Photoelectrochemical Stability of Triarylamine Doped Polycarbonate Layers

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Abstract

Photoelectrochemical stability (to corona charging + light exposition), light or heat stability, electrophotographic and spectral properties of charge transport layers (CTL) on the base of organic photoconductor (OPC) doped polycarbonate (PC-A) layers have been investigated.

An influence of electrical current transition and light exposure on CTL was studied in cells of a type "PETP-ITO-CGL-CTL-ITO-PETP". Charge generation layer (CGL) on the base of TiOPc was used.

Products of photoelectrochemical, photochemical and thermochemical reactions of triarylamines (TAA) in the layers or in solutions were investigated with Gas Chromatography-Mass-Spectrometry (GC-MS), High Performance Liquid Chromatography (HPLC) and UV-Vis spectroscopy.

It was shown that the electrochemical and photoelectrochemical processes give the same main products of OPC's molecules conversion as photochemical and thermal processes but in different amounts. Cyclic fatique of investigated CTLs can be caused first of all by minor (including colored) products of the processes.

Introduction

Cyclic stability of OPC doped polymer layers (to corona charging, to light or to the both of these factors), electrophotographic and spectral properties of these layers have been investigated earlier[1-2]. The influence of organic photoconductor structures and possible mechanisms of cyclic durability of CTL have been investigated and discussed[2]. As it was shown[1] light, corona and light+corona influence on electrophotographic characteristics – values of residual potential V_R and dark decay DD are increased and values of sensitivity are decreased. These changes are partially reversal, and strongly influence on properties of the OPC drums. The effect of corona charging and light exposition (separately) on values of residual potential, dark decay and sensitivity considerably increases with increasing of both light, and corona intensities. The total effect a corona + light on these values greatly depends on intensity of a corona, and especially greatly - on light intensity. Possible reasons of the fatigue of organic photoreceptors in this case can be photochemical processes in charge transfer layers (CTL)[2]. As it was been supposed the fatique of CTL is connected mainly with holes drifted in CTL. In this connection it was interest to investigate an influence of an electrical current transition and a light exposure on CTL's characteristics (including processes that has been in a cell of a type "PET-ITO-CGL-CTL-ITO-PET"), and to determine products of chemical reactions formed herewith in CTL's.

Experiment

Samples studied by photoelectrochemical method (cells of a type "PET-ITO-CGL-CTL-ITO-PET") consisted of (consecutively) an polyethylene terephtalate (PET) film substrate, transparent electroconductive layer (ITO layer, 3000 Om/cm^2) deposited on PET film, CGL of 0.5-1.0 microns thick, CTL of 35-40 microns thick, ITO layer and PET film substrate.

The CGL was composed of a titanyl phthalocyanine pigment (TiOPc, ST10.10/2 of SynTec GmbH) dispersed (2:1) in copolymer vinylchloride and vinylacetate VAGH (Du PONT de NEMUR). The CTL was Tris(4-tolyl)amine (TTA), Phenyl-4-tolyl-2-naphtylamine (PTNA) and Di-4-tolyl-1- naphtylamine (DTNA) doped (1:1) polycarbonate PC-A (PC-3, PO "Zarya", Russia).

An electrical field (800 V) was applied between two ITO layers of the cells so that negative electrode was contacted with CTL. Cells were illuminated with tungsten lamp (500 W, 36,000 Lx) on the side of CTL (Variant 1) or on the side of CGL (Variant 2). Light filter passed light only with wave length more than 440 nm was used in Variant 2, so the quantity of light passed (through the filter and CGL) in CTL was negligible. Dark I_D and light I_L electrical currents and their ratio I_L/I_D as function of time were measured in the both variants.

PET-ITO-CTL films with the same CTLs (45-50 microns) were treated with UV-Vis light (240 W high pressure lamp, 5000 Lx, 100 hours). Toluene solution of TAA were treated with UV-Vis light (8 000 Lx, 720 hours).

Chemical composition of initial TAA (powder), TAA and products of their decomposition in cells, in films and in the solutions were determined by Gas Chromatography-

Mass-spectrometry (GC-MS) and by High Performance Liquid Chromatography (HPLC, Detector: Gilson UV 115, 254 nm. Column: Hypersi ODS (HP), 25x4. Mob. phase: 1 ml/min, MeOH/$CHCl_3$).

UV-Vis spectra of initial and treated TAA were measured in toluene solutions with SF-26 spectrometer (LOMO).

Result and Discussion

An influence of an electrical current transition plus a light exposure on values of dark I_D and light I_L electrical currents flowed through cells (in a cell of a type "PET-ITO-CGL-CTL-ITO-PET") and their ratio I_L/I_D on the initial stage (600 minutes) is shown in Table 1.

Table 1. Time dependence of I_L/I_D values flowed through the cells in Variant 1 and 2.

Time min	TTA		PTNA		DTNA	
	V.1	V.2	V.1	V.2	V.1	V.2
0	470	140	2000	310	670	800
120	8	22	33	21	6	16
180	7	17	15	20	4,5	10
600	6,4	10	7	33	4,3	11

As is seen from Table 1 there is a sharp decrease of I_L/I_D values when a cell was exposed on the side of CTL (Variant 1). On the other hand I_L/I_D values changed more slowly when a cell was exposed on the side of CGL (Variant 2) when the quantity of light passed in CTL through the filter and CGL was negligible. These results confirm early obtained data[1,2] that simultaneous effect of electrical current and active light (what can be absorbed by OPC molecules) passed through CTL causes increased fatique of them.

For analysis of photochemical and electrochemical processes going in the CTLs of the cells, UV-Vis spectra of TAA and products of their decomposition extracted from CTLs of these cells with toluene (at initial state, after 24 hours of treating in Variants 1 and 2) were measured.

UV-Vis spectra of TAA and products of their decomposition extracted from CTLs (in PET-ITO-CTL films) with toluene after acting on the films of UV-Vis light (100 hours), and UV-Vis spectra of toluene solutions of TAA treated with sunlight (30 hours) were measured too. Obtained data are shown in Fugures 1-3.

Chemical composition of initial OPC, OPC and products of its decomposition in cells, in films and in solutions were determined by HPLC and GC-MS.

The data of GC-MS are shown in Table 2.

Some of HPLC data for initial and treated OPC are shown on Figures 4 - 5.

As shown from the obtained results (Figures 1-5), data of UV-Vis spectroscopy, HPLC and GC-MS good correlate among one's and with data of Tables 1, 2 and papers[1,2].

These data shows that effect of light and current transition on OPC more large when a cell is exposed on the side of CTL than on the side of CGL.

The date confirms the ones of Table 1 and earlier obtained data[2] , that effect of charge carriers passed throw CTL on OPC Drum fatigue is grate when OPC simultaneously absorbs an active part of light (where the molecules of OPC have absorption).

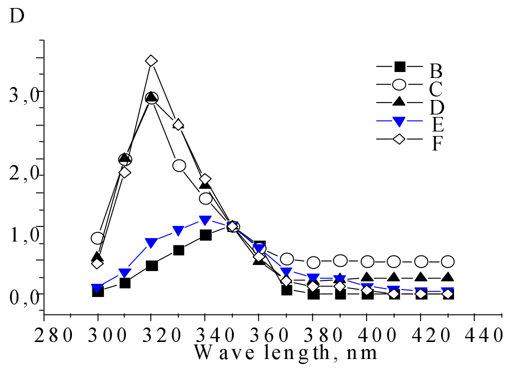

*Figure 1. UV-Vis spectra of TTA in toluene: (**B**) - initial TTA; (**C**) and (**D**) – TTA from the cells, Variant 1 and 2 ; (**E**) – TTA treated with UV-Vis 100 h in the film; (**F**)- TTA treated with sunlight 30 h in toluene solution.*

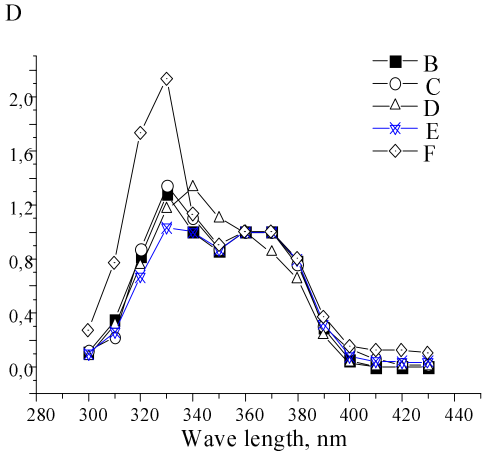

*Figure 2: UV-Vis spectra of PTNA in toluene: (**B**) - initial PTNA; (**C**) and (**D**) – PTNA from the cells, Variant 1 and 2 ; (**E**) – PTNA treated with UV-Vis 100 h in the film; (**F**)- PTNA treated with sunlight 30 h in toluene solution.*

As is resulting from received data the main processes of photoelectrochemical, light- and heat transformations of the OPC's molecules are shown in Figure 6. As shown in Table 2 and Figure 6 the OPC molecules undergo oxidative cyclization with different effectiveness. On this effectiveness effect a structure of the molecules (as was shown in earlier paper[3]) and the combination of acting factors.

Data of Tables 1,2, Figures 1-5 show that the stability of molecules are grows in a line – TTA - PTNA – DTNA, that confirm conclusions that were done in the paper.[3]

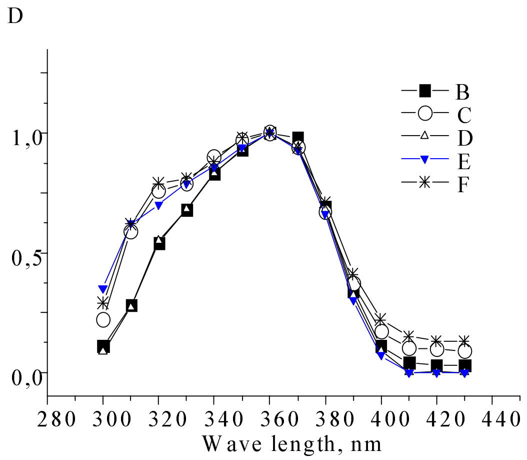

*Figure 3. UV-Vis spectra of DTNA in toluene: (**B**) - initial DTNA; (**C**) and (**D**) – DTNA from the cells, Variant 1 and 2 ; (**E**) – DTNA treated with UV-Vis 100 h in the film; (**F**)- DTNA treated with sunlight 30 h in toluene solution.*

Table 2. Results of GC-MS analysis of initial and treated OPC, contention of substances (%, on the base of peak areas).

OPC	**TTA**	**PTNA**	**DTNA**
Initial OPC	TTA– 100 DTPA*- traces	PTNA -100	DTNA-100
Cell, Var. 1	TTA- 99,85 DMTC, - 0,15	PTNA- 99,6 PBC- 0,27 TBC- 0,18	DTNA-100
Cell, Var. 2	TTA- 100 DTPA - traces	PTNA- 100	DTNA-100
Film, UV, 100 h	TTA- 94,84 DMTC- 5,16 DTPA - traces	PTNA- 100	DTNA-100
Heat 200^0, 30 min	TTA – 95,0 DMTC- 4,82 DTPA- 0,18	PTNA– 100	DTNA-100

*- [DTPA (Di-4-tolyl-phenylamine), m/e= 273 – as an admixture to initial TTA; TTA, m/e=287; PTNA, m/e=309; DTNA, m/e=323; DMTC (3,6-Dimethyl-N-(4-tolyl)carbazole), m/e=285; PBC (N-phenyl-3-methyl-benzocarbazole), m/e=307; TBC (N-(4-tolyl)-benzocarbazole), m/e=307].

Electrochemical studies of analogous substances have shown,[4] that the same cyclic products had formed in solutions as the main products of the electrochemical cyclization reaction. But rates of these processes in films were much less than the ones in solutions. So the products practically were not detected by GC-MS in our investigation.

But UV-Vis spectra of OPC treated in the cells (Variant 1 and 2) show presence of reaction products in more short and in more long spectral diapason than for initial OPC molecules absorption.

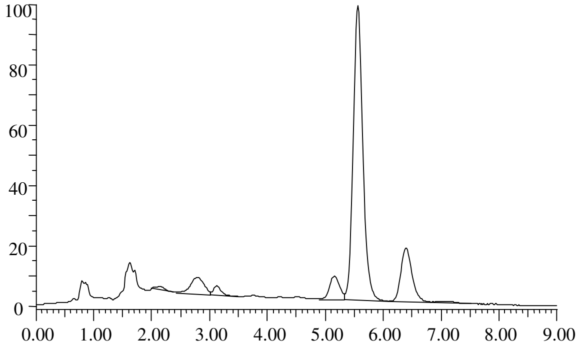

Figure 4. HPLC data of TTA treated in film UV-Vis, 100 h. Peaks (Area %) with retention times 2.14 (0.83%), 2.78 (5.55%), 3.12 (1.85%) are unknown polar substances (non-volatile or unstable in GC-MS); Peak 5.56 (70.19%) is TTA (may be, with DTPA); Peak 6.38 (14.98%) probably is DMTC; Peaks 5.15 (5.86%) and 7.06 (0.75%) are unknown substances (invisible in GC-MS too);

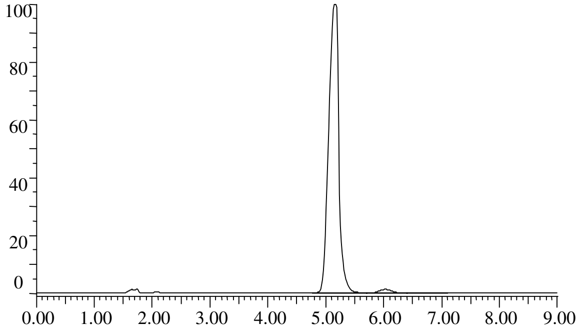

Figure 5. HPLC data of PTNA treated in the sell (Variant 1). Peak (Area %) with retention times 5.18 (98,07%) is PTNA; Peak 6.01 (1.69%) is a mixture of PBC and TBC; Peak 6.81 (0.24%) is an unknown substance (invisible in GC-MS).

Thus possible reasons of cyclic fatique of the CTL on base of the investigated OPC in principle may be:

a) Formation of colorless inactive molecules as shown in Table 2 (that can leads to hole mobility reduction and to a reduction of drum's sensitivity too but only at large degrees of conversion). But all these molecules have I_p values large than ones for appropriate initial OPC molecules and consequently can't be hole traps. Indeed AM1 calculation (CS ChemOffice, v.5) gives for isolated molecules (TTA; DTPA; DMTC/ PTNA; PBC; TBC / DTNA) values of I_p = 7,79; 7,99; 7,85 / 7,86; 8,05; 8,05 / 7,97 respectively.
b) Formation of unknown minor products (including colored - redish-brown, brown ones) in small amounts, that couldn't be determined with GC-MS at our conditions (too small amounts of them, unvolatile molecules and so on). Presence of these substances can

indicate HPLC data and UV-Vis spectra - it is seen small peaks of unknown polar substances at little retention times (Figures 4, 5) and grows of optical densities at more long waves then the main peaks (Figures 1-3).

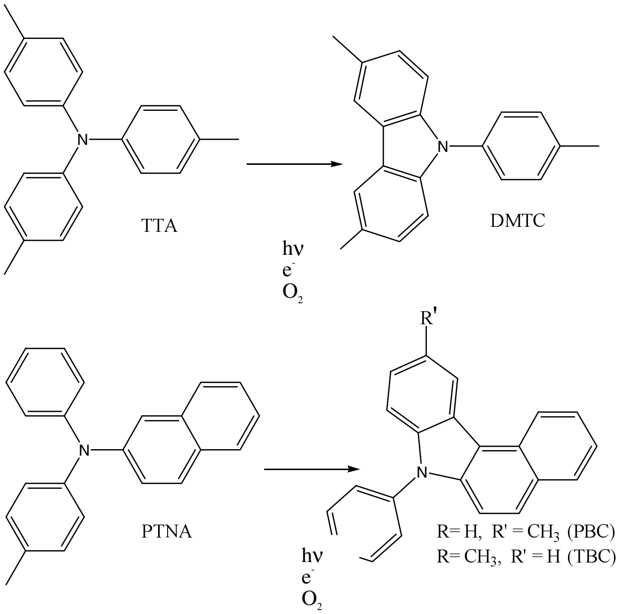

Figure 6 . Main processes and products of photoelectrochemical transformations of the OPCs.

Usually CTL of the drums that were used in a copier long time (or tested in a big amount of cycles “charging-exposition”) are visually colorless, but they can have a clearly fatigue effect (especially high values of V_R or DD).

And the exposition on these CTLs is not so large as used in present work.

Consequently investigation of minor “active” substances (and processes of their formation) that can cause fatigue of the CTLs must be continued.

Conclusion

The electrochemical and photoelectrochemical processes give the same main products of OPC’s molecules conversion as photochemical and thermal processes but in different amounts.

Cyclic fatique of investigated CTLs can be caused first of all by minor (including colored) products of the processes.

References

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Biography

Konstantin K. Kochelev graduated from the Novosibirsk's State University on the field of Chemistry in 1971.

In 1971 - 1980 he has researched polymer complexes in solutions in the Institute of Petroleum Chemistry of the Academy Sciences of the USSR. Since 1980 he researched and developed electrophotographic materials (films, plates, drums) at the Pereslavsky Filial of GOSNIIKHIMFOTO-PROECT (In 1996 converted in the NIFTI - Scientific Research Phototechnical Institute of the Company Slavich). Doctor of Chem. Sci., a member of the IS&T. ca. 150 patents and publications.