Photoelectrochemical Stability of Layered OPC Drums

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Abstract

Photoelectrochemical stability (to corona charging + light exposition), light 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 with drums of a type "Al-ITO-CGL-CTL". Charge generation layer (CGL) on the base of titanyl phthalocyanine (TiOPc) was used.

Products of photoelectrochemical and photochemical reactions of 4-diethylaminobenzaldehyde N,N-diphenylhydrazone (DEH) and triarylamines (TAA) in the layers were investigated with Gas Chromatography-Mass-Spectrometry (GC-MS), Thin Layer Chromatography (TLC) and UV-Vis spectroscopy.

It was shown that the photoelectrochemical processes in drums give the same main proucts of OPC's molecules conversion as photochemical processes in the films but in different amounts. An addition of a stabilizer - 2,3,5,6-Tetramethylpyrazine (TMP) leads to more stability of OPC molecules in CTLs and to decreasing of light absorption at wave lengths more than 410 nm These data confirm the earlier done supposition that the minor products with the light absorption at wave lengths more than 410 nm are the base products caused the OPC Drum cyclic fatigue.

Introduction

Photoelectrochemical stability of triarylamine (TAA) doped polymer film layers, electrophotographic and spectral properties of these layers have been investigated earlier[1]. It was shown[1] 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. It was supposed that cyclic fatique of the investigated triarylamine doped polycarbonate layers can be caused first of all by minor (including colored) products of the processes. It was interested to investigate more thoroughly these processes in layers on the base of different OPC's placed in OPC Drums and in corresponding films, and an influence on these processes of little amounts of a stabilizer - 2,3,5,6-Tetramethylpyrazine, tested earlier[2] as anti-fatique additive.

Experiment

The CGL was composed of a titanyl phthalocyanine pigment (TiOPc, ST10.10/2 of SynTec GmbH) dispersed (2:1) in polyvinylbutiral (PVB). The CTL was DEH, 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). The CTLs consisted of 0, 1, 3 or 6 wt% of TMP (Fluka, purum).

Electrophotographic characteristics of these drums were tested by usual way.[1,2]

The "corona charging+ light exposition" stability (cyclic stability) of samples were investigated by using a special rotate machine. Initial characteristics of OPC drum ($S_{1/2}$, V_R, $DD_{5\%}$) were determined. The rotating drum was then treated by light (Intensity was 8000 Lx /670 W/m^2). and corona discharge (at initial surface potential minus ca. 1000 V). After 10 000 revolutions (cycles) the electrophotographic characteristics were determined immediately. Finally, the drum was dark-rested for 24 hours and measurements were repeated. All measurements were carried out at room temperature.

Other samples of the OPC drums were placed too in modified cartridge and treated 150 000 cycles with corona (-1000 V) and light exposition (Halogen Lamp, 20000 Lx).

PET-ITO-CTL films with the same CTLs (30-40 microns) were treated with UV-Vis light (UV-Vis lamp, 130 W/cm2, 80 hours). Films were inserted in transparent watertight polyethylene bags and placed in a vessel with cooled water – to exclude an effect of CTL layers heating with the UV-Vis lamp.

Other samples of the OPC drums and PET-ITO-CTL films with the same composition were treated with sunlight (10 days).

Chemical composition of untreated and treated drums and films (OPCs and products of their decomposition in drums and in films) were determined by chromatographic methods. Quantitative GC-MS of volatile substances in TTA layers gives the initial TTA and small amounts of 3,6-Dimethyl-N-(4-methylphenyl)carbazole (DMTC), in the layers PTNA and DTNA no other volatile products were determined. Quantitative analysis of DEH layers by GC-MS is impossible because of DEH is present as broad decomposition peak (m/z = 169, diphenylamine (DPA). We have used TLC (“Armsorb KSKG UV-254”, $C_6H_5CH_3$ eluent) for quantitative analysis of DEH layers. The spots of DEH (R_f = 0.50) and 1-Phenyl-3-(4-diethylaminophenyl) indazole (IND) (R_f = 0.25) each were eluted from plates with 4 ml of ethanol and subjected to quantitative UV analysis (at 358 nm extinctions of both DEH and IND are approximately 23000). Also, traces of 1-Phenyl-3-(4-ethylaminophenyl)-indazole (EAIND) (Rf = 0.10) and of colored substances R_f = 0.00 – 0.01 were present. (PC-A, R_f = 0.00-0.01, makes analysis of these products impossible).

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

Results and Discussion

The “corona+light” stability (cyclic stability) of OPC Drum samples on the base of different OPC with and without addition of TMP are shown on Figures 1,2.

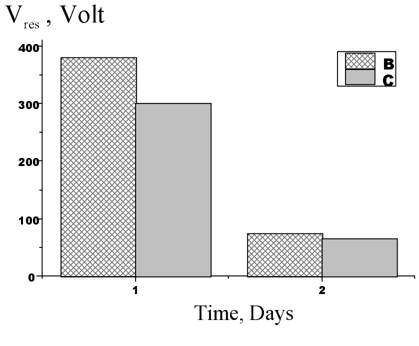

Figure 1. Residual potentials V_{res} for OPC Drums on the base of DEH without TMP (B) and with 1 wt.% TMP (C), immediately after 10 000 cycles (1) and after 24 hours (2).

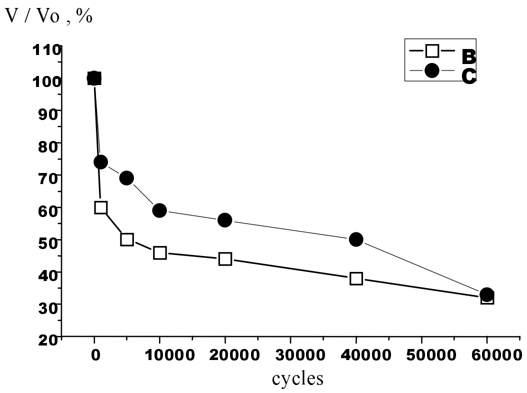

Figure 2. The surface charging potentials drop (%) vs amount of “charging - light exposition” cycles for OPC Drums on the base of TTA without TMP (B) and with 1% TMP (C).

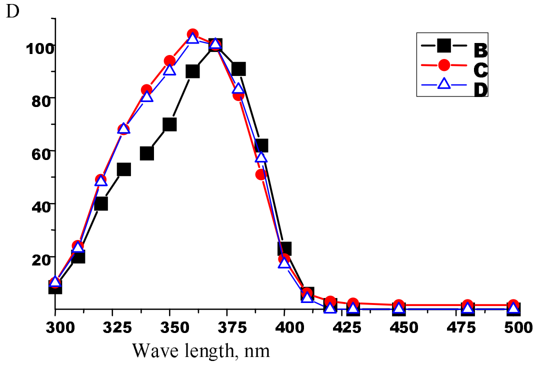

Figure 3. UV-Vis spectra of film’s CTL layers dissolved in 1,2-dichloroethane before (B) and after (C, D) UV-Vis exposition (80 hours, in water). CTLs are DEH+PC (B, C), DEH+PC+1% TMP (D).

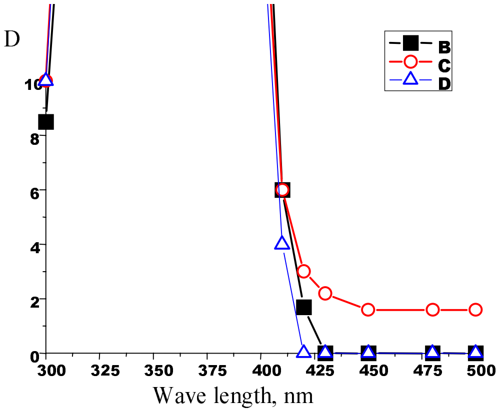

Figure 4. Spectra from the Figure 3, but at enlarged scale of D – in the range of D = 0 -10.

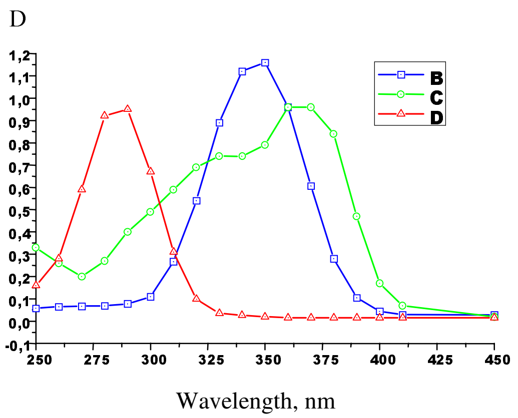

Figure 5. UV-Vis spectra of pure substances dissolved in 1,2-dicloroethane: B – IND, C – DEH, D -Diphenylamine DPA.

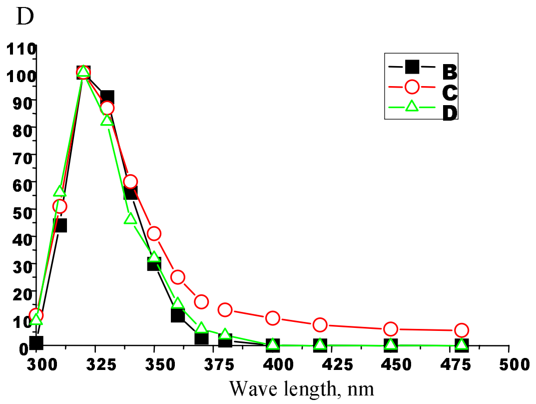

Figure 6. UV-Vis spectra of film's CTL layers dissolved in 1,2-dichloroethane before (B) and after (C, D) UV-Vis exposition (80 hours, in water). CTLs are TTA+PC (B, C), TTA+PC+1% TMP (D).

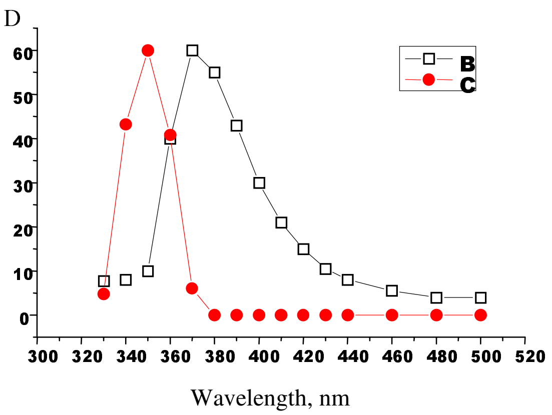

Figure 7. UV-Vis spectra of films with thin CTL (TTA+PC+1% TMP) before (B) and after (C) UV-Vis exposition (80 hours, in water). The spectrum C was obtained by subtraction of the spectrum B from the specrum of the identical film, but UV-Vis exposed (the date are only qualitative).

As shown in the pictures an addition of TMP leads to more slowly changes of surface charging potentials V_o and residual potentials V_{res}. In other words an addition of TMP slows the processes of weariness in investigated samples.

UV-Vis spectra of OPC (DEH, TTA) and products of their decomposition extracted from CTLs (in PET-ITO-CTL films) with 1,2-dichlorethane after acting on the films of UV-Vis light (80 hours) are shown in Fugures 3-7. As can be seen from the Figures 3-4, UV-Vis exposition of the investigated CTLs on the base of DEH leads to grows of optical density D values in the region 310-360 nm and at wave lengths more than 410 nm. As is shown in Figure 5 an absorbing of light in the region of 310-360 nm may be caused mainly by formation of IND,[1,2] the nature of substances absorbed light at wave lengths more than 410 nm are unknown.

Table 1. Chemical composition of initial OPCs and their products

OPC in CTL (OPC+PC-A, 1:1)	Method of threating	Composition of threated layer and method of analysis
TTA	Halogen lamp	100% TTA (GC-MS)
TTA	Sunlight	99.74% TTA, 0.26% DMTC (GC-MS)
98%TTA 2% TMP	Halogen lamp	100% TTA (GC-MS)
98% TTA 2% TMP	Sunlight	99.79% TTA, 0.21% DMTC (GC-MS)
PTNA	Halogen lamp	100% PTNA (GC-MS)
PTNA	Sunlight	100% PTNA (GC-MS)
DTNA	Halogen lamp	100% DTNA (GC-MS)
DTNA	Sunlight	100% DTNA (GC-MS)
DEH	Halogen lamp	96.73% DEH 3.27% IND traces EAIND traces products $R_f < 0.01$ (TLC-UV)
DEH	Sunlight	54% DEH 46% IND traces EAIND traces products $R_f < 0.01$ (TLC-UV)
98% DEH 2% TMP	Halogen lamp	99.17% DEH 0.83% IND traces EAIND traces products $R_f < 0.01$ (TLC-UV)
98% DEH 2% TMP	Sunlight	57.5% DEH 42.5% IND traces EAIND traces products $R_f < 0.01$ (TLC-UV)

UV-Vis spectra of CTL layers on the base of TTA are shown in Figures 6,7. The nature of substances absorbed light at wave lengths more than 410 nm are unknown too. These results confirms earlier obtained data[1,2].

Chemical composition of initial OPC, OPC and products of its decomposition in drums and in were determined by GC-MS or TLC-UV and these data are given in Table 1.

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

As is resulting from received data the main processes of photoelectrochemical and light transformations of the OPC's molecules are shown in Figure 6 of paper[1]. As shown in the paper and confirmed in this investigation the OPC molecules undergo oxidative cyclization with different effectiveness. In controlled conditions (337 nm, 10 ns light pulse) only cyclisation of DEH to IND and EAIND occured with continuous decreasing of photoconductivity[3]. In the conditions similar to these in real work of drums, when broad range of UV light acts on a layers of drums the processes with formation of other products absorbing at more than 410 nm occurs too.

Addition of a stabilizer – in this case TMP - leads to more stability of OPC molecules in CTLs and to decreasing of light absorption at wave lengths more than 410 nm. These data can to confirm the supposition[1] that the products with the light absorption at wave lengths more than 410 nm are the base products caused the OPC Drum cyclic fatigue.

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

Conclusion

The photoelectrochemical processes in drums give the same main proucts of OPC's molecules conversion as photochemical processes in the films but in different amounts. An addition of a stabilizer - 2,3,5,6-Tetramethylpyrazine leads to more stability of OPC molecules in CTLs and to decreasing of light absorption at wave lengths more than 410 nm. These data confirm the supposition[1] that the minor products with the light absorption at wave lengths more than 410 nm are the base products caused the OPC Drum cyclic fatigue.

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. 160 publications and patents.