

ACTIVATION OF THE SURFACE OF POLYMER HEAT-SEALABLE MATERIALS IN CORONA-DISCHARGE PLASMA TO ENHANCE ADHESION PROPERTIES AND PRINT QUALITY

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Annotation

The article presents materials on methods for activating the surface of polymers in order to increase their surface energy and adhesion, which leads to a significant improvement in the quality of the printed image. The corona-discharge treatment method is the most widely used in industry and consists in bombarding the polymer surface with free atoms, radicals, and electrons, which results in the cleavage of covalent bonds and the scission of polymer macromolecular chains with the formation of numerous open bonds as well as free valencies. It has been established that printable polymer films (polyethylene, polypropylene) treated with corona discharge at voltages of 10 and 12 kV acquire sufficient hydrophilic properties and exhibit a substantial increase in wettability, thereby predetermining high print quality with uniform distribution of the ink layer on the print.

Keywords

Polymer, adhesion, activation, corona discharge, film, polyethylene, polypropylene, ink, voltage.

Introduction. An important component of the rapid growth of the global economy in various industrial sectors (food, pharmaceutical, cosmetic) is the intensive development of the packaging industry, whose products perform a set of critical functions: protecting goods from external influences; ensuring reliable conditions for storage and transportation; providing consumers with the necessary information; creating product competitiveness through its appearance and, consequently, facilitating the processes of distribution and sale; addressing environmental challenges related to protecting the environment from pollution.

The rapid growth and continuous improvement of packaging technology [1–3] are based not only on the use of modern composite materials instead of traditional ones (paper, cardboard, fabric, etc.) and on new structures (monolayer, multilayer, metallized, etc.), but also on advances in printing technologies used in packaging production. At present, in the printing industry, oriented and non-oriented

polymer materials in the form of thin films are widely used for printing on packaging substrates, including polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and others. Oriented polymer materials obtained by stretching in one or two directions exhibit increased strength and elasticity due to molecular orientation.

To fulfil their informational function, modern packaging materials must be compatible with printing processes and ensure the production of high-quality prints. However, polymer materials such as PE, PP, PET, and others, when used as printable substrates, are non-absorbent, which requires a specific technological approach to ensure proper ink receptivity during printing. The main challenge in printing on polymer films is the accurate transfer of graphic and textual information onto the surface of the printable material without distortion, while meeting the requirements for precise tonal and colour gradations.

To improve adhesion properties of polymer materials, activation of their surface layers is performed by special surface treatment [4,5], leading to an increase in wettability and the ability to retain printing ink. Adhesion largely depends on the polymer surface structure and its free energy. The magnitude of adhesion is significantly influenced by the microgeometry of the polymer material surface.

The importance of creating adhesive interaction in polymer materials is dictated not only by ensuring the printing process, but also by the production of multilayer and composite films used in the packaging industry. An increase in adhesive interaction is often achieved through preliminary modification of the contact surface. The most common method, apart from mechanical and chemical treatment, is the treatment of polymer films in corona discharge plasma [6,7].

Methodological part. Corona discharge, like brush, spark, and arc discharges, belongs to one of the types of gas discharge observed at normal and high pressures [8], and occurs in a gas located in a strongly non-uniform electric field, i.e., near electrodes with small radii of surface curvature. During corona discharge, gas ionization and its glow occur only in a relatively small area adjacent to the coronating electrode with a small radius of surface curvature and forming the so-called coronating layer.

During the treatment of polymer films with corona discharge, charged particles, moving towards the surface of the treated material with acceleration under the action of an electric field, carry out impact interactions and cause breaks in the polymer macromolecular chains with disruption of covalent bonds, simultaneously forming numerous open terminal bonds and free valency. These latter circumstances are fundamental in enhancing adhesion properties due to the

formation of active centers with high reactivity, which also depend on the geometric factor of the microprofile parameters of the treated surface [9].

The main process parameters for treating polymer films in corona discharge plasma are: voltage (kV), current strength (A), interelectrode gap (mm), frequency (kHz), processing time (s), which depends on the rotation speed of the grounded electrode. By varying the values of corona discharge parameters, it is possible to achieve varying degrees of activation of the polymer material surface, expressed in enhanced adhesive interaction between contacting bodies, which is particularly important, for example, in the printing process during ink transfer to the printable material. Enhancing the adhesion properties of materials to be joined is also a necessary condition for creating multilayer and composite materials in packaging production.

Results and discussion. The main types of fiber-forming polymers (PE, PP, PET) used in the printing process, and some characteristics of their structure. Polymers PE and PP belong to carbocyclic aliphatic, PET-aliphatic-aromatic polymers. Polymer fibers are distinguished by the fact that the original polymers in them are in an oriented state due to strong drawing.

Important indicators of the molecular structure of fiber-forming polymers are the characteristics of macromolecular flexibility (rigidity), i.e., the ability to change their conformation under the action of intramolecular thermal motion of units (equilibrium or thermodynamic flexibility) or as a result of external mechanical forces (kinetic or mechanical flexibility).

The maximum achievable degree of crystallinity of fibers is determined by the molecular structure of the polymer, the thermo-fluctuation nature of crystallization processes, and the reasons for thermodynamic and kinetic nature that limit the size of crystallites relative to those of amorphous regions. At the same time, the orientation of crystallites is always higher than the orientation of amorphous regions at the same draw ratio. Table 1 shows the characteristics of the crystalline structure of polymers used as printable materials.

Table 1

Characteristics of the crystalline structure of aliphatic (PE, PP) and aliphatic-aromatic (PET) polymers

Polymers	Length of the elementary cell, Å	Number of units along the length of the elementary cell	Cross-sectional area of the chain, Å ²	Number of chains per 1 cm ² cross-section, n × 10 ⁻¹⁴
Polyethylene	2,534	1	18,2	5,5

Polypropylene isotactic	6,5	3	34,5	2,9
Polyethylene terephthalate	10,75	1	20,3	4,9

It should be noted that the cross-sectional area of the polypropylene chain is almost twice as large as that of polyethylene, which should affect the mechanical strength of the chain to rupture. The difference in the cross-sectional area of the chain for polyethylene (PE) and polyethylene terephthalate (PET) polymers is small and amounts to 10.3-11.5%.

Table 2 summarizes the main available data on the energies of interatomic bonds, obtained from data on the temperature dependence of strength (mechanical dissociation) and thermal dissociation of polymers [10, 11]. In this table D_i - energy of intermolecular bonds; D_{sp} - specific volumetric energy (energy density) of intermolecular bonds, determined by the formula.

$$D_{sp} = D_i/V_m = D\rho/M_{e.u} \quad (1)$$

Where V_m - volume of the polymer corresponding to one mole of elementary units;

$M_{e.u}$ - molecular mass of the elementary unit;

ρ - density of the polymer.

Table 2

Energetic characteristics of the structure of fiber-forming polymers

Polymers	Energy of bond dissociation in the chain, kJ/mol		Energy of intermolecular interaction, kJ/mol		
	Thermal decomposition	Mechanical destruction	in crystallites		in amorphous regions
			D_M	D_{yH}	
Polyethylene	251-318	250-293	8,4-10,5	0,3-0,37	4,5-5,2
Polypropylene isotactic	255-272	230-234	12,5-16,7	0,28-0,37	8,9-12,2
Polyethylene terephthalate	261-287	-	46-61	0,35-0,46	-

The study of any process from an energy perspective is based on thermodynamics, which determines the quantitative relationships between various forms of energy that exist or arise in a given thermodynamic system. This branch of science is based on two laws-postulates [12,13] the correctness of which has been established empirically and confirmed by the experience of human practical activity.

The first law (beginning) of thermodynamics represents the law of conservation (equivalence) of energy in its most general form and indicates that changes in the internal energy U of the system always sum up from the amount of heat Q supplied to the system from outside and the amount of work A performed on the system. In this case, the concept of work encompasses all types of energy except thermal (work of electrical, mechanical, and other forces). Thus, in any process, the following relationship holds:

$$Q = U + A \tag{2}$$

In the case of an infinitely small change in the state of a thermodynamic system, the relationship below is true:

$$\delta Q = dU + \delta A, \tag{3}$$

where δQ - small amount of heat transferred to the system;

dU - infinitely small increase in the internal energy of the system (polymer);

δA - elementary work performed against external forces.

The internal energy of the system represents the sum of the kinetic and potential energies of its constituent particles. The elementary work in the simplest case is expressed as the work of the system against external pressure $\delta A = p dV$. In the general case, the work of the system is performed against external forces of various natures - electrical, mechanical, magnetic, gravitational, etc. The elementary work δA is expressed in general form as

$$\delta A = \sum_{i=1}^n X_i dx_i, \tag{4}$$

Where X_i - so-called generalized forces;

x_i - generalized coordinates.

Generalized forces may include electric field strength E and magnetic field strength H , mechanical stresses σ_i , pressure p , internal friction forces, etc., while generalized coordinates correspondingly include electric induction D and magnetic induction B , deformation ε_i , volume V , etc.

From the first law of thermodynamics, as a consequence, follows the existence of a state function - internal energy U , which is a function of generalized coordinates $U=U(x_1, x_2, \dots, x_n)$. Unlike heat and work, internal energy is characterized by a total differential.

$$dU = \frac{\partial u}{\partial x_1} dx_1 + \frac{\partial u}{\partial x_2} dx_2 + \dots + \frac{\partial u}{\partial x_n} dx_n \tag{5}$$

The first law of thermodynamics, expressed by relations (2) - (4), is applicable for analysing energy relationships during activation in corona discharge plasma of polymer films used in the printing process. Under the action of high voltages 7-24 kV in the interelectrode gap, a non-uniform electric field arises and gas ionization occurs under corona discharge conditions, while accelerated charged particles, reaching the polymer surface, break their molecular chains.

The heat generated during corona discharge, acting as an external disturbing factor like external forces, causes displacement of atoms when the amplitudes of atomic vibrations become larger compared to interatomic distances (equilibrium position), which leads to violation of Hooke's law and thermal vibrations become asymmetric (anharmonicity phenomenon) [11].

Energy analysis of polymer treatment by corona discharge for surface modification to dramatically improve adhesion properties is expediently conducted from the general position of energy consideration of the polymer body destruction process [12].

Electronic breakdown occurs as a result of the destruction of the polymer dielectric by an electron avalanche formed by the interaction of an electron flow with the elements of the dielectric structure at high voltage values. Unlike thermal breakdown, the probability of which is high at large voltages and during prolonged voltage interaction, electronic breakdown is most probable during short-term exposure to high voltage and relatively low temperatures, which is characteristic of corona discharge. Thus, during electronic breakdown, material destruction occurs by electrical forces.

The expectation time of rupture τ_* of any chemical bond in the polymer chain is equal to [11]:

$$\tau_* = \tau_0 \exp[(U_0 - \lambda_m f)/kT], \tag{6}$$

Where k – Boltzmann constant;

T – absolute temperature;

τ_0 – period of atomic vibration, determined experimentally by IR spectroscopy (from the infrared absorption line);

U_0 – potential barrier at $f=0$, which must be overcome during bond rupture (often assumed that $U_0 \approx U_d$, where U_d – dissociation energy);

λ_m – distance between the minimum and maximum of potential energy;

f – constant external tensile force.

Formula (6) shows that the higher the temperature, the smaller the required force f to achieve a certain expectation time for the rupture of one bond in the polymer chain. If the polymer chain contains n bonds and is considered in isolation, then the expectation time for chain rupture at any point will be n times smaller and will be:

$$\tau_* = (\tau_0/n) \exp[U_0 - \lambda_m f/kT]. \tag{7}$$

In accordance with the first law of thermodynamics (2) or (3), the elementary work δA , performed against external forces during corona discharge treatment of polymer film, is equivalent to the activation energy of polymer destruction U_0 (Table 4). This energy for polypropylene exceeds that for polyethylene by more

than two times. Therefore, the value of the process parameter responsible for the amount of heat Q , supplied to the system in the interelectrode space must be higher. Thus, during corona discharge treatment of polyethylene films for printing, a voltage of 10 kV ensures strong adhesion with alcohol-based inks, exhibiting better polymer surface wettability and, consequently, improved print quality [9]. However, a voltage of 10 kV and the corresponding power does not provide sufficient bonding of the polypropylene polymer film surface with printing ink after corona discharge treatment. It was found that only treatment at 12 kV provides uniform ink distribution on the surface of the printable material, indicating sufficient surface activation after treatment.

It can be assumed that one of the reasons for the higher voltage required for polypropylene treatment is the greater molecular mass of the elementary unit (Table 1): for polypropylene - 42,081, for polyethylene - 28,054 kJ/mol. However, the main reason, in our opinion, is the higher activation energy of polymer destruction U_0 (Table 4) and the energy of intermolecular interaction (kJ/mol) (Table 3).

The molecular mass of PET (Table 1) is 192,16, which will require an even greater voltage U_k on the coronating electrode. This conclusion is supported by data on the energy of intermolecular interaction (kJ/mol) (Table 3), where among the compared polymers PET has the highest value of 46-61 kJ/mol. Therefore, for corona discharge activation of polyethylene terephthalate, an even higher voltage will be required than for polypropylene under otherwise equal processing conditions (gap, mm; frequency, kHz; duration, s). According to data [6] for PET surface activation, treatment at voltage $U_k = 16$ kV is necessary for water-based latex inks.

Conclusion. Thus, the analysis of polymer film treatment by corona discharge, which is an effective means of surface activation to improve adhesion properties upon contact with printing ink, should be based on a thermodynamic approach, since corona discharge is characterized by energy transformations in a thermodynamic system consisting of a coronating electrode with high voltage, the interelectrode space, and a polymer film located on a grounded dielectric electrode. It has been established that, in addition to the molecular mass of the polymer elementary unit, the main process parameter of corona discharge—coronating discharge voltage U_k is influenced by energy characteristics (activation energy U_0 , energy of polymer chain rupture U_D , energy of intermolecular interaction, kJ/mol), as well as the structural chain parameter—cross-sectional area of the chain, $\overset{\circ}{A}^2$.

REFERENCES:

1. Packaging Products Made of Polymer Film [Electronic resource]. – Access mode: <https://e-plastic.ru/news> .
2. Yeshbayeva U. Zh., Safaeva D. R. Analysis of Current Trends in the Technology of Packaging Polymer Materials in the World and Uzbekistan // *NamMTI Scientific and Technical Journal*. – Namangan, 2021. – Vol. 6, No. 1. – pp. 276–280.
3. Dmitriev Ya. V. Features of Flexographic Printing with UV-Curable Inks on Non-Absorbent Surfaces : Abstract of the PhD (Engineering) dissertation. – Moscow, 2013. – 24 p.
4. Nazarov V. G. Surface Modification of Polymers. – Moscow : MGUP Publishing House, 2008. – 474 p.
5. Berlin A. A., Basin V. E. Fundamentals of Polymer Adhesion. – Moscow : Khimiya, 1974. – 320 p.
6. Bakanov V. A. Properties of Polymer Films Activated by Corona Discharge and Features of Their Application in Packaging Production : Abstract of the PhD (Engineering) dissertation. – Moscow, 2008. – 21 p.
7. Ananyev V. V., Peretokin T. N., Zaikov G. E., Sofyina S. Yu. Modification of Adhesion Properties of Polymer Films by Corona Discharge Treatment // *Bulletin of Kazan Technological University*. – 2014. – No. 3. – pp. 116–119.
8. Yavorsky B. M., Detlaf A. A. *Physics Handbook*. – Moscow : Nauka, 1971. – 939 p.
9. Safaeva D. R. Investigation of Printing and Technical Properties of Packaging Material (Polypropylene) Using the Gravure Printing Method : Abstract of the PhD (Engineering) dissertation. – Tashkent : TITLP, 2022. – 48 p.
10. Perepelkin K. E. *Structure and Properties of Fibers*. – Moscow : Khimiya, 1985. – 208 p.
11. Bartenev G. M. *Strength and Fracture Mechanisms of Polymers*. – Moscow : Khimiya, 1984. – 280 p.
12. Gul V. E. *Structure and Strength of Polymers*. – Moscow : Khimiya, 1978. – 328 p.
13. Novikov I. I. *Thermodynamics*. – Moscow : Mashinostroenie, 1984. – 592 p.