SURFACE MODIFICATION OF POLYCARBONATE IN LOW-PRESSURE ABNORMAL DC GLOW DISCHARGE PLASMA FOR ADHESIVE BONDING

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Abstract - The article presents the results of a comprehensive study of the impact of ion-plasma modification in a low-pressure abnormal DC glow discharge on the surface physicochemical properties and mechanical performances of polycarbonate single lap adhesive joints. It has been established that ion-plasma treatment leads to a radical decrease in the contact angle from the initial value of 74° for the untreated sample down to the minimum of 17° for the optimal treatment mode, particularly glow discharge`s power of 50 W, exposure time of 180 s, the cathode-substrate distance of 20 mm at a gas pressure in the reactor of 13 Pa. It was shown that the polycarbonate surface treatment on this mode leads to a simultaneous increase in surface microroughness from 0.012 – 0.015 μm up to 0.156 – 0.164 μm and the polar component of its free surface energy due to the generation of active functional groups. This causes a multiple increase in the thermodynamic work of adhesion at the interface from W_a = 92.9 mJ/m^2 up to 142.42 mJ/m^2. Studies of the strength properties of adhesive joints have shown that the change in the thermodynamic characteristics of polycarbonate surfaces after their plasma treatment significantly affects the operational performances of the structure. It is shown that the initial chemical inertness and hydrophobicity of polycarbonate surfaces dramatically limits the strength of its single lap adhesive joints at the level of 1.6 MPa with a typical adhesive type of failure. After ion-plasma modification with optimal technological parameters, the shear strength of polycarbonate adhesive joints increases by 5 times and reaches the maximum value at a level of 8.06 MPa with the dominant cohesive failure.

Keywords: Polycarbonate, Plasma surface modification, Abnormal glow discharge, Adhesive bonds.

1. Introduction

Polymeric materials have found extensive industrial applications owing to their flexibility, transparency, low density, and cost-effectiveness. Among this class of materials, polycarbonate (PC) occupies a prominent position as an amorphous thermoplastic characterized by an exceptional combination of high impact strength, optical transparency, thermal stability, and low weight [1,2]. These properties have led to its widespread use in mechanical engineering, the aerospace industry, biomedical applications, optical instrumentation, and numerous other technological fields.

However, the implementation of polycarbonate in advanced structural assemblies requires the formation of both homogeneous (polymer–polymer) and heterogeneous (polymer–metal) permanent joints. Conventional mechanical joining techniques, such as bolted and riveted joints, introduce localized stress concentrations and compromise the sealing integrity of the assembled structure [3,4]. Likewise, thermal welding often results in localized overheating, leading to thermal degradation of the polymer matrix and the development of residual thermal stresses [5]. Consequently, adhesive bonding of polycarbonate sheets has emerged as a promising alternative, providing a more uniform stress distribution, reduced structural weight, improved sealing performance, and electrical insulation while preserving the optical transparency of the assembly [6].

Nevertheless, like most polymers, polycarbonate exhibits low surface free energy and high chemical inertness, resulting in poor wettability and limited adhesive affinity [7,8]. Consequently, the direct manufacturing of high-strength adhesive joints is

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generally not feasible without prior surface treatment.

Among the available surface preparation techniques for polymer bonding, physical surface activation and modification methods, particularly those employing the distributed low-temperature plasma of an abnormal DC glow discharge, have attracted considerable attention as efficient, environmentally friendly, and highly controllable approaches [9-11]. The main advantage of plasma treatment is its ability to selectively modify the surface chemistry and morphology at the nanoscale while preserving the bulk mechanical and optical properties of the polycarbonate substrate.

When exposed to the low-temperature gas-discharge plasma, generated by an abnormal DC glow discharge, the polymer surface is simultaneously bombarded by a variety of chemically and energetically active plasma species. The energies of these species are sufficient to destroy existing chemical bonds, resulting in the formation of free radicals and new unsaturated bonds within the near-surface layer. Although the gas temperature in non-equilibrium "cold" plasma remains relatively low, it significantly affects the kinetics of plasma-induced surface reactions. At relatively low energies of the active plasma species, surface activation predominates and is primarily manifested by the removal of organic contaminants and the incorporation of oxygen- and nitrogen-containing polar functional groups. These processes increase the surface free energy, alter the wettability of the substrate, and modify both the chemical composition and molecular structure of the surface layer [12]. As the treatment dose increases, the depth of the modified layer also increases. Under these conditions, the near-surface region undergoes intensive formation and destruction of functional groups, cleavage of chemical bonds and polymer chains, generation of free radicals, formation of unsaturated bonds and intermolecular cross-links, as well as the evolution of low-molecular-weight volatile products. The latter is accompanied by partial material removal from the polymer surface, i.e., plasma etching [13].

The effectiveness of plasma surface modification, however, strongly depends on the appropriate selection of treatment parameters. Improper combinations of discharge current, treatment duration, and substrate position within the plasma can result in either insufficient surface activation or excessive plasma etching, leading to the formation of weak hydrophobic surface layers that diminish the beneficial effects of plasma treatment on adhesion.

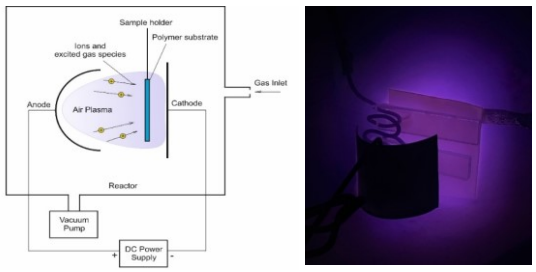
The objective of the present study is to investigate the influence of the energy-related parameters of low-pressure abnormal DC glow discharge plasma treatment on the mechanical performances of adhesive joints formed from polycarbonate.

2. Experimental Procedure

The studies were conducted on samples of monolithic transparent polycarbonate measuring 70×15×5 mm, cut from the same sheet. Before treating, all samples were washed with distilled water followed by ultrasonic cleaning for 5 min.

Plasma treatment of PC samples was carried out by low-pressure air plasma DC glow discharge at pressures of 13–26 Pa for 30, 60, 180 and 300 s. The discharge current varied in the range of 10–75 mA. The voltage drop across the discharge electrodes varied in the range of 600–1200 V. Thus, the discharge power varied from 6 up to 90 W.

The glow discharge was initiated according to a diode scheme in which the cathode was a plate made of S235J0 steel, measuring 50×40×0.8 mm. A hollow copper half-cylinder with a height of 50 mm, a wall thickness of 0.8 mm and a lateral surface radius of 25 mm was used as the anode. It was believed that such a geometry of the electrode system would provide a more focused movement of charged particles from the anode toward to the cathode. The experimental scheme and the treatment process itself are shown in Figure 1.



(a) (b)

Figure 1: Experimental scheme (a) and external view (b) of the treatment process of polycarbonate surfaces in a glow discharge plasma

The glow discharge was ignited using a modified URM-3 vacuum resistive deposition system, originally designed for the sequential deposition of thin-film components and electronic circuit elements that is given in Figure 2. The system was equipped with a dedicated DC glow discharge power supply and a gas delivery system to establish and maintain the required process atmosphere.

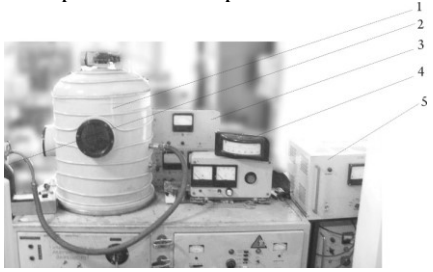


Figure 2: Experimental setup: 1 – vacuum chamber; 2 – gas supply equipment; 3 – VT-2A-P vacuum gauge; 4 – temperature control device; 5 – glow discharge power source

To identify the optimal glow discharge region for effective surface modification of PC, the samples were positioned at distances of 20 and 40 mm from the cathode surface. Under the selected discharge conditions, these positions corresponded to the cathode dark space and to the interface between the negative glow region and the Faraday dark space, respectively. A double sample holder was used, thus performing paired treatment in one working cycle. The interelectrode distance was fixed at 70 mm. The temperature of the cathode and samples while treatment was controlled by a K-type thermocouple.

The effectiveness of the surface treatment was evaluated by measuring the static water contact angle using the sessile drop method with an optical contact angle goniometer. Contact angle measurements were performed immediately after plasma treatment. Distilled water was used as the test liquid. The surface topography of the samples before and after treatment was investigated using a TMR-200 contact profilometer. The study was carried out on three areas of the sample, the measurement results were averaged.

Adhesive joints of polycarbonate samples were obtained using a one-component ethyl cyanoacrylate based adhesive Akfix 705. The adhesive was applied to one of the plasma-treated surfaces and uniformly spread using a special applicator to obtain a bond-line thickness of 0.2 mm. The specimens then were assembled with an overlap length of 20 mm and held under light compressive pressure to cure for 2 h. The lap shear tests of the adhesive joints were performed using a tensile testing machine for textile materials, as shown in Figure 3.

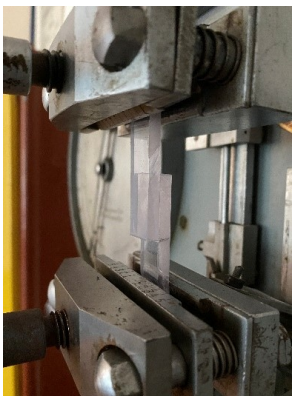


Figure 3: Experimental setup for mechanical tests

3. Results and Discussions

3.1 Hydrophilic Analysis of Plasma Treated Samples

The study of the activation effect of the glow discharge began with determining the impact of its energy characteristics on the wettability of the PC surface with distilled water depending on the exposure time when the discharge power was changed from 6 to 90 W.

In these experiments, the treated samples were positioned at 20 mm from the cathode surface. The gas pressure was maintained at 13 Pa. The initial (untreated) PC surface exhibited a water contact angle of 72–74°. The experimental results are presented in Figure 4.

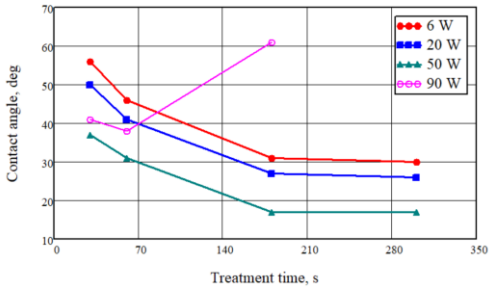


Figure 4: Dependence of the distilled water contact angle of PC specimen surfaces on the treatment time in air plasma DC glow discharge at powers of 6, 20, 50, and 90 W and a pressure of 13 Pa

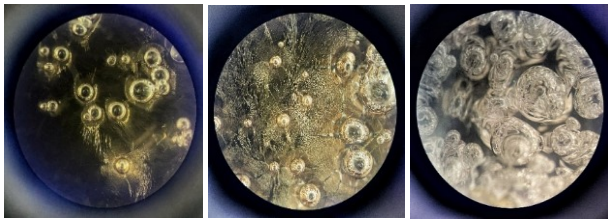
The graphs demonstrate that increasing the glow discharge power from 6 up to 50 W results in a significant decrease in the water contact angle throughout the entire investigated treatment time. Even the first 30 s of plasma exposure reduced the contact angle to 56–37°, corresponding to a decrease of 24–50% relative to the untreated samples when the glow discharge power was increased from 6 to 50 W. Increasing the treatment time under these conditions up to 180 s further enhanced the hydrophilicity of the PC surfaces, resulting in a pronounced reduction of the water contact angle to 31° and 17° at discharge powers of 6 and 50 W, respectively, which corresponds to a decrease of 58–77% compared with the initial (untreated) surface. The improvement in surface wettability is attributed to plasma-chemical activation of the polycarbonate surface in air plasma, accompanied by intensive cleavage of existing polymer bonds and the formation of polar oxygen-containing functional groups, such as carbonyl (C-O), hydroxyl (OH), and carboxyl (COOH) groups [14].

With a nearly twofold increase in glow discharge power to 90 W, a reduction in the surface activation efficiency is observed. After 30 s of treatment under these conditions, the water contact angle increased to 44°, compared with 37° obtained after treatment at 50 W. Extending the treatment time to 60 s still resulted in a certain improvement in surface wettability however, the contact angle increased to a value comparable to that obtained after treatment at a discharge power of 20 W, reaching 40°.

At the same time, the polycarbonate surfaces treated in the 90 W glow discharge plasma for 60 s exhibited a visually noticeable deterioration in optical properties, manifested as slight yellowing. This indicates a transition from surface functionalization processes to the initial stage of thermo-oxidative degradation of the polymer,

associated with carbonization of the near-surface layer. Further increasing the exposure time to 180 s resulted in significant surface rehydrophobization, accompanied by a rapid increase in the water contact angle to 61°.

The morphological analysis of the structure of polycarbonate after 180 s of treatment at a discharge power of 90 W revealed the presence of gas blisters and a microcracks network within the surface layer. The size and number of these defects increased dramatically with further extension of the treatment duration to 300 s as shown in Figure 5.



(a) (b) (c)

Figure 5: Morphological picture of the nucleation and growth of gas-induced blisters in a polycarbonate layer during high-energy treatment in glow discharge plasma for 180 s (a), 240 s (b) and 300 s (c)

Gas-induced blistering in the surface layer of polycarbonate results from the combined effects of radiation-chemical and thermal degradation of the polymer. During this process, localized cleavage of carbonate and ether bonds within the main polymer backbone occurs, accompanied by the formation and accumulation of gaseous degradation products, including CO, CO_2, H_2O, and low-molecular-weight organic compounds [15]. The accumulation of these products leads to a localized increase in internal pressure and the formation of characteristic globular blisters.

The macroscopic changes in the morphology and optical properties of polycarbonate observed during prolonged exposure at a 90 W glow discharge plasma indicate excessive energy input from charged plasma species, particularly working gas ions, onto the treated surfaces. As is well known, under abnormal glow discharge conditions, when the cathode area remains constant, an increase in discharge power can only be achieved through a further increase in the voltage across the electrode gap, with a significant fraction of this voltage being concentrated within the cathode fall region [16]. This results in an avalanche-like increase in the concentration of charged species and, consequently, in their energy due to the enhanced number of ionization events occurring within this region.

In turn, PC specimens positioned within the cathode fall region (in the present study, at 20 mm from the cathode) and located along the ion transport path act as an effective ion sink. Therefore, increasing their exposure time under high-intensity plasma conditions inevitably leads to excessive irradiation and overexposure of the polymer surface. In the present study, the energy of ions and chemically active atoms bombarding the substrate was determined by calculation using a modified version of the model proposed by Davis and Vanderslice given in [17].

$$\frac{d\mathrm{N}}{d\mathrm{E_i}} = \frac{N_\mathrm{i}}{2}\frac{L}{\lambda}\left[1-\frac{E}{U_\mathrm{c}}\right]^{\frac{1}{2}} \exp\left[-\frac{L}{\lambda}+\frac{L}{\lambda}\left(1-\frac{E}{U_\mathrm{c}}\right)^{\frac{1}{2}}\right], \quad (1)$$

where, N_i – the number of ions entering the cathode dark space; E_i – ion energy; U_c – cathodic potential drop; λ – the free path length of the ions; L – the width of the cathode dark space.

Then the average energy of ions bombarding the cathode surface can be defined as:

$$E_\mathrm{i} = U_\mathrm{c}\left[2\frac{\lambda}{L}-2\left(\frac{\lambda}{L}\right)^2+2\left(\frac{\lambda}{L}\right)^2\exp\left(-\frac{\lambda}{L}\right)\right], \quad (2)$$

and the energy of neutral atoms is as follows:

$$E_n = U_c\frac{\lambda}{L}\left[1-2\frac{\lambda}{L}+2\left(\frac{\lambda}{L}\right)^2-2\left(\frac{\lambda}{L}\right)^2\exp\left(-\frac{L}{\lambda}\right)\right], \quad (3)$$

In turn, the dark cathode space`s length is determined by the Child – Langmuir equation [18]:

$$L = \left[\frac{4\varepsilon_0}{9J}\right]^{\frac{1}{2}}\left[\frac{4q}{M}\right]^{\frac{1}{4}}U_c^{\frac{3}{4}}, \quad (4)$$

where, J – cathode current density; q – electron charge ($1.6\cdot10^{-19}$ C), M – ion mass (for air ions M ≈ $4.8\cdot10^{-26}$ kg); ε_0 – vacuum permittivity ($8.85\cdot10^{-12}$ F·m^{-1}).

At the same time, the free path length of ions in the gas medium will depend on the gas pressure in the reactor and is defined as follows:

$$\lambda = \frac{kT}{P\sigma}, \quad (5)$$

where, k – Boltzmann constant ($1.3\cdot10^{-23}$ J·K^{-1}); P – gas pressure, Torr; σ – ionization cross section ($0.5\cdot10^{-16}$ cm^2); T – cathode temperature, K.

The results of the calculated ions and neutral atoms energies for gas pressures of 13 and 26 Pa, obtained using Equations (2) and (3), are presented in Figure 6. It should be noted that under ion-plasma treatment conditions in a glow discharge, the substrate is exposed not only to ions and neutral atoms but also to quanta of radiative energy (photons) emitted during recombination processes in the negative glow region. Since it is not possible to quantitatively determine the number of photons reaching the substrate, the total energy delivered to

the material is conventionally attributed primarily to ions action.

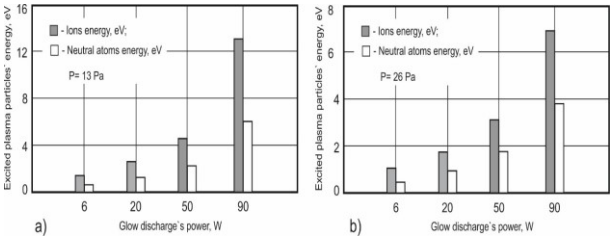


Figure 6: Dependences of ions and neutral atoms energy on the change in the glow discharge power from 6 to 90 W for gas pressures in the reactor of 13 Pa (a) and 26 Pa (b)

The calculations revealed that, with an increase in glow discharge power from 6 to 50 W at a gas pressure in the reactor of 13 Pa, the energies of ions (E_i) and neutral atoms (E_n) bombarding the substrate increased from E_i = 1.36 eV and E_n = 0.67 eV to E_i = 4.29 eV and E_n = 2.1 eV, respectively. The total energy contribution of plasma species to the substrate surface was estimated as E_{i+n} = 2.03 eV and E_{i+n} = 6.39 eV for discharge powers of 6 and 50 W, respectively. With a further increase in the glow discharge power up to 90 W, the kinetic energies of ions and neutral atoms increased approximately in three times, reaching values of E_i = 13.3 eV and E_n = 6.56 eV. The combined energy input of these species exceeded the dissociation energy of the main chemical bonds in polycarbonate (3.2–4.5 eV) by four times. Increasing the reactor gas pressure to 26 Pa resulted in a reduction of the mean free path of charged species from 8.039×10^{-4} m to 4.04×10^{-4} m, leading to an almost twofold decrease in their kinetic energy. However, even at a discharge power of 90 W, the energies of ions and neutral atoms remained sufficiently high, reaching E_i = 6.8 eV and E_n = 3.7 eV, respectively. The total energy input under these conditions still exceeded the dissociation energy of the polymer chemical bonds by more than a twice. Such high-energy bombardment initiates a series of destructive processes within the polymer, associated with cascade degradation and extensive scission of the polymer backbone, resulting in the breakdown of macromolecular chains to considerable depths.

Thus, treatment in glow discharge plasma at a power of 50 W can be considered optimal for polycarbonate surface preparation, as it provides a thermodynamic and kinetic balance between surface activation and thermal degradation of PC.

The impact of the spatial position of the specimens within the gas-discharge plasma and the working gas pressure on the wettability of the PC surface as a function of treatment time was investigated at a fixed glow discharge power of 50 W. The experiments were performed by varying the cathode-to-substrate distance ($L_{c\text{-}s}$) from 20 to 40 mm.

The gas pressure in the working chamber was varied within the range of 13–26 Pa. The experimental results are given in Figure 7.

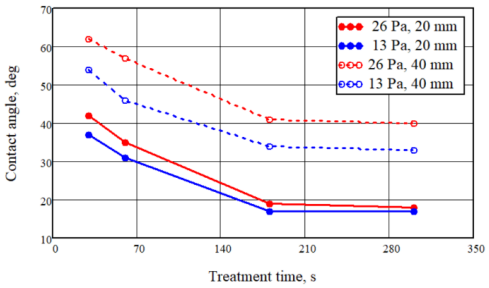


Figure 7: Dependence of the water contact angle of PC specimen surfaces on the treatment time in air glow discharge plasma at a discharge power of 50 W, with variation of the $L_{c\text{-}s}$ from 20 to 40 mm and gas pressure from 13 to 26 Pa

As was expected, increase in $L_{c\text{-}s}$ from 20 to 40 mm weakens the activation effect of the glow discharge. Under all investigated treatment conditions, the water contact angle increased by approximately 15–17°. At a gas pressure of 13 Pa in the reactor, moving the specimens from 20 to 40 mm away from the cathode shifts their position from the most energetic region of the glow discharge (the cathode fall region) into the negative glow region, which is characterized by a relatively low electric field strength. The most intensive volume ionization processes occur in this region. However, due to the absence of a significant accelerating potential, newly generated ions do not acquire sufficient kinetic energy to induce deep chemical activation of the polycarbonate surface.

As was demonstrated above, increasing the working gas pressure from 13 to 26 Pa reduces the mean free path of charged species, which intensifies volume recombination processes, decreases the discharge sustaining voltage, and causes geometrical contraction of the negative glow region toward the cathode. Under these conditions, specimens positioned at a distance of 40 mm are no longer located within the negative glow (NG) region but rather within the Faraday dark space, where volume ionization processes are absent. Most ions generated in the NG region recombine in this area, returning to neutral gas molecules [19]. This significantly complicates the conditions for ion-plasma surface activation, resulting in an additional increase in the water contact angle of PC surfaces by 8–10°. On average, these values are approximately 15% higher than those ones obtained after treatment at a gas pressure of 13 Pa.

Therefore, increasing the gas pressure from 13 to 26 Pa at a cathode-to-substrate distance of 40 mm represents an additional adverse factor that deteriorates the conditions for effective PC surface modification.

3.2 Work of Adhesion Calculations

The reduction in the water contact angle after glow discharge plasma treatment indicates a significant restructuring of the energetic state of the polycarbonate surface. To provide a more detailed evaluation of this interaction, the work of adhesion (W_a) was calculated as a quantitative parameter characterizing the strength of interfacial interactions in the "activated PC–liquid" system. According to the calculations, the work of adhesion for the untreated specimen with a contact angle of 74° was W_a = 92.9 mJ/m^2.

In Figure 8 the dependences of the work of adhesion on glow discharge power for exposure time ranging from 30 to 180 s under fixed gas pressure of 13 Pa and cathode-to-substrate distance of 20 mm are given.

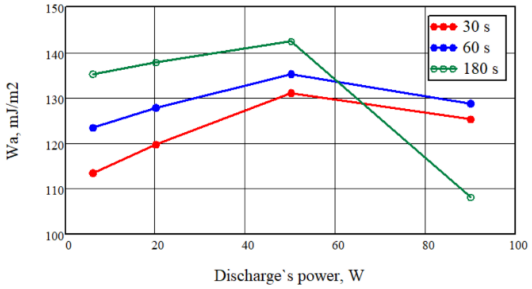


Figure 8: Dependences of the work of adhesion of the PC surface on the power of the glow discharge for different treatment time: t = 30 – 180 s, P = 13 Pa, Lc-s = 20 mm

The calculated thermodynamic characteristics of the PC surface after glow discharge plasma treatment are in full agreement with the previously obtained kinetic dependences of the water contact angle. Increasing the glow discharge power from 6 to 50 W resulted in a linear increase in the work of adhesion, reaching a maximum value of W_a = 142.42 mJ/m^2, which corresponds to the minimum water contact angle of 17°. A further increase in discharge power to 90 W led to deterioration of the thermodynamic surface characteristics of polycarbonate, manifested by a reverse increase in the water contact angle and, consequently, a decrease in the work of adhesion. Moreover, prolonged exposure for 180 s at a discharge power of 90 W resulted in a substantial reduction in the work of adhesion to W_a = 108.1 mJ/m^2, corresponding to the maximum water contact angle of 61°. This decrease indicates that instead of the expected accumulation of polar active sites under these treatment conditions, chemical degradation and surface erosion occur, which suppress the contribution of the polar component of the surface energy.

In Figure 9 the dependences of the work of adhesion on the cathode-to-substrate distance for gas pressures ranging from 13 to 26 Pa under fixed discharge power of 50 W and an exposure time of 180 s are shown.

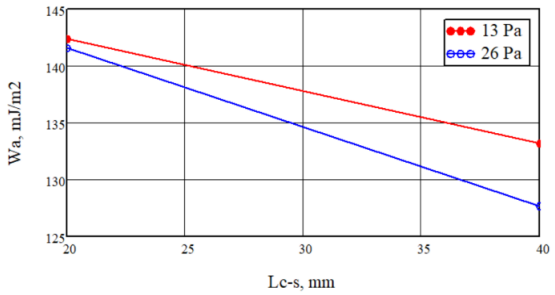


Figure 9: Spatial dependence of the work of adhesion (W_a) on the cathode-to-substrate distance (L_{c-s}) at pressures of 13 and 26 Pa, with a discharge power of 50 W and a treatment time of 180 s

The obtained results demonstrate that, at a fixed discharge power of 50 W and a treatment time of 180 s, increasing the cathode-to-substrate distance from 20 up to 40 mm at a gas pressure of 13 Pa leads to a decrease in the work of adhesion from W_a = 142.42 mJ/m^2 to W_a = 133.2 mJ/m^2. In contrast, increasing the gas pressure in the discharge chamber to 26 Pa under the same treatment conditions results in a more pronounced deterioration of the adhesive properties of the PC surface. In this case, increase in the L_{c-s} from 20 to 40 mm reduces the work of adhesion from W_a = 141 mJ/m^2 to W_a = 128.6 mJ/m^2. It should be noted that at L_{c-s} = 20 mm, the effect of gas pressure variation from 13 to 26 Pa on the energetic characteristics of the PC surfaces is negligible. This can be attributed to the fact that, despite the contraction of the cathode region of the glow discharge caused by increasing the pressure from 13 to 26 Pa, the specimens positioned 20 mm from the cathode remain within the high-energy region of the discharge, namely the cathode fall region, and continue to experience intensive bombardment by ions and chemically active radicals.

3.3 Surface Roughness of Plasma Treated Samples Measurements

Another important surface characteristic that determines the actual contact area between two solid bodies, adhesion strength, wettability, and other interfacial phenomena is surface roughness. As was already mentioned above, during ion-plasma modification, the polymer surface is continuously bombarded by accelerated ions and other active gas species, which is accompanied by plasma-chemical etching processes at the microscale. This results in the development of surface topography and an increase in the effective contact area with liquids. Therefore, the next stage of this study involved experimental measurements of the surface microroughness (R_a) of PC specimens after glow

discharge plasma treatment. The measurements were performed using a TMR-200 contact profilometer at three different locations on each specimen, and the obtained values were averaged.

In Figure 10 the dependences of PC surface roughness on the treatment time in glow discharge plasma operated at discharge power of 6, 20, 50, and 90 W, a gas pressure of 13 Pa, and a cathode-to-substrate distance of 20 mm are given. The surface roughness of the untreated PC specimens was within the range of 0.012–0.015 μm.

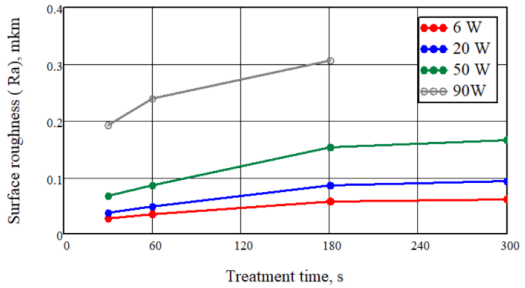


Figure 10: Dependences of the PC`s surface roughness, plasma treated at the glow discharge power of 6, 20, 50, and 90 W, P = 13 Pa, $L_{c\text{-}s}$ = 20 mm on treatment time

Analysis of the obtained surface topography evolution after glow discharge plasma treatment revealed both regions of controlled radiation-induced plasma-chemical modification and associated with destructive erosion of the polymer matrix. The results show that, within the discharge power range of 6–20 W, controlled changes in the PC surface microtopography occur, with maximum roughness values reaching 0.062 and 0.097 μm, respectively, after a treatment duration of 300 s. Increasing the discharge power to 50 W resulted in a rapid increase in surface microroughness, followed by the formation of a plateau at R_a = 0.156–0.164 μm for exposure time of 180–300 s. Such surface morphology is considered optimal for liquid adhesion because it provides a homogeneous wetting mode with a minimum contact angle of 17°, thereby creating favorable conditions for achieving the maximum work of adhesion of W_a = 142.42 mJ/m^2.

In contrast, a further increase in glow discharge power to 90 W initiated a transition toward high-intensity ion etching, resulting in pronounced plasma-chemical erosion of the near-surface layer of PC specimens. The surface morphology obtained under these conditions was characterized by an anomalous increase in microroughness, reaching R_a = 0.307 μm after 180 s of plasma exposure. This excessive development of surface topography is considered to be the reason for the increase in the water contact angle to 61° and the corresponding decrease in the work of adhesion to W_a = 108.1 mJ/m^2. These results demonstrate that, to achieve reliable adhesive bonding of polycarbonate surfaces, the operating parameters of the air plasma of abnormal DC glow discharge should be limited to a discharge power level of approximately 50 W.

In Figure 11 the dependence of the PC`s surface microroughness on the spatial position of the specimens during glow discharge plasma treatment at a discharge power of 50 W and a treatment duration of 180 s for gas pressures of 13 and 26 Pa is shown. The observed trends in the evolution of the PC surface microtopography with variations in the $L_{c\text{-}s}$ and gas pressure during glow discharge plasma modification are in good agreement with the results obtained from the wettability and work of adhesion measurements. As shown in the graphs, increasing the $L_{c\text{-}s}$ from 20 to 40 mm, i.e., moving the specimens toward the anode, is accompanied by a pronounced reduction in the effectiveness of the gas-discharge plasma in modifying the surface microtopography of the PC specimens.

The gas pressure in the reactor has a significant impact on this behavior. At a gas pressure of 13 Pa, the higher energy of the charged species bombarding the substrate (see Figure 6) promotes the development of a well-defined surface microrelief, resulting in a surface roughness of R_a = 0.084 μm even at $L_{c\text{-}s}$ = 40 mm. This value is nearly six times higher than the roughness of the untreated polycarbonate surface. In contrast, increasing the gas pressure in the reactor up to 26 Pa causes contraction of the characteristic glow discharge regions and a reduction in the mean free path of the excited plasma species [20,21]. Consequently, at a cathode-to-substrate distance of 40 mm, the intensity of plasma-surface interactions decreases to a negligible level, and the resulting surface roughness does not exceed R_a = 0.028 μm, approaching that of the untreated material.

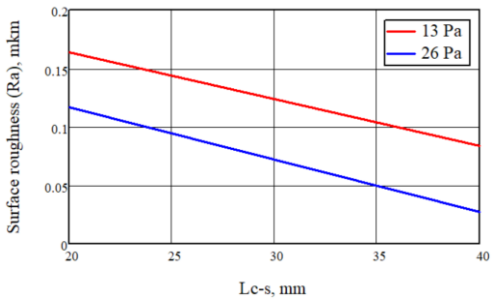


Figure 11: Dependences of the PC`s surface roughness on the spatial position of the specimens, plasma treated at discharge power of 50 W, exposure time 180 s at a pressure in the reactor of 13 and 26 Pa

3.4 Lap Shear Testing of Polycarbonate Single-Lap Adhesive Joints

The combined analysis of the wettability thermodynamics and profilometric characterization of polycarbonate surfaces following treatment in

abnormal DC glow discharge plasma makes it possible to establish the relationship between the structure of the ion-modified surface and its adhesion capability. However, this relationship provides only an indirect indication of the potential strength of adhesive joints. Therefore, the next stage of this study involved a series of mechanical tests to establish a direct correlation between the physicochemical state of the surface and the failure load of single-lap adhesive joints manufactured from polycarbonate specimens treated in glow discharge plasma for 30, 60, and 180 s at discharge powers of 6 and 50 W and a reactor gas pressure of 13 Pa. The bonded area kept constant for all specimens and was equal to 300 mm^2. The obtained results were compared with those for adhesive joints prepared from untreated PC specimens.

In Figure 12 the results of the lap shear tests of the single-lap adhesive joints as a function of plasma treatment time at discharge powers of 6 and 50 W under constant working gas pressure of 13 Pa are given.

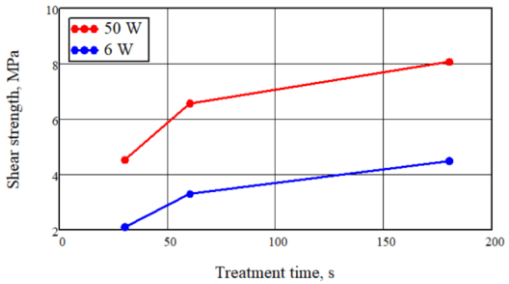


Figure 12: Dependances of shear strength of PC`s single lap adhesive joints on treatment time at discharge powers of 6 and 50 W and pressure in the reactor of 13 Pa

Analysis of the obtained curves reveals the discharge power as the dominant parameter governing the mechanical performance of polycarbonate adhesive joints. At a discharge power of 50 W, the adhesive strength increased markedly throughout the investigated treatment time. After only 30 s of plasma exposure, the lap shear strength reached 4.53 MPa, which is nearly three times higher than that of the untreated joints (1.6 MPa). Extending the treatment time to 180 s further increased the joint strength up to 8.06 MPa, corresponding to a maximum failure load of 2418 N. In contrast, reducing the glow discharge power down to 6 W decreased the effectiveness of surface modification by approximately 30–45% compared with the 50 W treatment. After 30 s of plasma exposure under these conditions, the lap shear strength reached only 2.1 MPa, slightly exceeding the value of the untreated sample. As was discussed above, such low-energy plasma treatment provides a relatively low rate of surface decontamination and generation of adhesion-active sites.

Consequently, increasing the treatment duration to 180 s under these conditions did not produce a substantial improvement in joint strength, which did not exceed 4.5 MPa.

In Figure 13 the fracture morphology of the single-lap adhesive joints after lap shear testing are given. Fractographic analysis of the fracture surface of the untreated PC specimens (see Figure 13a) revealed a purely adhesive type of failure. The fracture micrograph clearly shows complete debonding of the adhesive layer from the polymer substrate. The peripheral regions of the joint contain a large number of cyanoacrylate crystallization dendrites, which are attributed to the relatively high contact angle and poor adhesion of the adhesive layer. These factors prevented the formation of a continuous molecular contact interface throughout the bonded region.

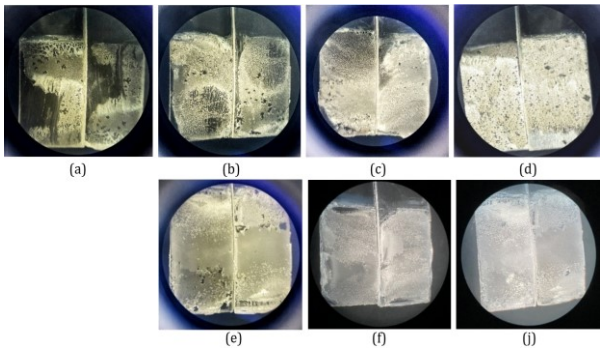
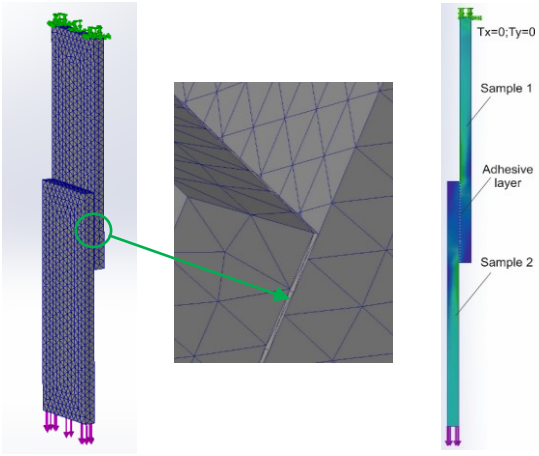


Figure 13: Adhesive failure of untreated PC samples (a); (b), (c), (d) cohesive failure after modification at discharge power of 6 W; (e), (f), (j) cohesive failure after modification at discharge power of 50 W during 30, 60, and 180 s respectively

In contrast, analysis of the fracture surfaces of the PC adhesive joints after plasma modification demonstrates a transition from adhesive to cohesive type of failure. As shown in Figure 13 b,e, the specimens treated for 30 s at both discharge powers exhibit no pronounced regions of adhesive debonding and a significant reduction in dendritic defects compared with the untreated specimens. Increasing the plasma treatment time up to 180 s resulted in further homogenization of the adhesive layer. Nevertheless, the fracture surfaces of the specimens treated at a discharge power of 6 W for 180 s (see Figure 13d) still exhibited local adhesive chipping and micro pull-out of the adhesive layer. By contrast, the fracture surfaces of the specimens treated at 50 W for 180 s were characterized by a uniform adhesive interface over the entire bonded area with a characteristic matte texture that is shown in Figure 13j. The fracture surfaces also exhibited localized micro-shear ridges and edge chipping near both ends of the overlap region, indicating a non-uniform stress distribution that developed during failure of the adhesive joint.

3.5 Stress and Strain Analysis of PC`s Single Lap Adhesive Joints

To investigate the stress–strain state and identify the locations of failure initiation in polycarbonate adhesive joints, finite element simulations were performed using the SolidWorks environment. The finite element model of the single-lap adhesive joint is shown in Figure 14a. The minimum mesh element size, concentrated within the adhesive layer, was 0.15 mm. The upper adherend was fully constrained (Tx = 0; Ty = 0) while tensile failure loads obtained from the experimental tests were applied to the lower adherend (see Figure 14b). Owing to both the geometric nonlinearity of the joint configuration and the nonlinear mechanical behavior of the constituent materials, a static nonlinear finite element analysis was employed throughout the simulations.



(a) (b)

Figure 14: Finite element model (a), boundary conditions and load of joints (b)

In Figure 15 the simulation results for the stress distribution in the polycarbonate adhesive joints under the experimentally determined failure load of F = 2418 N (8.06 MPa), corresponding to the optimum plasma surface modification conditions is given.

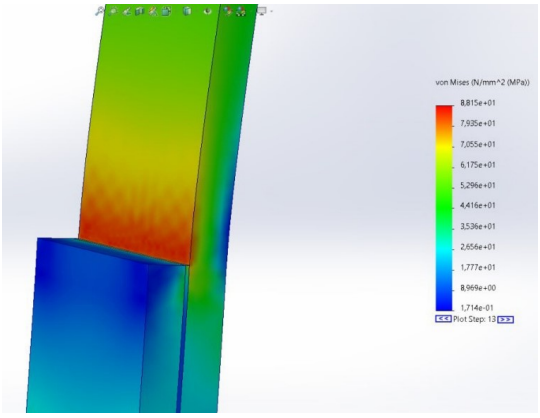


Figure 15: Equivalent stress distribution in PC samples for adhesive joints loaded with F = 2418 N

As can be seen, the maximum equivalent (von Mises) stress calculated for the mentioned above failure load reaches of 88 MPa, which is about 40% higher than the yield strength of bulk polycarbonate (60–65 MPa). It should be noted that these stress concentrations are localized in the immediate vicinity of the edges of the adhesive layer. This indicates that the edge regions of the adhesive joint experience pronounced stress concentrations, causing the polycarbonate adherends to exceed their elastic limit and undergo significant plastic deformation prior to failure.

In Figure 16 the distribution of resultant displacement in the polycarbonate adhesive joint is given. The simulation analysis shows that the maximum displacement immediately before joint failure reaches 2.37 mm, indicating significant plastic deformation of the polycarbonate adherends under mechanical loading. It should also be noted that the deformation process is accompanied by the coupled bending of the polycarbonate adherends due to the bending moment generated by the eccentric application of the tensile load, which is characteristic of single-lap adhesive joints.

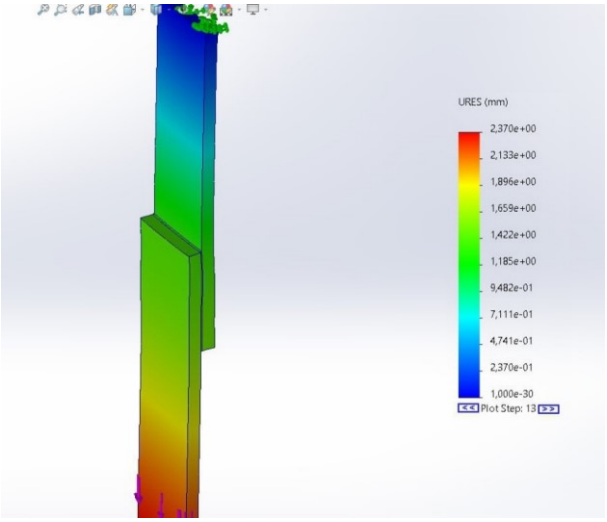


Figure 16: Resultant displacement distribution in the joint loaded by force F = 2418 N

The stress–strain state simulation results presented above correspond to the polycarbonate adherends. However, the load-bearing capacity of adhesive joints is primarily governed by the magnitude and distribution of stresses directly within the adhesive layer.

Analysis of the equivalent stress distribution within the adhesive layer, presented in Figure 17, revealed a local stress maximum of approximately 32 MPa, which is ~40% higher than the tensile strength of the Akfix 705 adhesive itself (15–22 MPa).

To gain a better understanding of the stress field developed within the adhesive layer, a stress distribution profile along the overlap length of the

joint was constructed (see Figure 18). In figure the X-axis is placed in adhesive layer.

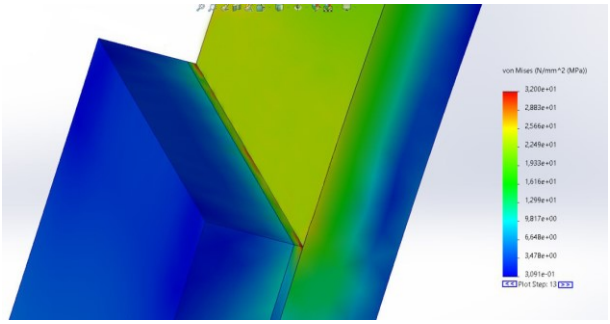


Figure 17: Equivalent stress distribution in adhesive layer

Figure 18: Equivalent stress value as a function of X coordinate

Analysis of the obtained stress distribution curve along the adhesive overlap length (X coordinate) reveals that major part of the mechanical load during joint failure is carried by the edge regions of the adhesive layer. At the left edge of the adhesive layer, located 0.1 cm from the overlap end, a local stress maximum of approximately 32 MPa is observed. In the central region of the joint, within the range of 0.4–1.6 cm, the stress level remains minimal and stabilizes at approximately 5–7 MPa. This indicates that the adhesive layer in this region operates predominantly within the elastic deformation mode.

The right edge of the adhesive layer is characterized by a gradual increase in equivalent stresses, reaching a maximum value of approximately 42 MPa. Such an asymmetric stress distribution along the overlap edges is associated with the development of plastic deformation in the polycarbonate adherends. As discussed above, local equivalent stresses in the polycarbonate reach approximately 88 MPa, accompanied by a complex deformation state with a maximum resultant displacement of 2.37 mm.

4. Conclusions

The obtained results demonstrate that the improved hydrophilicity of polycarbonate surfaces following low-pressure DC glow discharge plasma treatment results from the combined effects of surface modification and the development of its microtopography. It was established that the discharge power and exposure time have the most significant influence on surface wettability. Increasing these parameters from 6 to 50 W and from 30 to 180 s, respectively, leads to a substantial reduction in the water contact angle and an increase in surface microroughness.

It was shown that reducing the gas pressure from 26 to 13 Pa and decreasing the cathode-to-substrate distance from 40 to 20 mm further enhance the efficiency of plasma modification by increasing the energy of the plasma species bombarding the substrate. Under treatment conditions of a 50 W glow discharge in air plasma at a gas pressure of 13 Pa for 180 s, and a cathode-to-substrate distance of 20 mm, the maximum hydrophilization of the polycarbonate surface was achieved, as evidenced by a reduction in the contact angle from an initial value of 74° to 17° and an increase in surface microroughness to Ra = 0.156–0.164 μm. These results identify such a treatment mode as the optimal for polycarbonate surface activation prior to adhesive bonding.

It was experimentally demonstrated that glow discharge plasma modification of the polycarbonate surface layers has a direct impact on the mechanical performances of its adhesive joints. The lap shear strength of adhesive joints produced from untreated polycarbonate did not exceed 1.6 MPa and was characterized by a brittle adhesive failure mode. In contrast, ion-plasma surface activation under the experimentally established optimum treatment conditions increased the lap shear strength by a factor of five, reaching 8.06 MPa, which corresponds to a failure load of 2418 N. Furthermore, the failure mechanism changed from adhesive to cohesive, indicating a substantial improvement in interfacial adhesion.

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