

# Physical and Chemical Aspects of Glow Discharge Reaction on Synthetic Fibers

YU. I. MITCHENKO, V. A. FENIN, and A. S. CHEGOLYA,  
*Institute for Synthetic Fiber, Kalinin, USSR*

## Synopsis

Polyethylene terephthalate (PET), polypropylene (PP), polyamide fibres, and films have been discharge treated. The resulting surface modifications analysed via ESR, IR, UV contact angle measurements. Discharge treatment introduces radicals and OH groups into the surface. But it does not correlate with wettability. Discharge treatment also produces the changes in conformation of macromolecules and roughness. This process is largely responsible for the wettability.

## INTRODUCTION

Glow discharge treatment of polymers brings along changes in a number of very important properties such as: wettability, friction factor, adhesion, adherence, etc. A number of papers describe polymer properties after glow discharge treatment.<sup>1,2</sup> At the same time the complexity of physico-chemical processes taking place when the glow discharge interacts with polymer surface, up to now does not allow to give a unique interpretation of such property changes. The most frequently applied cause of changes in polymer properties, for instance hydrophilicity, is the change in polymer chemical structure.<sup>3</sup> However the unique relation cannot be considered established.

The aim of this paper is to analyse the relationship between the changes in different physico-chemical characteristics of polymer surface and polymer properties. As hydrophilicity is to be considered the most important property of synthetic polymers, attention will be drawn to this very feature.

## EXPERIMENTAL PART

Polycaproamide (PCA), polyethylene terephthalate (PET), polypropylene (PP) fibers and films were treated with glow discharge in argon, helium, hydrogen, oxygen, ammonia, and residual air. The samples were treated with operating gas under pressure (130–65 Pa) and using electrical field generator with frequency 40.6 MHz. Electronic microphotographs were received using scanning microscope ISM-50 A, IR spectra, disturbance of total internal reflection, and transmission were received by means of spectrometer UR-20, electronic paramagnetic resonance spectra—by means of spectrometer with wave length 3.2 cm, ultraviolet spectra—using the “Specord” instrument.

## RESULTS AND DISCUSSION

The effect of glow discharge upon materials made of synthetic polymers brings along sharp surface changes, transition of it from hydrophobic to hydrophilic. The changes in drop spreading time, moisture flow value before and after discharge are shown in Table I.

One can see from the table that the sharp changing characteristic is moisture transition rate.<sup>4</sup> The treatments leads to velocity increase of summary flow and flow, providing two-three order imbibition, the values of which are near the results corresponding to fabrics made of natural fibers.

Glow discharge treatment also brings along the changes in morphological structure of fiber surface. Originally flat surface acquires particularly expressed structure. Such changes were observed in a number of papers.<sup>2,4</sup> It is necessary to mention that the observed morphological structure is not the reflection of its own supermolecular organization characteristic for fibers.

However the above changes are the outer display of various physico-chemical processes taking place when glow discharge active components interact with polymer surface. It seems that the most important among these processes are the following: radical formation process, changes in polymer chemical structure and physical modification of the surface.

## RADICAL FORMATION

Radical formation is investigated for polymers with different chemical structure, containing no stabilizers. Glow discharge brings along the formation of free radicals, which are registered by electron paramagnetic resonance EPR spectroscopy in all polymers under discussion. Spectrum shapes of EPR-radicals formed with 77° and 293° K discharge are identical. The parameters of observed EPR-spectra for PCA, PP, PET correspond to radical spectra which were identified earlier by means of mechanical and photo polymer degradation.<sup>5,6</sup>

Figure 1 shows EPR signal intensity changes depending on time from the starting moment of discharge in absence of air at temperature 293°K. It is seen

TABLE I  
Moisture Transfer Characteristics

The type of fibre	The height of water rise (cm)	Drop spreading time (sec)	Water flow velocity (g/sec mm <sup>2</sup> )		
			Total	Absorption	Evaporation
1. PP					
Initial	0	1800	$7 \cdot 10^{-7}$	0	$7 \cdot 10^{-7}$
After discharge treatment	10-12	30-5	$(3-15) \cdot 10^{-5}$	$(1.8-7.2) \cdot 10^{-5}$	$(1.7-4.5) \cdot 10^{-5}$
2. PEF					
Initial	0.5	1800	$2 \cdot 10^{-6}$	$3 \cdot 10^{-7}$	$(2-5) \cdot 10^{-5}$
After discharge treatment	17-20	1800	$(1-3) \cdot 10^{-3}$	$(9-40) \cdot 10^{-4}$	$1 \cdot 10^{-6}$
3. Cotton	7.0	20-40	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$0.8 \cdot 10^{-4}$

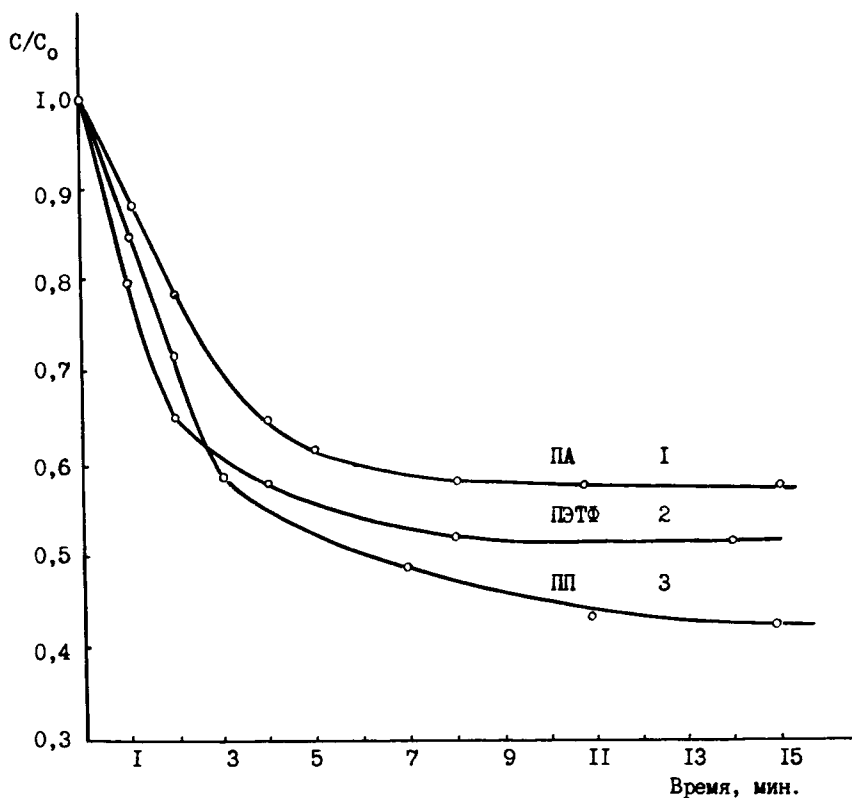


Fig. 1. The relationship of relative radical concentration and time after discharge switching off.

on the plots that 40–60% of originally registered radicals have not been destroyed for several hours which is characteristic for radicals with restricted kinetic mobility. Radical stabilisation in certain polymer volume is verified by the fact that oxygen leak-in into the reactor at 77°K brings no changes either in character or intensity of EPR signal. The important feature of radical formation process is fast radical destruction on the surface and their stabilisation in polymer depth.

Thus radical formation is unlikely to change the chemical structure of polymer surface considerably after discharge treatment.

### CHEMICAL CHANGES DURING THE TREATMENT

Chemical transformations in polymer surface were registered by IR spectroscopy of different polymers after discharge treatment. Intensity changes were observed for 940, 1020, 1730, and 1640  $\text{cm}^{-1}$ , 1000  $\text{cm}^{-1}$ , 1170  $\text{cm}^{-1}$  bands. Evaluation of chemical changes in polymer depth based on transmission spectra showed that there is no 1020  $\text{cm}^{-1}$  bands in the spectrum, and the intensity of 940  $\text{cm}^{-1}$  bands is not changed. These bands correspond to conventional<sup>7</sup> and

illustrate formation of oxygen containing groups, double links, etc. Such measurements can be observed for PAN, PET.

Conformational changes were studied on the basis of PET with different original structure (Table II). In accordance with the results of the work<sup>8</sup> the following conformers were discussed:

- T<sub>1</sub>—838 cm<sup>-1</sup> band trans-conformation in irregular amorphous zone;
- T<sub>2</sub>—846 cm<sup>-1</sup> band trans-conformation in the zone of uni- and two-dimensional orders;
- T<sub>3</sub>—853 cm<sup>-1</sup> band trans-conformation in crystallites.

Treatment in discharge leads to the gosh-conformers number increase. Major changes for trans-conformers can be observed in T<sub>1</sub> and T<sub>2</sub>, trans-conformation in crystallites being the same. That means that the least regular polymer zones are influenced.

It seems that the combination of these results allows to consider surface chemical changes in discharge to improve wetting property of the materials. Actually wetting contact angles and water drop spreading time changed sharply after the discharge (Table III).

A number of additional experiments were carried out in order to clarify the role of chemical changes in wetting change process.

PP film was exposed to thermal oxidation. IR spectra of disturbance of total Inter Reflection show that such film similar to that after discharge treatment has 1650, 1730, and 940 cm<sup>-1</sup> bands. Thus the same chemical groups are present in the polymer in approximately the same amount as after discharge treatment. However water drop spreading time is 3000–3600 sec.

Thermal and oxidative influences are accurately registered by their UV-spectra. Figure 2 illustrates the changes in wetting angle and intensity of UV-

TABLE II  
Conformer Composition in PET Films After Discharge Treatment

The kind of specimen	Conformer	Initial		After discharge treatment	
			After washing		After washing
Nonoriented	T <sub>1</sub>	19	18	7	19
	T <sub>2</sub>	7	8	14	10
	T <sub>3</sub>	4	4	4	5
After heating at 433°K in vacuum		70	70	75	66
	T <sub>1</sub>	18	18	7	11
	T <sub>2</sub>	43	42	45	48
	T <sub>3</sub>	10	11	10	10
Biaxially oriented		29	29	38	31
	T <sub>1</sub>	12	11	13	15
	T <sub>2</sub>	60	61	55	60
	T <sub>3</sub>	6	6	6	8
		22	22	26	17

TABLE III  
Wettability Changes After Discharge Treatment

The kind of polymer	Initial		After treatment		After washing	
	Wetting time (sec)	Contact angle (deg)	Wetting time (sec)	Contact angle (deg)	Wetting time (sec)	Contact angle (deg)
Polypropylene	3600	81	1	33	120	72
Polyethylene terephthalate	3600	70	1	25	90	51

absorption at 200 nm frequency for samples treated with discharge at different periods. On the figure one can see that wetting angle reduction accompanies UV-absorption intensity increase caused by chemical transformations in the polymer.

At the same time, it turns out that sharp increase of the wetting contact angle along with stable UV-absorption intensity is highly relevant for the polymer under water treatments. The increase of wetting contact angle under water treatments is a characteristic feature for all polymers under discussion.\*

It's obvious that the effect of wetting angle increase under water treatments by itself is an evidence of impossibility in this very situation to relate wetting to stable chemical transformations of polymer molecules. Created stable chemical transformations, as for example, during postpolymerization<sup>9,10</sup> will not change under water treatment.

Thus, regardless of the stable chemical polymer structure the wetting angle is changed, that means that not only alterations in chemical structure influence its value.

It was noted earlier that glow discharge alters the morphological structure of polymer surface. Basing on some papers<sup>11,12</sup> we can say that roughness increase can also lead to drop spreading time reduction. A number of polymers (PET, PP) were subjected to mechanical and chemical etching, that created a certain morphological structure (Fig. 2). Nevertheless wetting contact angle measurements show that these treatment have not changed contact angle value considerably.

Consequently we can assume that chemical and morphological (roughness creation) changes are not the main reason of sharp decrease in the value of wetting contact angle.

At the same time intensity changes in IR bands, 1000, and 1170  $\text{cm}^{-1}$ , observed in PP, which are not connected with some new chemical groups and belong to conformational features of the chain allow to assume that conformational condition of macromolecules in surface polymer layer is altered considerably under glow discharge. The changes of conformational characteristics are highly illustrative in PET.

Results listed in Table II, show the increase of gosh-conformers under glow discharge, that is molecule coiling. It seems natural to assume that molecule

\* Water treatment was executed by exposing the sample into distilled water for 10 min with subsequent drying.

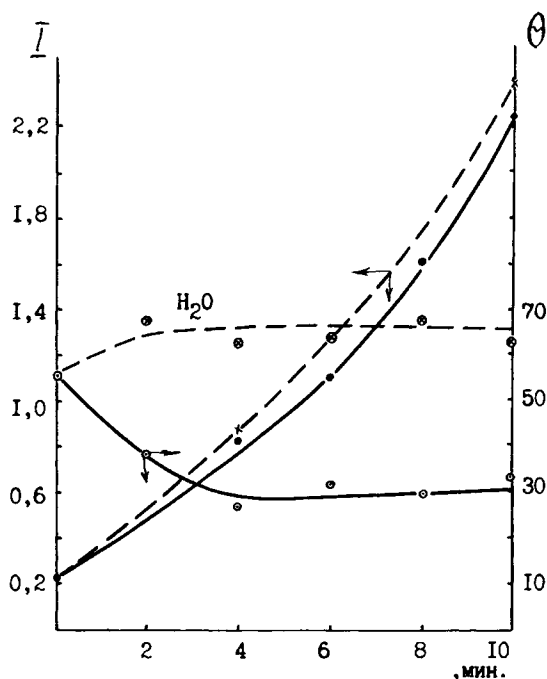


Fig. 2. Change of UV radiation intensity ( $I$ ) and contact wetting angle ( $\theta$ ) in relation to glow discharge time (immediately after treatment —), (after washing ----).

coiling is a consequence of structure changes in surface layer (i.e., its loosening). In good correspondence with this assumption are the results received during the study of water reaction on polymer films. If in original PET films water treatment causes no changes in conformational structure, then in samples after glow discharge treatment the decrease in gosh-conformers and increase in trans-conformers is clearly seen. That means that when evaporating water from samples after glow discharge treatment reverse conformational transformation takes place.

Thus we should assume that as a result of glow discharge the surface polymer layer is loosened a well developed microcapillar system is created in it. Water penetrates into such microcapillars and this is the cause of its higher spreading rate and higher rise level. After drying because of high surface tension, which is characteristic of water, the system contracts considerably causing the enclosure of most microcapillars; it means that the system returns to the condition, next to its original one. Changes of chemical structure observed in this situation are secondary auxiliary processes.

### References

1. A. T. Bell and I. R. Hollahan, *Techniques and Applications of Plasma Chemistry*, New York, Wiley Intersc., 1974.
2. W. Rakowski and M. Okoniewski, *Lenziger Berichte*, **47**(5), 174, (1979).
3. A. P. Stenwshin, V. I. Yakutin, and S. S. Vlasov, *Vysokomol. Soedin., Ser. B*, **11**, 866 (1976).

4. Yu. I. Mitchenko, A. G. Tarasova, V. V. Krylova, S. A. Kukushkina, and A. S. Chegolya, *Khimicheskie Volokna*, **4**, 34, (1982).
5. V. A. Roginski, E. A. Shanina, S. P. Yarkov, and V. B. Miller, *Vysokom. Soedin. ser. A.*, **24**, 1241.
6. F. Szöcs, I. Becht, and H. Fisher, *European Polym. J.*, **7**, 173, (1971).
7. I. Dechant, R. Danz, W. Kimmer, and R. Schmolka, *Ultrarotspektroskopische Untersuchungen an Polymeren*, Akademie—Verlag, Berlin, 1972.
8. S. A. Baranova, *Vysokomol. Soedin., Ser. B.*, **23**, 104, (1981).
9. D. A. Kritskaya, A. D. Pomogailo, A. N. Ponomarev, and F. S. Dyaschkovskii, *J. Appl. Polym. Sci.*, **25**, 349, (1980).
10. N. A. Plate, E. D. Alieva, and A. A. Kalachev, *Vusokomolec. Soedin., Ser. A.*, **23**, 640 (1981).
11. A. A. Berlin and V. E. Vasin, *Osnovy Adgesii Polymerov*, M. Khimiya, 1974.
12. B. D. Summ and Yu. V. Gorunov, *Physiko-Khimicheskie Osnovy Smachivaniya i Rastekaniya*, M. Khimiya, 1976, p. 73.

Received April 17, 1989

Accepted November 6, 1989