

Electrophotographic and Mechanical Properties of OPC doped Polycarbonate Layers

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Abstract

Charge carrier mobility and mechanical properties of organic charge transport layers (CTLs) for xerography have been investigated. The CTLs were based on molecularly doped polycarbonate (PC) of different chemical structure (PC-A and PC-Z) and molecular mass. Low weight organic photoconductors (OPCs), in particular, DEH and phenyl-4-tolyl-2-naphthylamine (PTNA) were used as a dopant.

In the CTLs, it was found out that the hole drift mobility tends to decrease as the molecular mass of the PC-A increases from 3×10^4 to $(1.0-1.3) \times 10^5$. In particular, a two fold and ten fold decrease in mobility was observed for the PC/PTNA and PC/DEH layers, respectively.

Indentation hardness, density and durability of the CTLs were studied and some structural characteristics of the CTL components were also calculated. The structure and composition of the CTLs were shown to influence slightly on the mechanical properties of the layers under study. Characteristics of the xerographic drums layered with the CTL are presented and discussed.

Introduction

In previous papers,^{1,2} data on the hole transport and electrophotographic properties charge transport layer (CTL) based on DEH and PTNA doped polycarbonate PC-A (PC-1 and PC-3) and PC-Z (Iupilon Z-200, Z-300 and Z-400) of different molecular weight were reported.

For the DEH doped polycarbonate PC-3 and PC-1, values of the xerographic sensitivity S_L and the concentration dependencies of S_L were shown to be similar in the dopant concentration range of 10 - 50 wt.%.¹ Furthermore, hole mobility in fragile and inflexible PC-3 films was larger than that in flexible PC-1 films. This was supposed to be related with either different mobility of segments and lateral groups of the polymer or different structure of the films.

In this work we have continued the study of an effect of polymer characteristics (in particular, structure and molecular weight) on hole transport and xerographic and mechanical properties of OPC (PTNA, DEH) doped polycarbonate PC-A, PC-Z, and copolycarbonate APEC.

Experimental

Samples studied by xerographic method consisted of an aluminium substrate, a barrier-adhesion layer of 0.8 - 1.2 microns thick, a generation layer of 0.5 - 1.0 microns thick, and a CTL of 30 - 40 microns thick. Barrier-adhesion layer was cast from a solution of polyamide (PA 6/66/610). Titanium oxide phthalocyanine (TiOPc) or bisazo dyes (ST 1017, SynTec Co.) dispersed in polyvinylbutirale (2:1) were used as a charge generation layer (CGL). The CTLs were prepared from DEH or PTNA doped PC. The following PCs were used: PC-A (PC-1, PC-3 and PC-0,5 from PO "Zarya", Russia), PC-Z (Iupilon Z-200, Z-300 and Z-400 from Mitsubishi Gas Chemical Co.), copolycarbonate APEC (9201, 9203 and 9204 from Bayer) and polycarbonate Panlite TS-2050 from Teijin Chemicals Co.

Viscosity of polymer solution was measured with a capillary viscometer at room temperature. Specific viscosity μ_{sp} was obtained from:

$$\mu_{sp} = (\tau_s - \tau_0) / C\tau_0 \quad (1)$$

where τ_s and τ_0 are the time of outflow of solution and solvent, respectively, C is the concentration of solution. Methylenechloride was used as a solvent and C = 0,5 g/dl.

For PC-1 and PC-3, melting index (168 °C /1,2 kg) equals to ca 3.0 - 3.5g/10 min and 7.1 - 7.6g/10 min, respectively. For PC Z-200, PC Z-300 and PC Z-400, viscosity molecular weights equals to 20000, 30000 and 40000, respectively.

Layers were prepared by the dip coating of a solution.

Sensitivity $S_{1/2}$ ($lx^{-1}s^{-1}$) of samples to a Halogen lamp ($T_{color} = 2850$ K) radiation was determined by measuring the

exposure required to reduce the corona charged surface potential to its half-value.

Hole drift mobility in CTL was measured by the conventional time-of-flight (TOF) technique that have recently been reviewed³. Details of the experiment may be found in Ref.4. Sandwich type samples were prepared for these measurements. Corresponding solutions were cast onto the polished stainless steel substrate or glass substrate with the indium-tin-oxide (ITO) electroconductive layer and dried at 80 - 90° C. Thickness of the CTLs ranged between 4 and 7µm as determined by a microinterferometer MII-4 and calculated from a CTL's capacitance. A 0.2-0.3 µm thick generation layer of selenium or titanium oxide phthalocyanine was deposited on the CTL free surface. Finally, a top aluminium semitransparent electrode was deposited on the generation layer. Both the generation layer and the top electrode were deposited by thermal evaporation in vacuum of 10⁻⁵ Torr. The TOF measurements were made at room temperature. A 337.3 nm N₂ laser pulse of 10 ns duration absorbed by the generation layer was used for the photogeneration of the free charge carriers. Measurements were carried out at a small signal mode of the TOF method; that is, the maximum charge generated at the electrode surface was less than 0.05 CV, where C is the sample capacitance and V the applied voltage. The transient currents were measured with a digital oscilloscope Tektronix TDS 340A providing that $R_L C_c \ll t_r$ was always fulfilled, where R_L is the load resistor, C_c is the capacitance of circuit and t_r is a transit time. The transit time was determined from the intersection of the asymptotes to the plateau and the tail of the transient. This time corresponds to the moment of the carriers sheet front arrival to an opposite electrode. The drift mobility was determined from the conventional expression:

$$\mu = d/(F t_r), \quad (2)$$

where F is the applied field and d is the CTL thickness. Mobility values were obtained with an accuracy of 15%. Both xerographic and TOF measurements were carried out at room temperature.

Vickers hardness was measured by a hardness tester with a pyramidal diamond indenter which has a load of 20 - 80 g. at fixed times and pressure. Specimens were prepared onto an Al plate by the repeated coating and drying of the corresponding solution in methylenechloride. The total thickness of dried layer ranged between 300 and 400 µm.

Density was measured with a 5 ml densimeter in bidistilled water by standard procedure. Specimens were prepared as described above. The dried CTL was scraped off from substrate and dispersed in water containing a low concentration of non-ionogenic surfactant until all air bubbles were removed. This lead to more reproducibility of data on density. Industrial PC granules were also used in measurements.

Durability of xerographic layer was measured by the following method. All the layers (barrier layer, CGL and CTL) were coated onto a drum and dried according to the

standard method. The drum was 30 mm in diameter and 70 mm in length. The thickness of layers ranged between 35 and 40 µm. The drum was weighed with accurate up to 0.00005 g, $P = P_0$. Then rotated drum (15 RPM) was abraded with a moving (12 mm/min) strip of grinding paper (number "0", 10x140 mm²) under the standard pressure. After 165 revolutions the drum was weighed again, $P = P_1$. Durability (mg) was defined as the difference $\Delta P = P_1 - P_0$.

Results and Discussion

The obtained data on specific viscosity μ_{sp} for polycarbonate solutions in methylenechloride are shown in Table 1.

Table 1. The specific viscosity μ_{sp} for polycarbonate solutions.

Polycarbonate	C, g/dl	Viscosity μ_{sp} , dl/g
PC-3	0,5	0,78
PC-1	0,5	0,96
PC-0,5	0,5	1,88
PC Z-200	0,5	0,54
PC Z-300	0,5	0,99
PC Z-400	0,5	1,2
PC TS 2050	0,5	1,2
APEC 9201	0,5	0,7
APEC 9203	0,5	0,57
APEC 9204	0,5	1,53

At equal conditions (T, C, solvent, viscometer, type of polymer) the value of viscosity is known to be usually symbate to the value of molecular weight of dissolved polymer. Hence, the molecular weight of the PC-A increases in the order of PC-3, PC-1, PC-0,5; that of the PC-Z increases in the order of PC Z-200, PC Z-300, PC Z-400; that of the PC APEC increases in the order of APEC 9203, APEC 9201, APEC 9204.

The influence of polymer binder (PB) molecular weight on hardness, density and durability of CTL are shown in Table 2. The influence is unclear.

Figs. 1-2 show the hole mobility as a function of electric field strength for DEH and PTNA doped PC-A (1:1) of different molecular weights (MW). The hole drift mobility increases with increasing electric field. As follows from the obtained data the mobility depends on the PC-A molecular weight - the higher MW the lower mobility. And the influence is more distinctly for DEH than for PTNA. At the same time all types of PC doped with DEH (or PTNA) have the same value of $S_{1/2}$. The similar data have been reported in the earlier papers^{1,2,5}. So the correlation between values of μ and $S_{1/2}$ is not found.

Seemingly^{2,6}, drift mobility depends on some following different factors: the nature of OPC and polymer binder; the technology of sample preparation (by means of a solvent composition; OPC concentration in solution; the

terms of drying of the coated layers) and so on. These factors can influence on free volume of the CTL polymer and consequently on the drift mobility.

Table 2. Properties of pure and OPC doped polycarbonate layers.

Polymer Layer	Hardness, Hv , kg/mm ²	Density, g/cm ²	Durability, mg
Pure PB			
PC-3	24	1,05*	
PC-1	26	1,18*	3,0
PC-0,5	17	1,24*	
PC Z200	25		1,3
PC Z300	23	1,20	
PC Z400	21		
PB + DEH, 1:1			
PC-3	30	1,08	33/51**
PC-1	29	1,11	2,4
PC-0,5	30		
PC Z200	30		2,6
PC Z300	30		2,3
PC Z400	30		2,2
APEC 9201			2,6
APEC 9203			2,3
APEC 9204			2,1
TS 2050			1,5
PB + DEH, 2:1			
PC-3	27	1,06	
PC-1	32	1,14	2,6
PC-0,5	27		
PC Z200	26		2,3
PC Z300	29		
PC Z400	29		
PB + DEH, 3:1			
PC-3	29	1,05	
PC-1		1,06	
PC-0,5	30		
PC Z200	28		
PC Z300	28		
PC Z400	28		
PB + DEH, 5:1			
PC-3	27		
PC-1	29		
PC-0,5	26		
PC Z200	26		
PC Z300	31		
PC Z400	29		
PB + PTNA, 1:1			
PC-3	35	1,10	
PC-1	37	1,15	2,0
PC-0,5	35		
PC Z200	42		
PC Z300	42		
PC Z400	40		

PB + PTNA, 2:1			
PC-3	36	1,08	
PC-1	40	1,20	
PC-0,5	36		
PC Z200	41		
PC Z300	37		
PC Z400	41		
PB + PTNA, 3:1			
PC-3	30	1,10	
PC-1	40	1,16	
PC-0,5	37		
PC Z200	36		
PC Z300	36		
PC Z400	36		
PB + PTNA, 5:1			
PC-3	32		
PC-1	37		
PC-0,5	35		
PC Z200	42		
PC Z300	35		
PC Z400	32		
Pure Organic Photoconductors			
PTNA		1,14	
DEH		1,20	
OPC Drum			
Canon NP-1215 (Katun)			2,1
Canon NP-1215 (Integral)			2,4
H.P. 6L			2,2

* - the industrial polycarbonate granules.

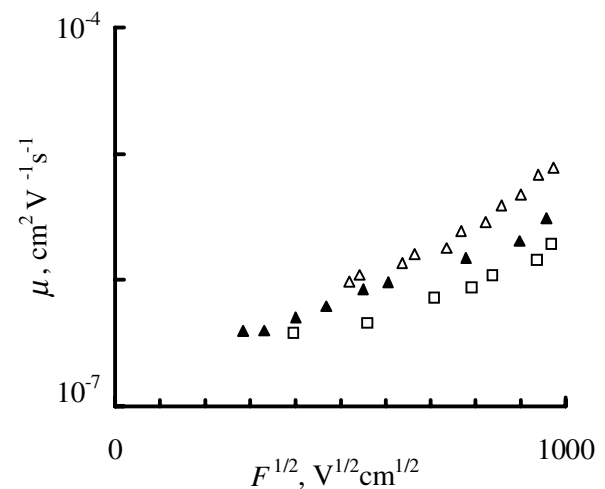


Figure 1. Field dependence of hole mobility in the PTNA doped PC-A of different molecular mass: PC-3, $MW \approx 3 \times 10^4$ (empty triangle), PC-1, $MW \approx 4.5 \times 10^4$ (filled triangle), and PC-0.5, $MW \approx (1.0-1.3) \times 10^5$ (empty square).

As was shown in Ref.7 the photoreceptor degradation depends on both polymer binder and OPC features, the degradation rate increases with an increase of OPC concentration. As follows from Table 2 there is no relation between the OPC concentration and the durability of CTL. But the durability of the CTL under study increases slightly with an increase of MW of OPC doped PC-A, PC-Z and copolycarbonate APEC.

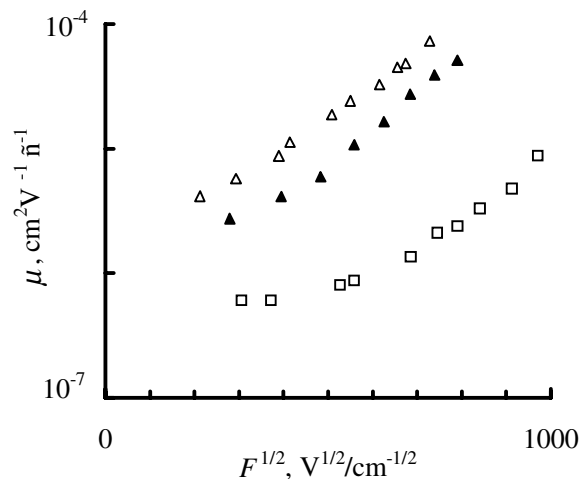


Figure 2. Field dependence of hole mobility in the DEH doped PC-A of different molecular mass: PC-3, $MM \approx 3 \times 10^4$ (empty triangle), PC-1, $MM \approx 4.5 \times 10^4$ (filled triangle), and PC-0,5 $MM \approx (1.0-1.3) \times 10^5$ (empty square).

One may suppose that the free volume of polymer in CTL can influence both on hardness and density of PB and OPC+PB films. Accordingly, hardness of the PC-3 and PC-1 is higher than that of the PC-0,5. Again, hardness for the PC-Z200 is higher than that for the PC-Z300 and PC-Z400. Densities of these polymers increase in the order of PC-3, PC-1, PC-0,5. For the DEH and PTNA doped PC-A, density of the PC-1 films is larger than that for the PC-3 films. So it may be concluded that there is the following correlation between hole drift mobility and density for the DEH and PTNA doped PC-3, PC-1, PC-0,5: the higher MW the higher density the higher durability and the lower mobility.

The correlation is more clear for DEH than for PTNA probably due to a different size of the molecules considered. The DEH molecule is larger than the PTNA molecule (Connolly Solvent-Excluded Volumes: 317 and 266 Angstroms Cubed correspondingly, calculated by CS Chem3D Pro, MM2).

Conclusions

Concentration of OPC and molecular weight of polymer binder influence on hole mobility and mechanical

properties of the CTLs. The correlation between hardness, microdensity, durability and hole drift mobility is observed.

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Biography

Konstantin K. Kochelev, Novosibirsk's State University (Chemistry), 1971. 1980 - Dr. chem. sci. degree in physical-chemistry (Tomsk's State University). Since 1980 he researched electrophotographic (EPG) materials at the Scientific Research Phototechnical Institute ("NIFTI", Pereslavl- Zalessky). His work has focused on Electrophotographic Drums and Toners and special polymer materials (EPG, PTP, heat mirror films and so on). Member of the IS&T. cca 150 patents and publications.

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