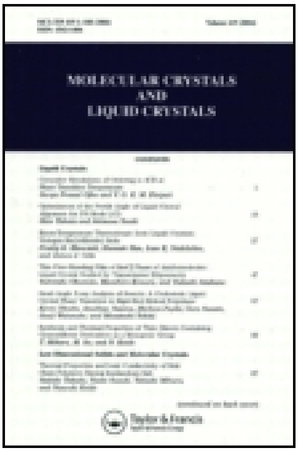

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Degradation as a Method of Modification of Polymeric Products

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Degradation as a Method of Modification of Polymeric Products

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Various researchers have given different examples of how degradation can be used as a method of modification of polymeric materials for achieving new materials with improved surface properties. Hydrolysis, ozonolysis and oxidation are acceptable for the modification of films, fibres, membranes and other polymeric materials. The authors recommend new methods for increasing the adhesion of films and fibres.

Keywords Adhesion; degradation; hydrolysis; oxidation; ozonolysis; polymers

Introduction

The stability of polymeric products towards oxidation and hydrolysis is one of the important factors determining their weather resistance [1]. However, in the 1970s researchers began to apply oxidation and hydrolytic destruction for surface modification of materials with the purpose of obtaining products with improved operational properties [2,3]. In this case it is necessary to stop the process of destruction at a specific stage so that there is no noticeable change in the various positive properties of a polymeric product. A thorough knowledge of the kinetic and diffusive changes taking place at degradation is required for the purpose of improving the surface properties of a product without deterioration of its bulk properties.

In many cases the surface properties of such products appreciably determine their operational properties. For this reason attention is increasingly being paid to the surface modification of polymeric products, which, along with radiation and chemical grafting, can be carried out by means of chemical destruction. Certainly, it would be better if modification by destruction occurred in those molecules of a product that really are in the surface layer (at a depth 10–15 Å). However, in reality the reaction proceeds not only on the surface, but also into part of the below-surface layer, the size of which depends on the relation between the rate of diffusion of an aggressive medium (oxygen, ozone, water, solutions of salts, basis, acids) and the rate of decomposition of the polymeric molecules affected by these substances. Let us now consider now separately hydrolytic and oxidising destruction.

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Hydrolytic Degradation

Polymers that are susceptible to hydrolytic destruction usually have heteroatoms in the main chain or in a side chain. The destruction of polymeric products by aggressive media (solvents) proceeds through the following main stages: adsorption of the aggressive medium onto the surface of a polymeric product; diffusion of the aggressive medium through a volume of the polymeric product; chemical reaction of the aggressive medium with chemically non-resistant links of polymer; and desorption of the destruction products from the surface of a product.

Generally, the rate of chemical decay of non-resistant links in polymers resulting from the concentration of the aggressive environment can be described by the following equation:

$$w = dc_n/dt = k\left(c_n^0 - c_n\right)c_s c_c \tag{1}$$

where c_n^0 is the initial chemical concentration of non-resistant links in a polymer; c_n is the concentration of the breaking links; c_c is the concentration of the catalytic agent; and c_s is the solvent concentration (e.g. H_2O) in a polymer.

If the solvent is spent during the chemical decay of non-resistant links in a polymer, its concentration can be found from the equation:

$$\partial c_s/\partial t = D_s \nabla^2 c_s - k\left(c_n^0 - c_s\right)c_s c_c \tag{2}$$

where D_s is the diffusivity coefficient of a solvent; and ∇ is the Laplace operator.

The problem of determining the rate of chemical decay of non-resistant links in a polymer therefore consists of a joint solution of Equations (1) and (2). However, consider the case where the rate of diffusion of the aggressive medium is much lower than the speed of the chemical reaction. Then the process of destruction occurs in some thin surface reaction zone or, as it is usually described, on the surface of a polymeric product, i.e. in the external diffusion-kinetic area. In this case the rate of breaking up of hydrolytically non-resistant links is solved by the equation:

$$dc_n^s/dt = k\left(c_n^0 - c_n^s\right)c_c^s c_s^s \tag{3}$$

where s designates values of concentrations in the surface layer.

It is not difficult to show [4] that

$$c_n^s = k_{eff}^s c_c^v c_s^v$$

where the index v corresponds to volume concentration. We shall consider how the mass of the polymer will change during destruction in this case. Irrespective of the type of decay undergone by the polymeric molecules, it is possible to write an expression for the mass change of the products formed:

$$m = k_{eff}^s c_c^v c_s^v t S \tag{4}$$

where S is the surface area of a polymeric product. If the polymer is a film, then its mass change will be determined by the following equation [4]:

$$m_n = m_n^0(1 - t/\tau) = m_n^0\left(1 - k_{eff}^s c_c^v c_s^v t S/m_n^0\right) \tag{5}$$

where τ is the time for complete decomposition of a film; and m_n^0 is the polymer mass before decomposition.

When destruction occurs in the external diffusion-kinetic region, it is necessary to take into account what the properties of the polymeric molecules in surface layers are, because as a rule, thy differ from those of the bulk molecules of a sample (molecular weight, degree of crystallinity, orientation, etc.). Generally, in micro volumes of polymer with various structures of chemically non-resistant links, there can be various concentrations of the components of the aggressive medium (c_c, c_s), which will lead to various rates of chemical destruction. All functional groups in a polymer can therefore be conditionally divided into "accessible" and "unavailable", and the degree of availability is unequal for different components of the medium. As has been shown experimentally for polyethylene teraphthalate (PETP) [5,6] the decay of a film in an alkaline solution has the following regularities: the reaction has a zero order on the polymer and the molecular weight of a polymeric film does not vary, right up to the termination of the process. In spectra from Fourier Transform Infrared Spectroscopy in the Attenuated Total Reflection Mode (IR-ATR) there are no absorption bands of carboxyl groups formed by the hydrolysis of the ester link. The value of an effective rate constant, calculated from the Eq. (5), varies depending on changes in the thermodynamic parameters of the media according to the equation:

$$k_{eff} = \frac{\left(k_u a_{H_2O} K_e/b_0 + k'_u a_{H_2O}\right)}{\left(1 + K'_e a_{H_2O}/b_0 + K'_e a_{H_2O}/b_0^2\right)}$$

which describes the hydrolysis of low-molecular-weight compounds in water solutions of alkalis [2,3,5]. In the above equation, a_{H2O} is the activity of water; b_0 is the basicity of a solution; K_e and K'_e are equilibrium constants of the process of formation of the ionised forms; and k_u and k'_u are appropriate rate constants. All these factors allow one to suppose that the reactionary zone comes closer to being a monolayer [2–6]. Micrographs of PETP filaments [2], obtained with the help of a raster microscope, confirm this supposition (Fig. 1).

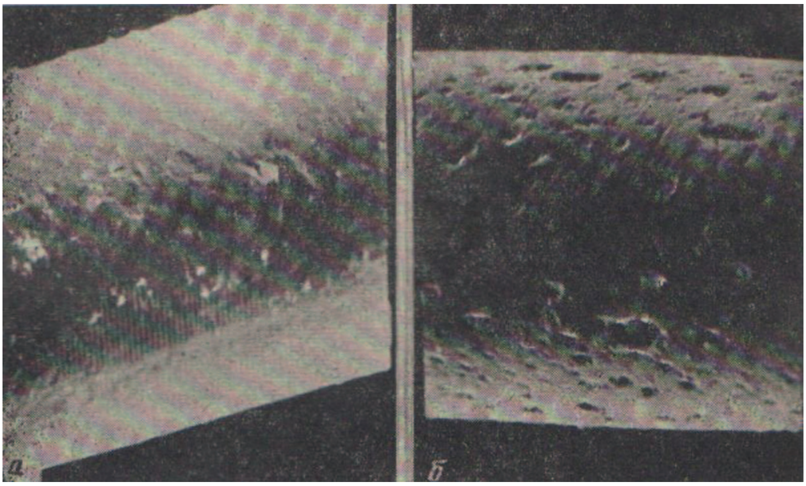


Figure 1. Microphotography of PETP-filaments: Left– initial, right– after degradation 5 min in 22% KOH solution at 88°C, x3000 [3,5].

Modifying Polyethers by Water Solutions of Alkalis to Obtain a Rough Surface

Polyethers (PE), PETP, polycarbonates (PC) and some other polymers are used as materials for synthetic paper pulp and related products. Recently, intensive development of technology for the production of rough films has been carried out. Rough films are used to produce a raw long-lived material for cards, drawings, copies, computers, video and sound recordings, etc. There are various ways of modifying the grain of polymeric films. For example, it can be achieved by treatment of films by a corona discharge [7], by orientation [8,9] or by chemical pickling of films [10,11], and also by coating the surface with a lacquer [12]. One of the most successful methods is pickling [13]. To find optimum methods for pickling films, it is necessary to understand the mechanism of this process, starting with all ways of achieving a rough surface and the dependence of the grain on time, temperature, the thermodynamic parameters of the medium, and the structure of the polymer.

PETP films. In the case of pickling a thick PETP film (Fig. 2), during the process the grain index, R_a, (the average arithmetic deviation of microjaggings from the basic line of a profile) first reaches a maximum and then remains practically unchanged before complete degradation of the film. Thus the maximum of a grain corresponds to the thickness of the pickling layer, from 25–30 μm. The maximum value of a grain, R_a^{max}, decreases with an increase in the degree of crystallinity (Fig. 3) and depends on the degree of orientation.

According to one of the present explanations, the roughness of a surface at pickling is achieved by preferential destruction of the amorphous part where the miscibility of water, alkalis and salts is quite high and naked crystal chips from the joggings observed. Apparently such a pickling mechanism can be used, but it is not observed in the case of PETP because the degree of roughness of amorphous films exceeds the degree of roughness of crystalline

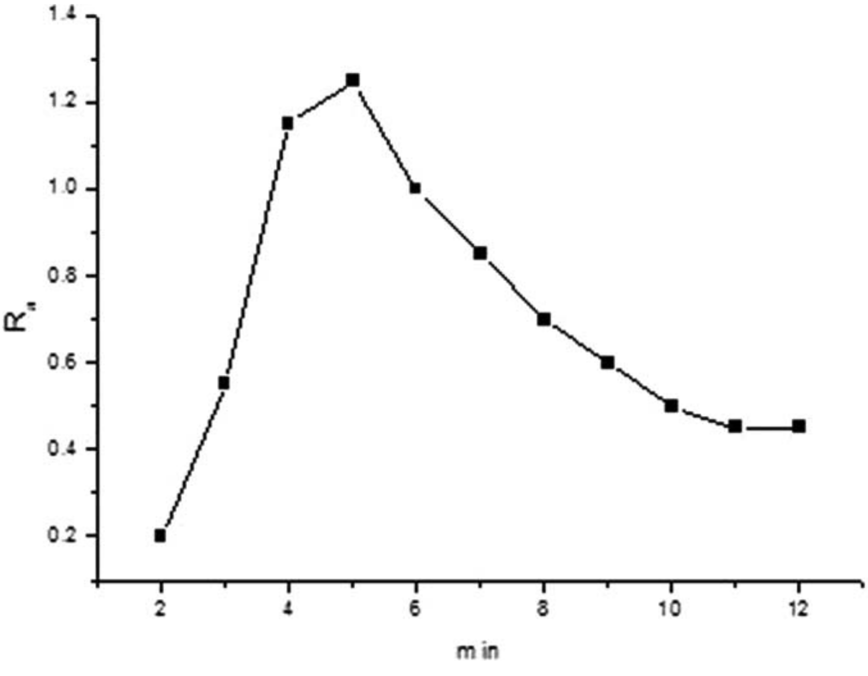


Figure 2. The dependence of grain (R_a) on time of pickling for a PETP-film [5]. Film thickness–550 μm, degree of crystallinity – 40%, [KOH] – 4,9%, 108°C.

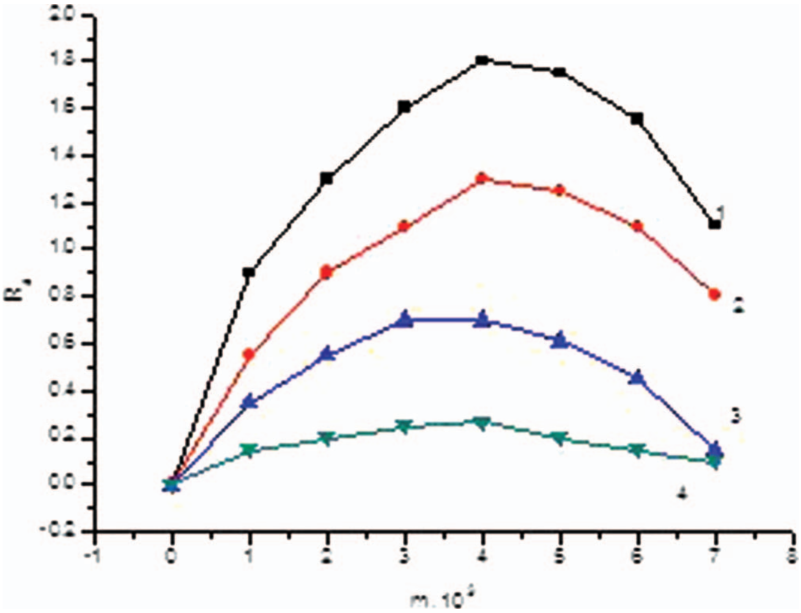


Figure 3. The dependence of grain (R_a) on the removed layer mass (m, moles) at different cristallinity%: 5(1); 30(2); 40(3); 50(4) [6].

films. It also appears that when PETP films were pickled by solutions of alkalis, under various conditions but with close degrees of crystallinity, various values R_a were obtained [3]. In this case the roughness achieved is probably determined by the opening up during pickling of micro-sized defects formed at the time that a polymer film was processed from a melt [14]. It is thought that the surface layers of films have a more friable structure, lower density and greater amount of defects [2,3]. With an increase in the degree of crystallinity, the chain length of the amorphous phase decreases and the defects in it are “cured”. All this results in a lower surfaces rough being obtained when films with a high degree of crystallinity are pickled. The greatest number of microdefects is thus at a depth 25–30 μm, which determines the maximum roughness obtained when such a layer is pickled.

The roughness value is defined only by the width of the pickling layer and does not depend on the temperature or on the concentration of alkali [2,3,5,6]. Therefore on thin (5–20 μm) PETP films one cannot obtain a sufficiently rough surface as these films apparently do not contain enough microdefects. For the formulation of economically sound and technologically optimum methods, it is necessary to take into account the influence of alkali concentration and temperature on the rate of pickling. According to the kinetic data, the change of mass of a film can be written as [2]:

$$m = m_0(1 - k_{eff}tS)$$

where m_0 is the mass of the initial film; and S is the surface of that film.

Based on the known mechanism of destruction of PETP [2–6], we can formulate an expression for an effective rate constant:

$$k_{eff} = k''_u a_{H_2O}/1 + K_e b_0$$

Since

$$k''_u = Ae^{-E/RT}$$

$$k_{eff} = Ae^{-E/RT} a_{H_2O}/1 + K_e b_0$$

Therefore

$$m = m_0 \left(1 - Ae^{-E/RT} a_{H_2O} tS/1 + K_e b_0\right)$$

At a site up to a maximum roughness of the curves of the pickling of films:

$$\Delta m = \alpha R_a$$

where α is the ratio coefficient, depending on the nature of a material.

From here

$$R_a = Ae^{-E/RT} a_{H_2O} tS/\alpha(1 + K_e b_0)$$

This equation shows the dependence of roughness on temperature, time and the thermodynamic parameters of the medium. By inserting substituted values of the parameters A, E, and K_e for PETP [2-6], we obtain

$$R_a = \frac{6{,}4 \times 10^6 \exp(-16500/RT) a_{H_2O} tS}{\alpha(1 + 4 \times 10^2 b_0)}$$

The optimum technological parameters for obtaining roughness on PETP films are as follows: degree of crystallinity >10%; concentration of KOH 46–49%; and temperature 105–110°C [5,6]. A graphical illustration of the optimum mode for obtaining maximum roughness is given in Fig. 4.

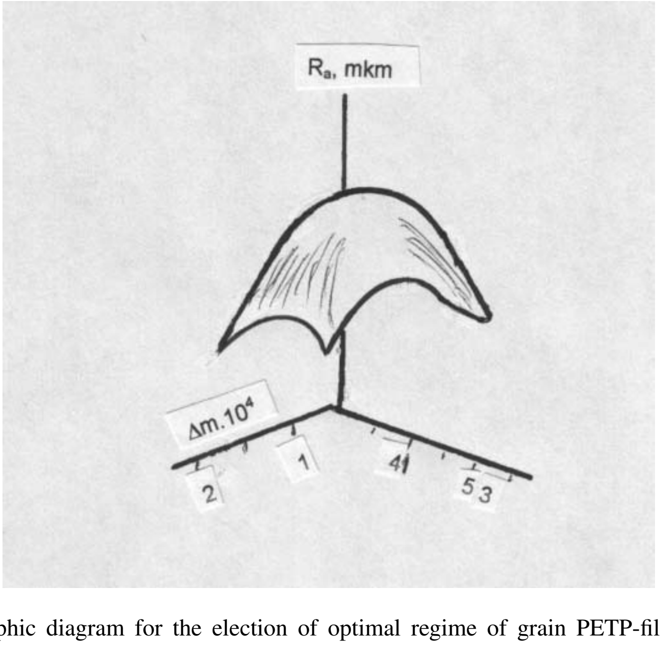


Figure 4. Graphic diagram for the election of optimal regime of grain PETP-film preparations (108°C) [2,6].

Polycarbonate films. When polycarbonate (PC) films, and PETP films, are pickled with alkaline solutions, a rough relief will be obtained on their surfaces [15,16]. The sources of this roughness are micro-heterogeneities of submicroscopic size in the structure of PC. Thus with a PC film the methods of solution pouring (PCP) and extrusion (PCE) will essentially give different results. A PCP film has a looser structure [16] and a more pronounced micro-relief is found on it after pickling than on a PCE film treated by extrusion.

An attempt was made to change the size of the microdefects by using swelling before pickling [15]. Chochlov et al. [17] treated films with a swelling agent (water solutions of acetone) [17].

Most likely water solutions of acetone affect the structure of PC films through the following mechanism [15]. At first there is intensive swelling (loosening of the structure), which increases the segmental mobility of the macromolecules, thereby creating conditions for their subsequent ordering in an even amorphous state. The subsequent decrease in sample mass is linked to partial forcing out of the swelling agent. At this stage there is still no crystallisation, which is evidence of pre-crystal ordering of the polymeric chains in the structure of amorphous PC; crystallisation starts later.

The rate of loosening of the PC structure at swelling and the rate of packing of aligned chains depend on the composition of the plasticiser (in this case the component ratio of acetone and water). In pure acetone all three sequential stages occur very fast. At addition of water, the rate of these processes is retarded, and each of the stages becomes separated from the others at a major time interval.

According to modern theory [18], the structure of amorphous polymers is heterogeneous (in the sense that it undergoes density fluctuations). Razumova et al. [15] postulated that this heterogeneity increases during the time the PC films are being treated by the plasticising additives. They attributed this to an increase in the packing of polymeric chains in areas of low density before crystallinity develops. For this reason it is possible to expect the most highly developed micro relief on the surface of pickled films that have swelled the most. This is also the method used in practice. From the data in Fig. 5 it is clear that, other things being equal, the highest roughness value is achieved when films are pickled beforehand by treatment with a plasticising solution.

Rather conveniently, the optimum duration of processing for a film though the use of solutions can be obtained from the time profiles of specific elongation at break of polymer samples: the moment of appearance of a maximum on these curves corresponds to the moment of maximum swelling of a film [15], and this in turn provides the maximum roughness value obtainable after pickling. In practice, it is not always possible to achieve enough swelling on oriented polymeric films. The method of chemical pickling of a surface is now one of the most suitable for creating roughness while preserving the positive properties of a product, including oriented structures [19,20]. From theories about the mechanism of derivation of roughness on PC films [15], and also about the structural changes in polymers at elongation [21,22], it is possible to suppose [20] that as orientation proceeds the defects of the molecular and supramolecular order in the bulk polymer are "healed" and there is a decrease in their effective size and amount. This means that the possibility that these microdefects in the polymer will result in "dimples" in the roughness after the oriented films have been pickled is reduced. To achieve reliable roughness of films it is necessary to control the directional action promoting the development of disorder in the structure of a polymer. The simplest means of control is the process of reorientation of oriented films [20].

The regularities of PCE films having initial anisotropy, roughness formation and other changes were researched by Vlasov [23], especially with regard to a change of roughness in pickled films oriented in a transverse direction up to various coefficients, K, of film

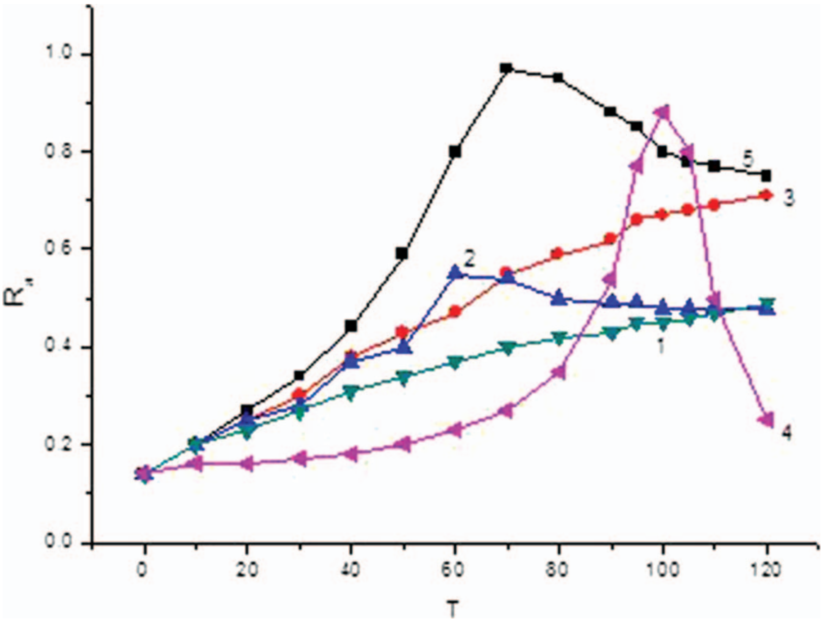


Figure 5. Difference in a roughness R_a at the pickling by 50% NaOH solutions at 50°C PC-films, treated by 80% acetone solutions [20]. Time of a treatment by acetone (T, min): 1 – untreated 2 – 15; 3 – 30; 4 – 60; 5 – 120.

elongation. As shown in Fig. 6, on the surface of films thus modified it is possible under certain conditions to create a rough relief with $R_a = 0.5–1.0\ \mu$m. In this case the optimum roughness value was obtained at K = 2.0. The friability and increase in structural defects obtained at K = 2.0 can be attributed to intensive reorientation in the structure of the polymer [24]. The critical value, *K*, at which there will be intensive reorientation in various films, should depend on the initial structure and anisotropy of a film [20].

At further elongation of a film, up to critical values of *K*, compaction of the polymer structure and “healing” of defects again occur. The creation of roughness continues up to the critical value, which is characteristic of films oriented along a direction of potential expansion during extrusion.

Modification of the Surface of a Filament of Cellulose Diacetate by Water Solutions of Alkalis

The disadvantages of synthetic filaments, including polyesters, are their hardness, strong electrostatic properties (EP) and dirt adherence (DA). The formation of static electricity charges during treatment creates technological and operational difficulties. So, for example, the charges on the surface of a polymer attract dust and other foreign impurities to end products, and the dirt adhering to clothes made of an electrified fabric can sometimes exceed by 300–500 times the dirt adhering to clothes made from cotton fabric. The negative consequences of static electricity on human beings are also known [25]. To neutralise static electricity charges, people try to use both physical and chemical methods [2,3]. The introduction into polymers of antistatic agents reduces static electricity, but, as a rule, such

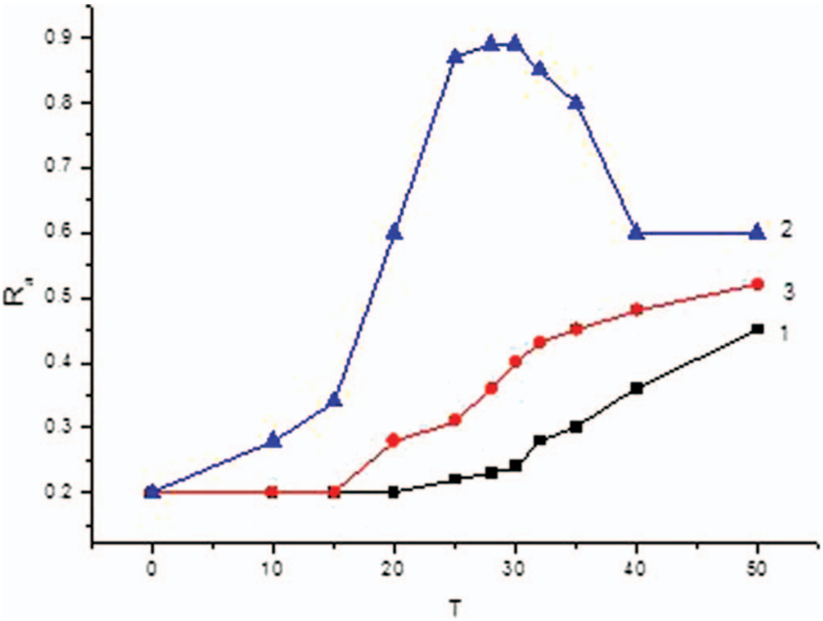


Figure 6. Changing of a roughness PC-films oriented across extrusion direction at the pickling. (Degree of elongation: 1 – 1,5; 2 – 2; 3 – 2,5; T–time of pickling, min.) [20].

antistatic agents irritate the skin and mucous membranes of the eye and are removed when a polymer fabric is washed.

Rudakova and co-workers [26,27] carried out a detailed study of one of the chemical methods of neutralising static electricity on a sample of a filament widely used in industry, namely cellulose diacetate (DDA). The difficulty of neutralising charges chemically consists in modifying the filament while retaining its positive properties. It is well known that charges are concentrated mostly on the surface of polymers (although this will depend on their thickness). Therefore, the main task consists in modifying the surface layer to render it less electrified. If the surface layer of a DDA filament is replaced by strongly polar acetate groups through hydrolysis of hydrophilic hydroxyl groups, this layer is converted to cellulose and the EP are some orders lower. For such modification to be acceptable, the water solutions of alkalis must be used in concentrations that do not cause destruction of the glycoside bonds in a basic chain of macromolecules.

Figure 7 shows the typical S-shape curve of hydrolysis of DDA filaments. The concentration of the broken ether links in DDA c_n can be found from the equation

$$\partial c_n/\partial t = k\left(c_n^0 - c_n\right)c_{NaOH}$$

where k is the specific reaction rate of hydrolysis of ether links; c_n^0 is the initial concentration of ether links in a polymer; and c_{NaOH} is the concentration of alkali in a polymer, which can be calculated from the equation

$$\frac{\partial c_{NaOH}}{\partial t} = D_{NaOH}\nabla^2 c_{NaOH} - k\left(c_n^0 - c_s\right)c_{NaOH}$$

where D_{NaOH} is the effective diffusion coefficient of alkali in a volume of polymer.

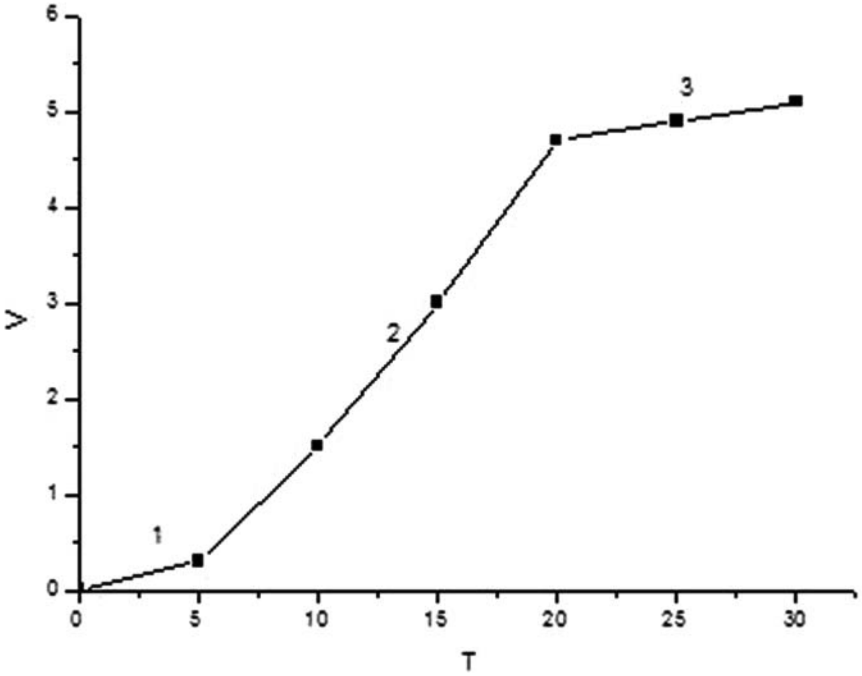


Figure 7. The kinetics curve of alkali demand in process of DDA-filaments degradation (T – min, 70°C, NaOH – 0,15% water solution, 1, 2, 3 – selected areas of curve) [27].

This set of equations has no analytical solution, but can be solved with the help of numerical calculations. Also these equations can be solved if one uses various assumptions and suppositions to simplify the reaction schema. From the end part 3 of the kinetic curves in Fig. 7 it is possible to calculate an effective rate constant of hydrolysis of ether links, k_{eff}, supposing that at this site the filament was completely saturated with alkali and the reaction occurred in a kinetic area. The change in the value k_{eff} as a function of temperature and alkali concentration is featured in the following equation:

$$k_{eff} = 10^{10} \exp(-18000/RT) c_{NaOH}$$

The whole task is reduced to finding conditions at which the rate of hydrolysis would be much higher than the rate of diffusion, in other words to finding conditions for the most effective destruction process in the narrowest reactionary zone. Such conditions can be reached by two paths: (1) use of an alkali with a large volume of cations, for example $(C_4H_9)_3NOH$, that is decreasing $D_{OH}-$ while retaining a constant rate of hydrolysis; and (2) use of concentrated solutions of strong alkalis which increase the rate of hydrolysis at a constant rate of diffusion $D_{OH}-$ (as is visible on electronic micrographs of transverse sections of a DDA filament, the width of the regenerated cellulose layer at a conversion of $\sim$3% is 0.5–0.6 μm. See Fig. 8). Figure 9 shows data for the dependence of the electrical resistance of the surface of a DDA fabric on the degree of transformation of acetate groups (C) after treatment by alkalis with various volumes of cations.

Table 1 shows data indicating the influence of the degree of transformation of groups on the mechanical characteristics and electrical resistances of DDA filaments. It is clear that during the process of destruction the electrical resistance of a filament is considerably

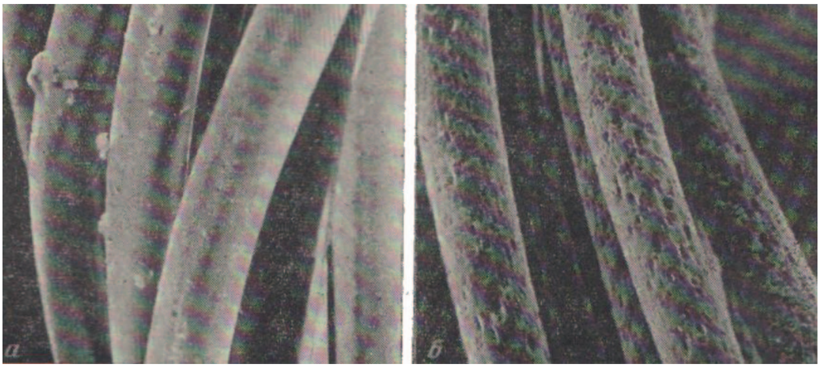


Figure 8. Electron microscope photography of DDA-filaments: Initial (left) and modified (right) [5,27].

reduced by even a small deterioration in the mechanical characteristics [29]. On the basis of the kinetic regularities described above it is possible to choose the optimum regime for the modification of DDA filaments by hydrolysis.

The Influence of Alkaline Treatment on the Properties of PETP Filaments

The destruction of PETP filaments and films proceeds from the surface [4,28–31]. When PETP molecules are destroyed in alkali, the decay follows the usual mechanism [2,3] with

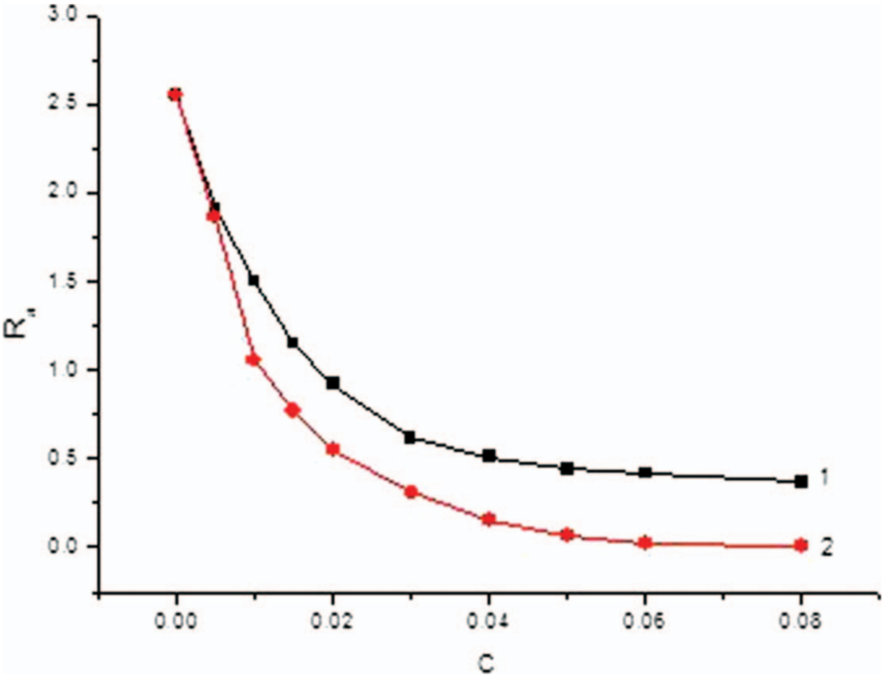


Figure 9. The dependence of surface DDA electrical resistance R_a on C for hydrolysis by NaOH (1) and (tert-C_4H_9)NOH (2) [28].

Table 1. Influence of a degree of acetic group transformations in a DDA-filaments on the tensile characteristics and electrical resistance [29]

Degree of transformations	Tearing strength, g/mm^2		Elongation,%		Electrical resistance, q.10^{-11}, ohm
	warp	weft	warp	weft	
0	109,3	115,8	22,7	25,5	24
0,01	108,2	109,0	22.0	22,5	14
0,03	105,9	100,5	21,3	20,3	4
0,08	102.7	91,3	20.5	18,4	3

subsequent depolymerisation. This means that on the surface area of a filament there will always be a constant concentration of ester bonds c_n^0, and the loss of polymer mass will be proportional to the number of broken ester bonds:

$$-dm/dt = k'_{eff} S \tag{6}$$

where $k'_{eff} = k_{eff} c_n^0$; and S is the surface area of a filament for a filament of $S = 2\pi \mathrm{rl}$ and $m = \pi \mathrm{r}^2 l\rho$, where r is the average radius, l is the length of the filament, and ρ is the density of PETP.

It is possible to find the change in the average radius of a filament with time from the following equation:

$$r = r^0 - 2k'_{eff} t/\rho \tag{7}$$

where r^0 is the initial average radius of a filament.

Integrating Eq. (6) and taking into account Eq. (7), we get

$$m_t = m_0\left[1 - 2k'_{eff} t/\rho r^0\left(1 - k'_{eff} t/\rho r^0\right)\right] \tag{8}$$

In this equation $k'_{eff}/\rho r^0$ is the inverse value of the time at which the degradation process will end. For small conversions Eq. (8) can be simplified thus:

$$m_t = m_0\left(1 - 2k'_{eff} t/\rho r^0\right) \tag{9}$$

Let us consider how k_{eff} will vary if we increase the alkali concentration in a solution. According to the mechanism of hydrolysis of ester bonds in PETP [2,3], for a small degree of ionisation

$$k_{eff} = k''_u b_0 a_{H_2O}/K_e \tag{10}$$

Having substituted the values of a number of parameters [5,29] in Eq. (10), we obtain the dependence of an effective constant rate of hydrolysis of ether links on the temperature and thermodynamic parameters of the medium:

$$k_{eff} = 1,6 \times 10^2 \exp(-1650/RT) b_0 a_{H_2O} \tag{11}$$

If we substitute Eq. (11) for Eq. (9), we obtain the general dependence circumscribing the change of mass of a PETP filament as a function of temperature, time and the thermodynamic parameters of the medium:

$$M = m_0\left[1 - \frac{1{,}6 \times 10^2 \exp(-1650/RT) b_0 a_{H_2O}}{p r_0}\right] \tag{12}$$

Experiments were carried out in equipment for dyeing under pressure. The time of treatment was 60 min. During alkaline treatment of PETP, the electrical resistance of the filaments does not change [29] because, as a result of hydrolysis, the surface area of the PETP filaments remains constant (Table 2). The stress load and stress elongation are reduced during alkaline treatment of a filament (Table 2), but such treatment considerably reduces the adherence of dry dirt to a fabric (the Kubelka-Munk index decreases by 1.00 up to 0.6). It is worth noting that alkaline treatment results in a considerable improvement in the depth of colour of a fabric dye [29]. Using the data obtained from kinetic research, it is possible to find optimum conditions for the alkaline processing of a PETP fabric [2,5. 29]. Since the destruction occurs on the surface layer, the value of the fabric's tensile strength, σ, remains almost constant:

$$\sigma = P/\pi r^2 \tag{13}$$

where P is the stress load.

Having combined Eqs (7), (11) and (13), we obtain an expression describing changes in P as a function of time, temperature and the thermodynamic properties of solutions of different alkalis:

$$P = \pi\sigma\left[r_0 - \frac{1, 6 \times 10^2 \exp(-1650/RT) b_0 a_{H_2O} t}{\rho}\right]^2$$

Oxidising Destruction

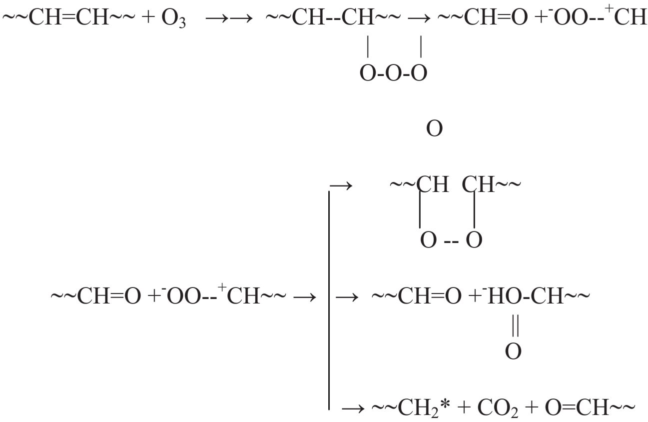
In addition to hydrolytic destruction for the modification of polymers, methods of oxidising destruction have been widely used [32,33]. Homogeneous oxidisation of PE dissolved in toluene, both in the presence of the catalytic agent cobalt acetate [34] and in the uncatalysed mode [35] has been described as a method of introducing polar groups into PE to increase its adhesive strength. Wittaker's 1946 patent [36] gives data on the processing of PE on mixing rollers at 160–200°C in air. As a result of such processing, functionalised PE with oxygen contents of 0.1–0.5% by weight was formed. It was used as a finish on textiles due to its ability to form spontaneous emulsions [37].

The processes of oxidising destruction of polypropylene have been described [38,39]. With deep oxidising degradation, atactic [40] and isotactic [41] polypropylenes were obtained which were similar to wax products. The chain reactions involved in the oxidisation of macromolecules by oxygen proceed rather slowly. To speed up the process engineers in industry treat polymer materials with high-energy particles [42,43], with an open flame [44,45], by electric discharge [44, 46, 47], with oxygen atoms [48] or with ozone [49]. The action of high-energy particles in the presence of oxygen is accompanied by the destruction of polymer chains; in the absence of oxygen, cross-linking processes predominate [50,51]. When cellulose or its derivatives are treated in an inert atmosphere, there is intensive destruction [51,52], and at a dose of ~100 MRad the products become completely soluble in water. The radiation method of treating cellulose derivatives is applied to obtain graft copolymers of cellulose and its ethers [53,54].

Table 2. Influence of processing PTEP fabrics by 16% water solution NaOH on its properties [2,9]*

Samples	Tearing stress, kG		Tearing elongation,%		Electric resistance, ohm. 10^{-12}	Kubelka-Muny Index after		Weight loss
	warp	weft	warp	weft		Soiled	Washed	
Initial fabric Fabric treated at:	52		28	33	5,5	1,00	0,06	0,0
100	48	32	28	34	6	0,65	0,08	6
110	46	28	25	30	5,2	0,59	0,05	14,4
120	38	20	22	24	6	0,78	0,07	33,1
130°C	19	9	17	15	5	—	—	61,4

The treatment of polymer surfaces by an open flame is also very effective as a method of oxidising modification. Fig. 10 shows the schema of flame surface treatment of a polymeric film. To obtain reproducible results it is necessary to move the film at a constant speed (mostly 30–80 m/min) and at fixed ratio of air to combustible gas (usually natural gas or propane). Air is the major component for the creation of an oxidising environment (25:1–32:1). The action of a flame and hot gases on the surface layer of a polymer causes chain oxidisation to proceed, which at a first approximation can be presented as in the Scheme 1 [55]. This shows the main paths of polar functional group (carboxyl, hydroxyl and carbonyl) formation, which determine the surface properties changes. It can be observed that the change of surface layer properties of a composite is very dependent on the intensity of processing. As an example, Fig. 11 gives the test data for the adhesion of ink to the surface of a PE treated by a propane flame at different doses (the air delivery was constant) [56].



$$\sim\sim CH{=}CH\sim\sim + O_3 \rightarrow\rightarrow \sim\sim \underset{\text{O-O-O}}{CH{-}{-}CH}\sim\sim \rightarrow \sim\sim CH{=}O + {}^{-}OO{-}{-}{}^{+}CH\sim\sim$$

$$\sim\sim CH{=}O + {}^{-}OO{-}{-}{}^{+}CH\sim\sim \rightarrow \begin{cases} \rightarrow \sim\sim \overset{O}{\underset{O\,-{-}\,O}{CH\quad CH}}\sim\sim \\ \rightarrow \sim\sim CH{=}O + {}^{-}HO{-}\underset{\|\atop O}{C}H\sim\sim \\ \rightarrow \sim\sim CH_2{}^{*} + CO_2 + O{=}CH\sim\sim \end{cases}$$

Scheme 1.

It is seen that adhesion increases from 1 (very poor) up to 5 relative units (good); 3 corresponds to an acceptable level. Similar outcomes can be achieved by skipping a film of polymer between two metal electrodes, to which an alternating current of 8–20 kV is applied. The installation method for treatment by electric discharge is given in Fig. 12.

The polymer film or filament is slipped through a zone of barrier discharge, where it is exposed to the complex action of charged particles, atoms of oxygen, ozone or nitric oxides [57,58]. The process temperature usually does not differ greatly from room temperature. The chain reaction progresses fairly slowly and the functional groups that accumulate during treatment form mainly because of isomerisation and the decomposition of peroxide radicals (reaction III of the scheme). The dynamic properties that change during treatment by electrical discharge are characterised by a wider plateau at the maximum in the field (Fig. 11, curve 2) in comparison with flame treatment, which is an important technological advantage. Many other oxidising agents have a similar effect. So, for example, extensive oxidation of the surface of PE (being one of the most chemically inert polymers) is achieved by oxidising a hot surface with concentrated hydrogen peroxide, 8% oleum, 9.5% chlorosulphonic; with fluorosulphonic, chromic or nitric acids; with a solution of potassium bichromate in sulphuric acid; and with an acid-water solution of potassium permanganate and gaseous ozone [50]. Despite the large variety of chemical reactions that proceed as a result of the action of these oxidising agents on the surface of a polymer material, the final outcome is

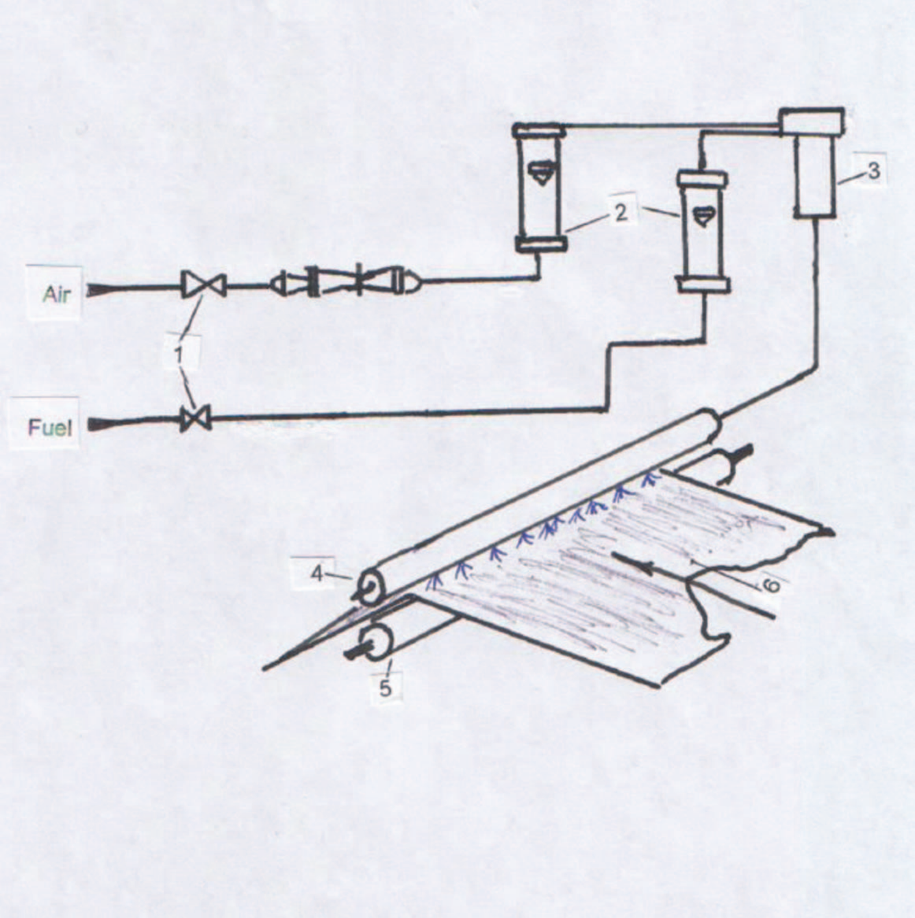
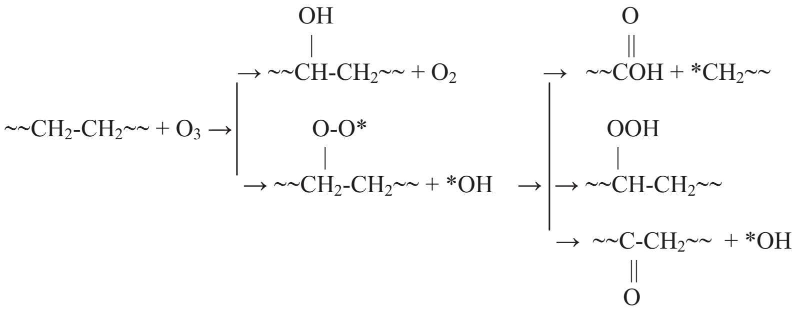


Figure 10. Scheme of flame surface treatment of polymeric films. 1 – regulation taps; 2 – flow meter; 3 – mixer; 4 – burner; 5 – supporting valve.

mostly of a similar nature. It is possible to deduce that all the effects on a polymer surface layer are due to the formation of peroxide radicals in it. Further transformation will depend on the nature of the polymer, the processing temperature and, to a lesser extent, on the nature of the oxidising agent used. In the surface layer molecules are partially degraded and this leads to the accumulation of oxygen-containing functional groups [59–63].

Sometimes surface polymer macromolecules have reactive double bonds. Ozone reacts with such bonds easily, producing ozonides, acids and aldehydes [64]. The decomposition of ozonides to acids and aldehydes occurs mainly through the ionic mechanism and is accompanied by destruction. However, in parallel, small amounts of free radicals are formed and these can initiate the polymerisation processes. For this reason previously ozonised rubbers can be easily modified by grafting [65,66].

Ozone does not react as easily with C—H bonds as with double bonds; it produces alcohols, ketones, acids and peroxides (Scheme 2) [60, 61,64]. The ozone reaction usually produces $\sim$2 functional groups in the reacted ozone. Their concentration in the surface layer increases proportionately with the duration of treatment. The induction effect is not



$$\sim\sim CH_2\text{-}CH_2\sim\sim + O_3 \rightarrow \left| \begin{array}{l} \rightarrow \sim\sim \overset{OH}{\overset{|}{C}}H\text{-}CH_2\sim\sim + O_2 \rightarrow \sim\sim \overset{O}{\overset{\|}{C}}OH + {}^*CH_2\sim\sim \\ \rightarrow \sim\sim \overset{O\text{-}O^*}{\overset{|}{C}}H_2\text{-}CH_2\sim\sim + {}^*OH \rightarrow \left| \begin{array}{l} \rightarrow \sim\sim \overset{OOH}{\overset{|}{C}}H\text{-}CH_2\sim\sim \\ \rightarrow \sim\sim \underset{O}{\underset{\|}{C}}\text{-}CH_2\sim\sim + {}^*OH \end{array} \right. \end{array} \right.$$

Scheme 2.

observed and the ratio of functional groups remains constant in the initial time period (Fig. 13).

As the conversion increases, more reactive peroxide, hydroxyl and carbonyl groups react with the ozone and transform into carboxyl groups. The transient formation of peroxide radicals in the system was detected in direct experiments on their EPR spectra [64,67].

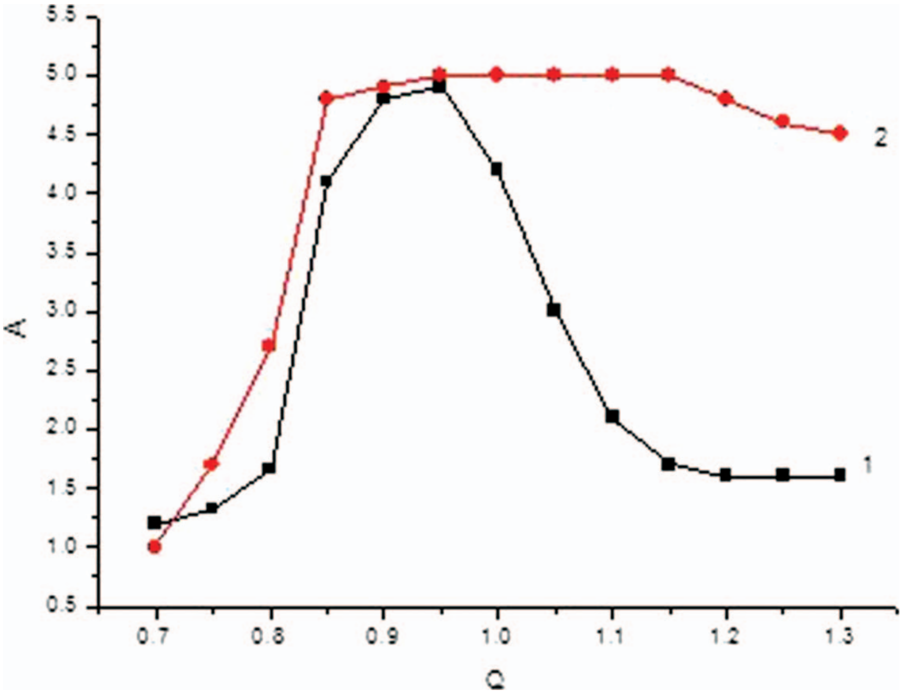


Figure 11. Ink adhesion (A) to PE surface treated by flame (1) and electric discharge (2). A – relative units; Q (for 1) – propane demand, m^3/hour, Q (for 2) – energy of discharge, 300 W.

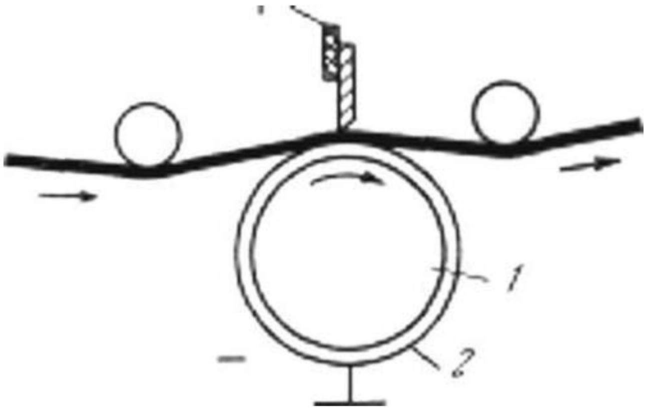


Figure 12. The scheme of a system for film surface treatment by barrier discharge. 1 – metal valve; 2 – dielectric cover.

Increasing Plastic Adhesion

The polyolefins, and many other plastics, are characterised by low adhesion to metals, paper and other surfaces [68,69]. This is due, among other reasons, to the absence of of macromolecular chains with functional groups capable of forming hydrogen bridges or charge transfer complexes with major electrostatic interaction capabilities. These interactions have

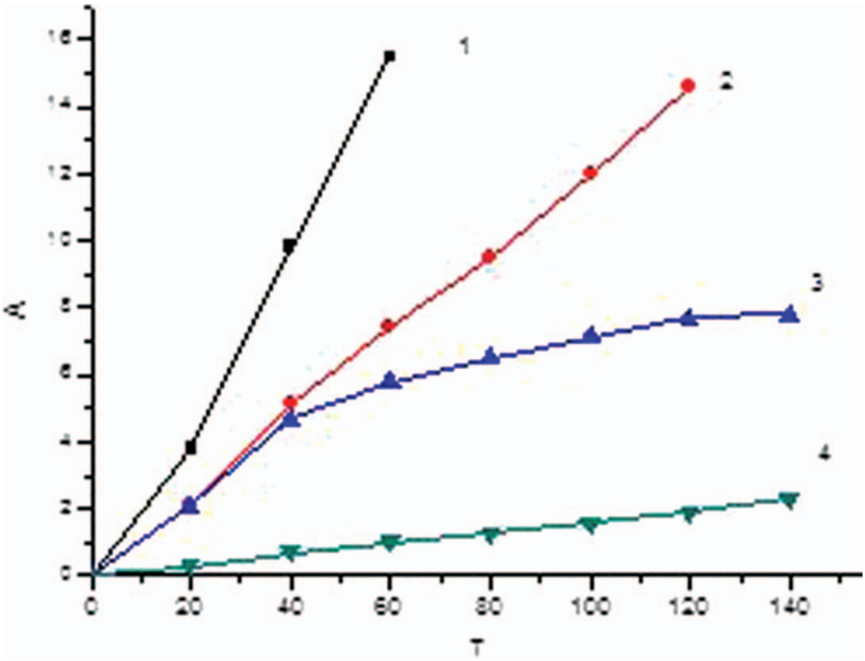


Figure 13. The kinetics of functional groups increasing at the action of O_3 on polystyrene, A – concentrations, mol/l × 10; T – min; 1 – O_3 absorbance; 2 – ~C(=O)~; 3 – —O—O—; 4 – ~C(=O)—OH.

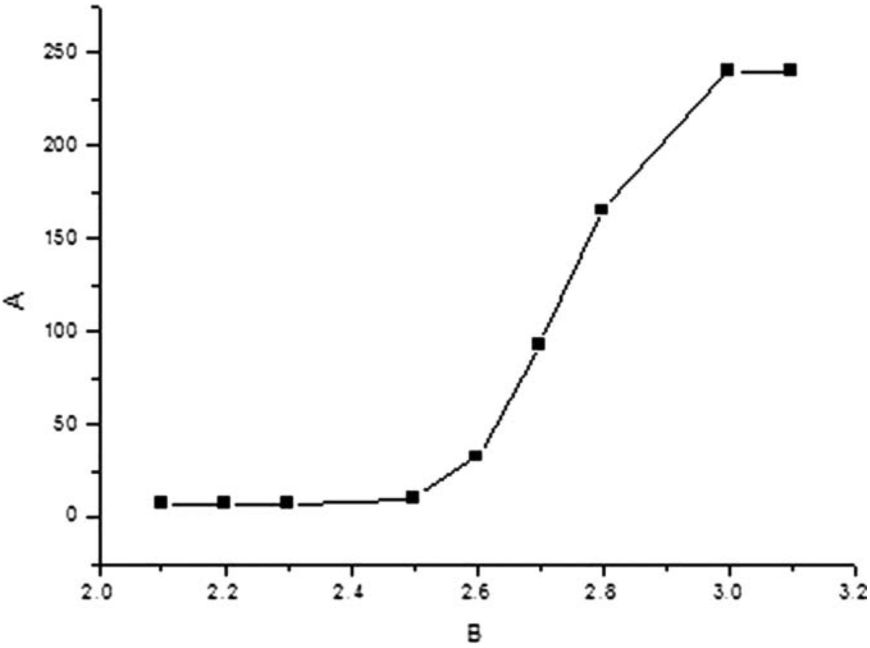


Figure 14. Influence of surface tension (B, N/m^2) on printing dyes adhesion (A, N/m).

an effect on the free surface energy, the energy of cohesion, interfacial tension and other related properties. Published data [70,71] give one an idea of how these interactions or other functional groups are likely to change the properties of a material. The results of measurement of the adhesion of dyes to a treated PE surface were compared with the results for surface tension, γ [72]. From the data given in Fig. 14 it appears that at $\gamma <\sim 2.8$ n/m^2, the adhesion is negligible, nut with a small increase in γ it grows rapidly, reaching maximum values at $\gamma \sim 3$–3,1 n/m^2.

It is possible to increase the adhesion of a surface coating to other materials by introducing polar units to macromolecules by copolymerisation of ethylene with vinyl acetate [73,74], acrylonitrile [75] or methyl methacrylate [76].

Alongside the modification of polymers by synthetic procedures, a wide variety of results was obtained in the above-described processes of oxidising modification [77]. For example, with regard to anti-rust coatings on metals, the method of flame spray coating simultaneously causes the destructive modification of particle surfaces, and as a result the adhesion of a polymer to a surface increases. The concentration of polar functional groups in a contact zone is observed to increase, as do the number of macromolecules strongly bound to the metal [78]. As an example, Fig. 15 shows the resistance to delamination of the connecting surface of PE–steel samples from the time of exposure at different temperatures.

Polar groups appearing in the course of thermo-oxidation in a contact layer can often participate in the formation of adhesive links due to the speed with which the maximum value of affinity forces is reached. The imprinting of decorative designs, the marking and artistic finishing of oil-cloth, packaging materials, etc., manufactured from PE or PETP give rise to major difficulties owing to the poor moistening ability of films and the poor cohesion of colorants [79]. However, the widespread use of treatment by electric discharge has appreciably solved this problem (Fig. 11). When treatment by electric discharge does

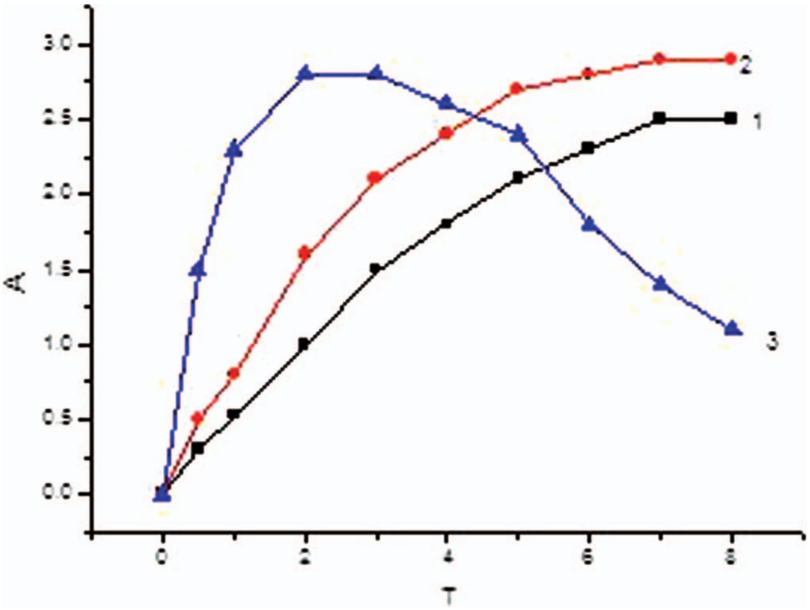
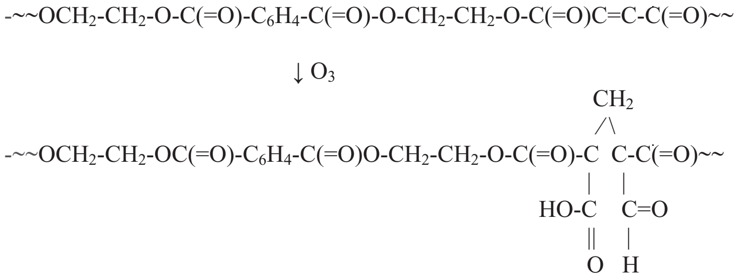


Figure 15. The dependence of resistance to delamination of connection surface PE-steel samples from time of exposure on air at different temperatures [78].

not produce the desired outcome, there are various ways of getting around the problem. In particular, in PETP films good outcomes have been obtained by the initial introduction to macromolecules of PETP fragments of unsaturated cyclic dicarboxylic acids and then subsequent destruction by ozone (Scheme 3) [80]. This allows a limited number of polar groups to form on the PETP, which decreases the electro-affinity of the surface. The above-mentioned ways of obtaining functional groups are used in the method of "active points" for the creation of reactive centres for grafting [81]. Surface treatment by hot air [82] or ozone [83,84] can be applied for the addition of various vinyl monomers to polyamides, polyolefins, starch and other substances.


$$-\sim\sim OCH_2\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}C_6H_4\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(=O)C=C\text{-}C(=O)\sim\sim$$

$$\downarrow O_3$$

$$-\sim\sim OCH_2\text{-}CH_2\text{-}OC(=O)\text{-}C_6H_4\text{-}C(=O)O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}\underset{\substack{|\\ HO-C\\ \|\\ O}}{C}\overset{CH_2}{\diagup\diagdown}\underset{\substack{|\\ C=O\\ |\\ H}}{C}\text{-}C(=O)\sim\sim$$

Scheme 3.

Modification of a Plastic Surface by Oxidising Pickling

Pickling processes are widely used for the plating of plastics [85,86]. Many goods are produced from metallised plastics. The activation of a surface before vacuum spraying of a decorative metal layer is usually carried out with the help of a flame or electric discharge [87,88], whereas before electrochemical plating of metal on a polymer surface it is usually prepared with solutions of chromates in sulphuric acid or other reagents [88,89]. For the manufacture of containers from silvered PE for the long-life storage of water it is recommended that the PE surface be treated with a chrome mixture to increase the water resistance of joints between the sprayed silver and the polymer [90]. The pickling of a surface of carbon filaments by nitric acid increases the strength of carbonic plastics and considerably improves other physical-mechanical indexes [91]. In scientific research pickling has been widely applied to investigate defects in crystal units. The detection of defects in such units is based on greater light permeability and higher solubility of the reagent in the less ordered zones of a partly crystallised material and, as a consequence, a higher rate of amorphous zone degradation [92]. The pickling of cellulose, polyethers and polyamides proceeds easily under the action of acids and alkalis.

Methods based on oxidising destruction have been designed for carbon chain polymers. In particular, optimum conditions for PE pickling by fuming nitric acid were developed [93]. Dicarboxylic acids were obtained as the main product after such treatment. Acids produced from highly crystallised PE were rather homogeneous and had identical chain lengths [94]. At low temperatures the molecular mass shows the greatest change, while the changes in density and degree of crystallinity are insignificant. All this implies that after a chain has been broken, the fragments do not vary. The decrease in the chain length of retained oligomer crystals frequently stops completely after a particular time.

Another reagent used for pickling is ozone [93]. It is a softer destructive agent than fuming nitric acid and it can be applied at room temperature, when even the poor crystallites are fairly steady. The products of reaction are mainly dicarboxylic acids, which are easy to remove by extraction. It was concluded from the determination of the molecular mass of disrupted polymers that macromolecules end up on the border of crystallites, mostly on tucks and in chains of oligomer acids appropriate to single and double widths of a crystallite [95]. The length of received acids at the time of pickling permanently decreased, mirroring the change in the boundary between accessible and inaccessible layers of crystallites. There are a number of specific reagents for disrupting the pickling of PETP, for example methylamine [96]. For pickling polyoxymethylene, heating is applied at high pressure [97].

In electron microscope research pickling is frequently done by gas discharge at pressures of 10^{-3}–10^{-4} Torr [98]. The oxygen atoms and ions generated during discharge destroy and erase the surface layers of a material. The rates of degradation depend on the degree of ordering [99]. The nylon 6,6 and PETP formed after pickling showing characteristic lamellar structure [100]. The method of pickling by gas discharge is usually more informative than methods based on solvent extraction [101,102].

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