttg\delta_{max}$		T_p		$tg\delta_{max}$		ε'	
Polymeric systems	init	ann	init	ann	init	ann	init	ann
VCVD	360	356	336	332	19,2	19,6	2,59	2,62
VCVD + 0,5% DOF	366	362	345	342	21,2	21,6	2,7	2,8
VCVD + 10% DOF	347	344	317	314	18,4	18,7	2,40	2,42
VCVD + 0,5% DOF + 20% $CaTiO_3$	363	360	340	337	19,9	20,3	2,96	2,99
VCVD + 10% DOF + 20% $CaTiO_3$	344	342	314	312	16,6	16,9	2,34	2,36

TABLE 3 Parameters of PVC with Plasticizer (0,5% DOF) and Filler ($CaTiO_3$) Annealed in Electric Field and Annealed Without Electric Field

	PVC		PVC + 0.5% DOF		PVC + 0.5% DOF + 20% $CaTiO_3$	
Parameters	pol	ann	pol	ann	pol	ann
ε' [298 K]	3,05	3,00	3,1	3,16	3,30	3,25
$tg\delta_{max} \cdot 10^2$	14,1	14,3	15,4	14,9	15,5	15,7
$\mu_{eff}10^{30}$, K · M;	1,48	1,43	1,44	1,5	1,77	1,64
T_p, K	345	342	348	351	354	352
$Ttg\delta_{max}$, K	377	375	379	383	389	388
$E_{a,n}$,κJ/mol	89,9	82,8	94,0	98,5	91,3	85,1
E_a,κJ/mol	332,8	306,3	348,7	368,8	338,5	315,8

In Tables 3 and 4 we give the parameters of the composites on the base of PVC and VCVD with 0.5% DOF and the $CaTiO_3$ filler annealed in the electric field and without it.

The character of changing the parameters of the composites which are given in Tables 3 and 4 shows exactly how the electric field influences the composition containing the plasticizer and the filler. As one can see from the tables, the electric field action on the composites leads to the retardation of processes running in the structure like the case of the initial polymer. The addition of the filler in the plasticized polymer reduced the electric field action. This is most obvious for PVC compositions with more rigid chains as compared with VCVD-based compositions. It is obvious that the influence of the filler is prevalent in the PVC-based composites with the filler and a small amount of the plasticizer, whereas the effect of the plasticizer is greater in the case of VCVD-based composites.

TABLE 4 Parameters of VCVD with Plasticizer (0,5% DOF) and Filler ($CaTiO_3$) Annealed in Electric Field and Annealed without Electric Field

	VCVD		VCVD + 0.5% DOF		VCVD + 0.5% DOF + 20% $CaTiO_3$	
Parameters	pol	ann	pol	ann	pol	ann
ε' [298 K]	2,66	2,62	2,76	2,80	3,04	2,99
$tg\delta_{max} \cdot 10^2$	19,4	19,6	22,1	21,6	20,1	20,5
$\mu_{eff}10^{30}$, K · M	1,36	1,30	1,44	1,74	1,74	1,67
T_p, K	335	332	340	342	338	337
$Ttg\delta_{max}$, K	358	356	360	362	361	360
$E_{a,n}$,κJ/mol	84,6	78,1	90,8	93,7	88,2	87,0
E_a,κ/mol	313,8	298,7	335,2	346,7	326,3	321,9

TABLE 5 Parameters of PVC with Plasticizer (10% DOF) and Filler ($CaTiO_3$) Annealed in Electric Field and Annealed without Electric Field

	PVC		PVC + 10% DOF	
Parameters	pol	ann	pol	ann
ε' [298 K]	3,05	3,00	2,36	2,33
$tg\delta_{max} \cdot 10^2$	14,1	14,3	13,5	13,6
$\mu_{eff}10^{30}$, K·M	1,48	1,43	0,93	0,9
T_p, K	345	342	319	317
$Ttg\delta_{max}$, K	377	375	356	354
$E_{a,n}$,κJ/mol	89,9	82,8	64,1	61,6
E_a,κJ/mol	332,8	306,3	247,3	234,5

In Table 5, we display the parameters for the composites of PVC with 10% DOF and the $CaTiO_3$ filler annealed in the electric field and without it.

The comparison of the data presented in Tables 3 and 5 shows that the electric field stimulates the reconstruction of the polymer with a small content of the plasticizer at annealing. The values of μ_{eff}, T_p, and $T_{tg\delta max}$ for annealed films are higher that those for polarized ones. The action mechanism of a small plasticizer amount was described in [2]. The electrical forces can retard the reconstruction of a polymeric composition with higher content of the plasticizer (Table 5). The values of T_p and $T_{tg\delta max}$ for polarized films are higher than those for annealed ones.

CONCLUSIONS

The ability of a polymer to transform its structure as a result of the action of an electric field and annealing depends on a few factors, among them we indicate the presence of other components in the system. Namely, small and large amounts of plasticizers influence differently: a small amount leads to the ordering of a polymer or a composition, whereas the large one causes the disordering. Electrical forces appearing on the polarization in the electric field stimulate the annealing effect at a small concentration of the plasticizer and decrease its action at its large concentrations. The addition of the filler in the plasticizer diminishes the electric field action. This is most obvious for the PVC-based compositions possessing more rigid chains as compared with the VCVD-based ones.

REFERENCES

[1] Van Krevelen, D. W., Hoftyzer, P. J. (1972). *Properties of Polymers. Correlations with Chemical Structure*, Elsevier: New York.

[2] Tager, A. A. (1978). *Physico-Chemistry of Polymers*. Khimiya: Moscow.