

Cyclic Stability and Electrophotographic Properties of OPC doped Polycarbonate

*Konstantin K. Kochelev, Vladimir N. Bulavka, Olga K. Kocheleva,
Vladimir E. Golovin, Galina A. Kocheleva
NIFTI-Slavich (Scientific Research Phototechnical Institute on Slavich Co.)
Box 34 Pereslavl-Zalessky-5, 152025, RUSSIA, nifti@slavich.ru*

Abstract

Cyclic stability (to corona charging, to light or to the both of these factors), electrophotographic and spectral properties of charge transport layers (CTL) have been measured. The CTL used were the various OPC (triaryl-amines, hydrazones) doped polycarbonates of different types with and without cyclic stabilizers. The influence of OPC and stabilizer structures and possible mechanisms of cyclic durability of CTL have been investigated and discussed. It has been found that cyclic stability of the CTL can be essentially increased by addition of some stabilizers to the CTL.

Introduction

Our previous papers^{1,2} reported on electrophotographic and hole transport properties of polycarbonates PC doped with organic photoconductors OPC and their light- and corona discharge stabilization. Effect of corona discharge and light intensities on electrophotographic characteristic of phenyl-4-tolyl-2-naphtylamine (PTNA) and 4-diethylamino-benzaldehyde-diphenylhydrazone (DEH) doped PC systems was studied. It was shown¹ that the effect of corona or of light (separately) on values of residual potential V_R and sensitivity $S_{1/2}$ increases considerably with increasing of both light, and corona intensities. The total effect of corona and light on these values greatly depends on intensity of a corona, and especially greatly - on light intensity. The residual potential and dark decay DD values (measured at once and after dark resting) vary more under the simultaneous action of both corona discharge and exposure, than under the action of each factor by individually. The previous investigations^{1,2} have also shown that a simultaneous use of antioxidants in both charge generating layer (CGL) and charge transporting layer (CTL) allows to increase sharply cyclic stability of drums to cycle "charging-exposition". That is, both of functional layers were responsible for a cyclic fatigue of a drum. Various types of light-, ozone- and corona discharge stabilizers and other additives in a charge transporting layer (CTL) and/or a charge generating layer (CGL) were used in the previous works^{1,2}. In a number of papers it was supposed, that the reason of a fatigue of CTL

is the photooxidation (especially UV-component of light)³ or oxidation of OPC in CTL by products of corona (ozone, nitrogen oxides, etc.)^{4,5}. In order to prevent above-mentioned harmful influences, in a number of the patents electron accepting compounds, hindered phenols or amines were added into a CGL⁶⁻⁸. However, the mechanism, which is responsible for the cyclic fatigue of the drums, has not been determined with certainty. To clarify influence of processes taking place mainly in CTL on a cyclic fatigue of drums the effective stabilizers was entered only into CGL, but CTL was used without stabilizers². The investigation of light-, corona- and light + corona influence on electrophotographic characteristics of OPC Drums with stabilized CGL and nonstabilized CTL have demonstrated, that a simultaneous effect of light and corona on CTL promotes a large reversible and irreversible fatigue of drums. The effect of wavelength of light on the characteristics of drums after cycle "charging-exposition" has been determined too. It was shown that an active part of a spectrum (300-440 nm), which is greatly absorbed by molecules of OPC, affected on the CTL especially effectively. It have been conditioned by photochemical reactions of monocation radicals and bication of OPC molecules, for example between oneself or between radical and neutral OPC molecule or with impurities involved in CTL. Such impurities and products of their reactions with radicals can operate as different types of traps for charge carriers, which can influence on CTL characteristics. It means that the nature of OPC molecules and methods of their purification must influence strongly on cyclic stability too. The observable facts were explained by existence of chemical reactions of photoexcited monocation radicals (B^{*+})* of OPC. These photoexcited monocation radicals can have reversible or irreversible interactions with the impurities or/and to couple between oneself. Some differences in behavior of investigated OPC (greater or smaller changes of values of V_R or DD, etc.) are possibly explained by existence of various types and amounts of impurities in CTL and also by influence of a chemical structure of the OPC. At present the most of produced Drums are Drums for Laser Printers, where triarylamine photoconductors (TPD and so on) are usually used. In this case the investigation of CTL on the base of triarylmines doped PC is topical problem.

Experimental

Samples studied by electrophotographic method consisted of an Al substrate, a barrier-adhesion layer of 0.8-1.2 microns thick, a generation layer of 0.3-1.0 microns thick, and a transport layer of 30-35 microns thick. Barrier-adhesion layer was cast from a solution of a polyamide (PA 6/66/610). The CGL was composed of a titanium phthalocyanine pigment (TiOPc, ST10.10/2 of SynTec GmbH) dispersed in copolymer vinylchloride and vinylacetate VAGH (Du PONT de NEMUR) or bisazo pigment (ST 1017 of SynTec GmbH) dispersed in polyvinylbutyral PVB (2:1). The layers were prepared by a dip coating method.

PTNA, Tris(p-tolyl)amine (TTA), Di(4-tolyl)-1-naphthylamine (DTNA), Phenyl-p-anisyl-1-naphthylamine (PANA), Di(p-tolyl)-(2,4-dimethylphenyl)amine (DTXA) were produced by Ullmann coupling of the appropriate diarylamines with corresponding aryl halogenides and refined by column elution chromatography. The structures and purity of the compounds were confirmed by GC-MS, ¹H and ¹³C NMR spectra. TPD (ST 16/1.2 of SynTec GmbH) was used without purification. Stabilizer S1 is Irganox 565 (Ciba-Geigy), S2 – 2,3,5,6-Tetramethyl-pyrazine (Fluka, purum), S3 – Difluoroboron-1-methyl-3-(4-amyphenyl)-1,3-propanedionate (PF-351 of NIFTI-Slavich). Polycarbonates PC-A are PC-1 and PC-3 (PO "Zarya", Russia)^{1,2}. Sensitivity $S_{1/2}$ (lx·s)⁻¹ for halogen lamp ($T_{color} = 2850$ K) was given by exposure $E_{1/2}$ required to reduce the corona charged surface potential to halfvalue, $S_{1/2} = 1/E_{1/2}$. Dark decay DD was determined by a decrease of the initial surface potential after left in the dark (% for 5 seconds). Residual potential V_R was determined by a surface potential after exposure $10 \times E_{1/2}$.

The "corona+light" stability (cyclic stability) of samples was 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 3000 Lx /250 W/m² or 8000 Lx /670 W/m²) and corona discharge (at initial surface potential minus ca.1000 V). After 5 000, 15 000 or 30 000 revolutions (cycles "corona+light") 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.

Drum of type I has ST-1017 + PVB (2:1) + phenozone-28 (5 wt.%) in a CGL; and OPC + PC-3 +PC-1 (1: 0.5: 0.5) in a CTL. Drum of type II has TiOPc +VAGH (2:1) + phenozone-28 (5 wt.%) in a CGL; and OPC + PC-3 +PC-1 (1: 0.5: 0.5) in a CTL. Drum of type III is the Drum of type I where stabilizer S (1 weight % to the sum of solid components) was added into a CTL.

Results and Discussion

On the base of the obtained results we have supposed², that the fatigue of CTL is connected mainly with holes drifting in CTL, i. e., with a following reaction (1):



where B and B₁ - neutral molecules of OPC, and B⁺, B₁⁺ - their monocation radicals.

In that case we can say that a fatigue of charge-generating material and a charge-transporting material is mainly due to a photoelectric current passing repeatedly through the photosensitive layer. In this case the processes in CGL and CTL are similar to ones carrying out in electrochemical systems during electrochemical oxidation.

Processes of electrochemical oxidation of triarylamines TAA were well investigated by some authors earlier⁹⁻¹³.

It is known that electrochemical oxidation of non-substituted and substituted tertiary aromatic amines TAA goes through some stages⁹⁻¹⁰. Non-substituted TAA, for example triphenylamine TPA is oxidized at ca. +0,90 V vs SCE to an unstable monocation radical TPA^{•+} (Stage 1). The cation dimerizes (couples) or reacts with parent rapidly to form tetraphenylbenzidine TPB (Stage 2). TPB is more easily oxidized than TPA and undergoes further oxidation under the applied potential to give the monocation radical TPB^{•+} (Stage 3) and finally to quinoidal bication TPB²⁺.

Then the monocation radicals (for example TPA^{•+}) can turn into bication TPA²⁺ (Stage 4) and then they can dimerize into quinoidal bication TPB²⁺ (Stage 5).

Relative stability of monocation radicals of substituted TAA is very different⁹. For example tris(para-substituted) compounds give very stable monocation radicals in MeCN. p-Benzidine formation cannot obviously take place without some group elimination. We might expect a statistically predictable inhibition of coupling by blocking of one or two of the p-aryl positions with some functional group. In addition it was found¹⁰ that effect of substituents cannot be ignored too. Thus tris(p-anisyl)amine and tris(p-tolyl)amine give very stable monocation radicals (and their EPR spectra showed practically no intensity decrease with time); 4-methoxytriphenylamine gives quite stable radical; but 4-nitro-triphenylamine and 4,4'-dinitro-triphenylamine give highly unstable radicals. Thus p-methoxy and methyl groups are highly "stabilizing" but Nitro group is highly "destabilizing" and promotes coupling. Coupling rates of mono-para-substituted TPAs are given in Table 1¹¹.

The rate constants of dimer cations formation of triphenylamines and effect of substituents are studied by pulse radiolysis. Rate constants of dimerization were estimated and given in Table 2¹².

Furthermore tris-para-substituted TAAs have very stable cation radicals. They are neither cyclize nor couple at detectable rates. But when these molecules are oxidized into the bications, rapid decomposition was found to occur by a number of different pathways (for example they can react with impurities).

It has been found¹³ also that para-substituted triphenylamines Ar₃N and diphenylamines can cyclize to form the corresponding carbazoles TAC (Figure 1).

The reaction occurs through the bication Ar₃N²⁺ and will take place only if the cation radical is stable. The similar reactions occur during the photochemical process, and a

comparison between the two pathways has been made. The second anodic process is seen to be irreversible.

Table 1. Coupling rates of mono-para-substituted triphenylamines.

Substituted triphenylamines	Coupling rates, k, liter per mole per second
R-Ph ₃ N, R =	
C ₆ H ₄ OMe	1.0
C ₆ H ₄ Ph	4.63×10^1
C ₆ H ₄ Me	1.46×10^2
C ₆ H ₄ Cl	9.6×10^2
C ₆ H ₄ (TPA)	2.4×10^3
C ₆ H ₄ NO ₂	1.3×10^4

Table 2. Rate constants of dimer cation formation of substituted triphenylamines in 1,2-dichloroethane.

Substituted triphenylamines	Coupling rates, k, liter per mole per second
TPA	13
2-Me-TPA	2.7
Tri-o-tolylamine	2.1
3-Me-TPA	4.7
Tri-m-tolylamine	3.2
4-Me-TPA	2.2
4,4'-diMe-TPA	0.63
Tri-p-tolylamine	Difficult to measure

There are may be other decomposition pathways competing with the intramolecular cyclization, for example hydrolysis and substituent elimination. Products distribution for arylamine bications in CH₃CN are shown in Table 3¹³.

Table 3. Product distribution for Arylamine dications.

Substituted triphenylamines	Carbazole formed:	Other products
Tris(p-anisyl) amine	+*	Some hydrolysis occurs
Tris(p-tolyl) amine	++	
Tris(p-chlorophenyl) amine	+	Tetrakis(p-chlorophenyl)benzidine
Tris(p-cyanophenyl) amine	++	

* - “+” represents a relatively higher yield than a “+”.

Electrochemical studies have shown¹³, that only tertiary aromatic amines with aromatic rings substituted at least with one alkyl group in para positions can be cyclized during the electrochemical reactions. These substituents must not be susceptible to substitution or elimination.

Furthermore substituted triphenylamines, for example tris(p-tolyl)amine can react with active oxygen to give N-oxides of amines (aminoxides). TPA in this situation gives only TPB¹⁴.

In accordance with the above mentioned data we can suppose that TAA can give a stable monocation radicals and biradicals, when:

a) All aromatic rings of TAA must be substituted in para positions by alkyl or/and alkoxy groups (to prevent of benzidines formation; and for elimination of reactions with active para positions);

b) At least one of the aromatic ring must be naphthyl group or 2,4- substituted phenyl group (to prevent of carbazoles formation; and for further stabilization of cations by a delocalization of electronic shells; and to complicate the aminoxides formation).

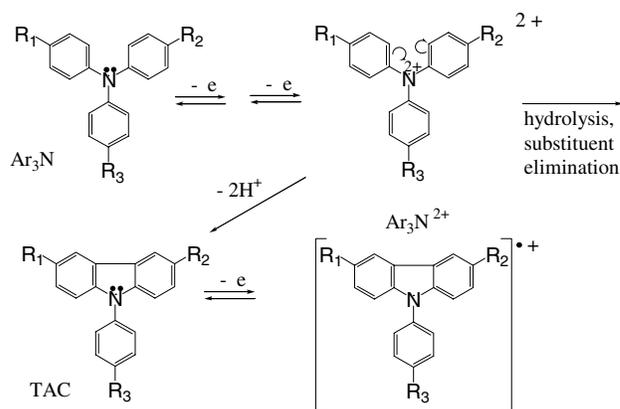


Figure 1. The reaction of cyclization of para-substituted triphenylamines Ar₃N.

The substances of such types doped in PC must really give CTLs with good cyclic stability. The obtained results are shown in Table 4.

As shown in Table 4 the cyclic stability of investigated drums is increased in the lines:

- Drum of type II: a) TTA – PTNA – DTXA – TPD – DTNA; b) PTNA – PANA – TPD – DTNA;

- Drum of type I: a) TTA – DTXA – PTNA – TPD – DTNA; b) PTNA – PANA – TPD – DTNA;

Thus the obtained results confirm well the supposition of the possible cyclic stability of substituted triarylamines. So tris-para- substitution of TAA by methyl or by methyl plus methoxy groups prevents monocations coupling. There is correlation between the cyclic stability of CTLs (Table 4) and the stability of monocation radicals (Tables 1,2). Additional ortho-methyl substitution of tris-para-substituted TAA or replacement of phenyl group by naphthyl or para-substituted diphenyl group can complicate carbazoles formation and reactions with impurities too. The combination of all these factors give a good results, since DTNA and TPD doped PC layers have a very good cyclic stability.

As it was shown previously^{1,2}, the adding of stabilizers - hindered phenols or electron acceptors into CTL allows to improve significantly the cyclic stability of drums. Molecules of stabilizers can interact on the following lines:

a) With impurities, reducing their reactivity;

b) With OPC molecules (B) or/and with their cation radicals B^{*+} ; or with molecules B and their cation radicals in photoexcited (*) forms B^* , $(B^*)^*$; or with biradicals (B^{++}) - facilitating their relaxation or/and complicating their reactions with impurities and between oneself too.

Table 4. The cyclic stability of OPC Drums of types I, II and III. Residual potentials V_R^0 , V_R^I , V_R^R and dark decays (% for 5 sec) DD^0 , DD^I , DD^R - were initial, immediately after 5000, 15000 or 30000 cycles of "charging-exposition" and after dark-resting for 24 hours correspondingly.

OPC	$V_R^I - V_R^0$	$V_R^R - V_R^0$	DD^0	DD^I	DD^R
Drum of type I, 15 000 cycles, 8 000 Lx					
TPA	No sensitivity				
TTA	360	100	1	2	3
DTXA	120	75	1	1	1
PTNA	325	110	5	7	6
DTNA	15	10	3	6	3
TPD	0	0	27	89	32
Drum of type III, 15 000 cycles, 8 000 Lx					
PTNA	325	110	5	7	6
PTNA+S1	115	80	1	2	2
PTNA+S2	50	30	2	2	2
PTNA+S3	0	0	1	1	1
Drum of type II, 5 000 cycles, 8 000 Lx					
TPA	No sensitivity				
TTA	105	30	4	6	2
DTXA	85	25	2	6	6
PTNA	20	10	5	10	4
DTNA	0	0	6	13	6
TPD	0	0	21	90	22
Drum of type I, 30 000 cycles, 3 000 Lx					
PTNA	160	90	16	20	20
PANA	115	50	14	39	18
DTNA	0	0	9	35	16
TPD	0	0	11	46	20
Drum of type II, 5 000 cycles, 3 000 Lx					
PTNA	70	35	1	2	0
PANA	10	10	2	2	2
DTNA	0	0	3	2	2
TPD	5	0	11	28	31

Really (Table 4, Drums of type III) stabilizer S3 (electron acceptor which forms charge-transfer complex with PTNA in solution) is better than stabilizers S1 and S2 (antioxidants which don't form the complexes) and gives CTLs with good cyclic stability.

Thus the obtained data of cyclic stability of CTL with and without stabilizers confirm the conclusion that the main factor of CTL fatigue for investigated OPC is electrochemical reactions in CTL (and CGL too) when charge carriers passed through the Layers.

Conclusions

As it was concluded, a fatigue of charge-generating material and a charge-transporting material is mainly due to a photoelectric current passing repeatedly through the photosensitive layer. The processes in CGL and CTL are similar to ones carrying out in electrochemical systems during electrochemical oxidation. Polycarbonate doped with triarylamines TAA can give a CTL with a good cyclic stability, when: all aromatic rings of TAA are substituted in para-positions by alkyl or/and alkoxy groups; at least one of the aromatic ring must be naphthyl group or 2,4-substituted phenyl group. The cyclic stability of the CTL can be increased essentially by addition of some stabilizers – electron acceptors to the CTL. The mechanism of stabilization by such substances has not been determined with certainty and requires further investigations.

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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. Member of the IS&T. ca 150 patents and publications.