Application of Radio Frequency Glow Discharge Plasma for Enhancing Adhesion Bonds in Polymer/Polymer Joints

B. Lapèíková,[1] L. Lapèík Jr.,[1] P. Smolka,[1] R. Dlabaja,[1] D. Hui[2]

[1]*Institute of Physics & Materials Engineering, Faculty of Technology, Tomas Bata University in Zlín, Nad Stráněmi 4511, CZ-760 05 Zlín, Czech Republic*
[2]*Department of Mechanical Engineering, University of New Orleans, New Orleans, Louisiana 70148*

ABSTRACT: It was found in this study, that air radio frequency glow discharge (rfGD) plasma is increasing surface roughness and is enhancing wettability of poly(propylene) (PP), poly(ethylene) (PE), and poly(carbonate) (PC). As an addition, the increased surface microhardness of PP and PE was found. Results indicate that rfGD air plasma treatment is very effective tool for improvement of adhesive properties of studied polymers as tested on single lap and double lap joints. The value of maximum load rise from 107 to 1926 N (approximately 18-fold increase) for 20-min-treated PE and from 314 to 834 N (approximately three-fold increase) for PP. Artificial accelerated ageing rapidly decreased the quality of adhesive joint. The value of maximum load decreased from 1926 to 221 N (approximately nine-fold decrease) in the case of 20-min-treated PE. This result indicates that the ageing of the adhesive joint of plasma treated polymers can be a limitation factor in the possible application of the final component because of the extremely high loss of its initially-enhanced mechanical properties. However, the strength of the thus prepared joints was higher in comparison to the plasma nontreated virgin samples. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1827–1833, 2006

Key words: adhesion; surface properties; mechanical testing; joints/joining

INTRODUCTION

In any product, there are generally several parts or components joined together to make the complete assembly. Main purpose of the joint is to transfer loads from one member to another, or to create relative motion between two members.

In the structure, a joint is the weaker area and most failures emanate from joints. Because of this, joints are eliminated in the construction by integrating the structure. Adhesive bonding is the most common type of joint used in composites manufacturing. In adhesive bonding, two substrate materials are joined together by an adhesive (e.g., epoxy, polyurethane, methyl acrylate, etc.). Joining of materials using an adhesive offers several benefits over mechanical joints:[1,2]

1. The load at the joint interface is distributed over an area rather than concentrated at a point.
2. Joints are more resistant to flexual, fatigue, and vibrational stresses.

3. Weight penalty is negligible compared to mechanical joints.
4. Adhesive not only bonds the two surfaces but also seals the joint, preventing thus corrosion.
5. Can be more easily adapted to join irregular surfaces than mechanical joints.
6. Provides smooth contours and creates virtually no change in part dimensions (design of aerodynamic shapes).
7. Is often less expensive and faster than mechanical joining.

Adhesive bonding has also several technological disadvantages, in comparison with mechanical joints. It requires surface preparation before bonding; heat and pressure may be required during the bonding operation, thus limiting the part size (autoclave etc.); with application of some adhesives, a long cure time may be needed; health and safety could be an issue because of the tightened legislation; inspection of bonded joint is difficult; requires more training and rigid process control than mechanical joint; creates a permanent bond and does not allow repeated assembly and disassembly.

Two major types of failure may occur when adhesively bonded joints are loaded by excessive tensile stress, the adhesive failure that is located at the interface between the adherent and the adhesive, and the cohesive failure that occurs in the adhesive or in the

substrate material. The latter cohesive failure occurs when the bond between the adhesive and the substrate material is stronger than the internal strength of the adhesive or substrate material. The goal of any good bond design is a substrate failure, i.e., the bond is stronger than the joining materials themselves.[2]

There is no single theory that explains the complete phenomena of adhesion. It is worth to mention the adsorption theory by which the adhesion results from molecular contacts between two joining materials and the surface forces that develop between these materials (secondary or van der Waals forces); in the mechanical theory, a bond formation is due to the interlocking of adhesive and substrate surfaces. Electrostatic theory explain the bonding by means of mutual interaction of electrostatic forces in the form of an electric double layer that are present at the adhesive/substrate interface, which create resistance against separation. It considers the adhesive and the adherent as a capacitor, where exists the charge separation across the interface.[3] By diffusion theory, the adhesion occurs due to the interdiffusion of molecules on the adhesive and substrate surfaces. By the last rheological theory, a performance of the bonded system is governed by the mechanical properties of the materials comprising the joint, and by the local stresses in the joint.

At the present time, increased demand for application of synthetic polymers in automotive industry and aeronautics is evident, mainly in utilization of polyethylene (PE), polypropylene (PP), or polycarbonate (PC) components of the interior, exterior, or the functional parts of the vehicle. Polymers were able to replace more traditional engineering materials, such as metals on account of their many desirable physical and chemical properties (e.g., high strength-to-weight ratio, resistance to corrosion, etc.) and their relatively low price.[4] Latter polyolefin polymers preserve due to their natural chemical structure extremely low adhesive properties, especially for different types of bonding agents or adhesives. This is accompanied also with their natural low wettability, which in many industrial applications is causing severe technological problems. Because of the fact that a precisely adjusted surface properties (e.g., sufficiently high surface energy or proper surface morphology and topology of the mutually bonded materials[5,6]) are vital for a successful creation of the mutual bond between two components of the polymer/polymer joint, application of the plasma processing seems to be both effective and economic. Important from the materials mechanics point of view is the fact that the applied plasma treatment is influencing only the near-surface regions without affecting the desirable bulk properties of the material.[7] Several methods have been used for improving adhesion, e.g., mechanical treatment,[8] chemical treatment,[9] exposure to flames,[10] corona discharges,[11] and glow discharge plasmas.[12] A common basic objective of the latter-mentioned treatments is to remove contaminated surface layer and to provide intimate contact between two interacting materials on a molecular scale. Of course, plasma processing as an addition has the ability to modify polymer surface via deposition, grafting or functionalization mechanisms,[13,14] what in particular cases might be positive for creation chemical bonds.

In this study, the effect of air plasma treatment of selected synthetic polymers on changes of contact angles of wetting, surface free energy, and hysteresis of contact angles with respect to the obtained adhesion strength of polymer/polymer joints after different modes of thermal ageing is offered.

EXPERIMENTAL

Materials

Poly(ethylene) Liten VL 10 (Chemopetrol Litvínov, Czech Republic) (PE), poly(propylene) Mosten PPB (Kaučuk, Kralupy nad Vltavou, Czech Republic) (PP), and poly(carbonate) Lexan 9030 sheet (GE Plastics, Pittsfield, MA) (PC) were used in this study. For dynamic contact angle measurements, all materials under study were used in the form of square coupons with the dimension of 20×20 mm^2 and thickness of 1.5 mm. As a wetting liquids, double-distilled water, ethylene glycol, glycerol, dimethyl sulfoxide, and N,N-dimethylformamide were used (ACS spectroscopy grade) (Aldrich).

Tested adhesives

Alkapren 50 (Czech Republic)—cautchouc bases, contact adhesive (used for PE, PP, and PC bonding), Helmicar 17027 (Czech Republic)—synthetic cautchouc bases, universal solvent base adhesive (used for PC bonding), Loctite E 406 (Henkel)—ethyl cyanoacrylate bases, with or without a polyolefin activator Loctite 770 (used for PE and PP bonding). For accelerated ageing, adhesive Loctite E 406 (for PE, PP joints) was used.

Methods

Plasma surface treatment

Plasma treatments of samples were performed by radio frequency glow discharge (rfGD) sources in a capacitatively-coupled reactor with a frequency of 13.56 MHz (VAKUUM Praha, Czech Republic). The reactor chamber consisted of a quartz cylinder of 80 mm inner diameter and 140 mm height, closed with two stainless-steel flanges. The substrates lay on the bottom electrode. A diffusion pump backed by rotary pump was used. The treatment period was 0–20 min. Elec-

trical power was ranging between 8 and 10 W and operating pressure was from 10 to 100 Pa. As a discharge gas we have used air, flow rate was kept at 50 cm^3/min. Apparatus consisted also from vacuum meter TPG 215 A (Pfeiffer), mass flow controller (Cole Palmer), and a matching RF unit.

Dynamic contact angles of wetting

Dynamic contact angles of wetting were measured on Tensiometer K12 (Krüss, Germany) by means of Wilhelmy plate method. Samples were immersed into three different wetting liquids and advancing and receding angles were measured at 20 °C. Four readings were averaged to obtain one contact angle value.

Microhardness measurements

Surface microhardness was measured according to the Czech standard ČSN EN ISO 2039–1 (Plastics—Determination of the hardness, Part 1: Sphere impressing method) by use of the testing instrument Zwick H 04.3106. Measurements were performed at 20°C. Method was based on impressing the sphere into the surface of the studied material at defined preload. Surface of the obtained imprint was calculated from the obtained depth. Microhardness was then calculated as the ratio: applied loading/obtained surface of the imprint. Measuring sphere was produced from the tempered steel with radius 5.0 ± 0.05 mm. Initial applied preload (F_0) was 9.8 N. Testing procedure was performed in the following way: tested body (flat plate, e.g., 50×50 mm^2, recommended thickness 4 mm) was placed on testing machine support; then the testing loading was adjusted from the series 49 N–132 N–358 N–961 N in such magnitude, that obtained depth of the imprint was ranging between 0.15 and 0.35 mm. Imprinted sphere depth was read after 30 s. Measured hardness H (N/mm^2) was then calculated:

$$H = \frac{1}{\pi} \frac{F_t}{h_r} \tag{1}$$

where F_t was reduced testing loading (N) and h_r was reduced impressed depth (mm). Reduced parameters were used to correct obtained values with respect to the deformation of the instrument's testing frame.

Scanning electron microscopy

Plasma-induced changes of surface morphology and roughness of the interface were characterized by scanning electron microscopy (FEG-SEM Hitachi S4100 microscope operating at 15 kV). Samples were covered with layer of black lead, and tilted 45° for better observation.

Adhesion joint tensile strength determination

The single lap and double lap joint test specimens were prepared in compliance with a standard ISO 4587. The specimen tensile tests were performed on universal tensile test machine Instron 4301 (5 kN) (UK) according to the standard EN ISO 527 in a push and pull arrangement. Fixing grips with swinging pivot were used to eliminate possible nonaxial loading. Tensile speed was 5 mm/min at the ambient laboratory conditions (25°C and 50% relative humidity). Samples prior to the testing were conditioned for 72 h at 23°C and 50% relative humidity. Acquired data were processed using Instron software and the maximum tensile load and elongation at break were determined. Ten separate readings of results were averaged to obtain one representative maximum load value and elongation at break.

Accelerated ageing of the samples

Accelerated ageing of the prepared adhesive joints was performed in compliance with conditions specified in the P-VW 1200 Volkswagen standard. The following temperature and humidity program was used: time at set temperature, 4 h; upper temperature, +80°C; lower temperature, −40°C; relative humidity of 80% at +80°C and 30% at the ambient temperature; velocity of the temperature change, 1 K/min; one cycle duration was 16 h. Totally 20 cycles were applied for each sample under study.

RESULTS AND DISCUSSION

Practical requirements for forming a strong adhesive joint are the absence of a weak boundary layers at the joined interfaces, i.e., the surface region is mechanically similar to the bulk of the material; fluid adhesive having its surface tension $\gamma_L < \gamma_c$ of substrates (where γ_c is the critical surface tension of wetting as extrapolated from Zisman plot[3]). It means that a substrate material should be perfectly wet by the adhesive. Important is also a successful formation of an extensive interfacial molecular contacts, displacing air from cracks and crevices, and finally setting of adhesive.[3,15] Because of the above-mentioned requirements, our initial effort was focused on optimizing the conditions of the plasma surface treatment and physicochemical characterization of the bonded substrate surfaces.

In plasmas that do not give rise to thin film deposition, the following major effects are observed on the surface, which alone or in synergistic combination, affect adhesion: surface cleaning, i.e., removal of organic contamination from the surfaces; ablation, or etching of material from the surface, which can remove a weak boundary layer and increase the surface area; crosslinking or branching of near-surface mole-

TABLE I
Dynamic Contact Angles of Wetting of Studied PE, PP, and PC Polymers after Different rfGD Air Plasma Treatment Times[a]

Plasma treatment time (min)	Dynamic contact angle (adv/rec) (°)								
	PE			PP			PC		
	Water	DMSO	DMF	Water	DMSO	DMF	Water	Ethy	Gly
0	105.6/82.2	63.5/50.9	48.2/37.3	105.1/86.0	62.1/52.5	42.8/40.7	89.0/57.0	63.7/41.2	86.0/49.9
1	46.0/16.2	11.9/8.5	11.4/9.1	75.9/23.4	42.3/15.9	38.3/18.7	55.6/36.8	9.0/7.3	68.8/1.5
5	56.8/30.9	17.6/15.6	21.1/18.4	60.2/16.2	30.6/13.9	27.7/8.8	51.5/23.2	11.5/9.5	75.6/4.8
20	30.2/18.0	10.5/3.9	8.5/7.5	57.1/16.9	23.0/13.2	26.2/7.4	42.8/21.4	17.5/11.3	66.1/0.0

Water, redistilled water; Ethy, ethylene glycol; Gly, glycerol; DMSO, dimethyl sulfoxide; DMF, N,N-dimethylformamide; adv, advancing contact angle; rec, receding contact angle.
[a] Measurements were performed in different wetting liquids at 20°C.

cules, which can cohesively strengthen the surface layer; modification of surface chemical structure, which can occur during plasma treatment itself, and upon re-exposure of the treated part to air, at which time residual free radicals can react with atmospheric oxygen or water vapor.[16–18] That is why the vigorous changes in the wettability, surface roughness, and the surface microhardness were obtained for all studied samples as will be discussed in the following separate sections.

Dynamic contact angles of wetting

There were studied plasma treatment time dependencies of advancing (adv) and receding (rec) contact angles of wetting for PP, PE, and PC samples. Different plasma treatment times ranging from 0 to 20 min were used for sample preparation. From the obtained data, vigorous changes of the originally hydrophobic behavior to more hydrophilic one of all polymeric surfaces under study were found. Summarized results are shown in Table I. The latter mentioned changes were most evident in the first 5 min of the plasma treatment, while longer treatment times do not show such a dramatic decrease of the contact angles. Interesting were the observations for glycerol as the wetting liquid. Here, the advancing angle was dropped from ~90° to 60°, while the receding angle after 1 min treatment time was nearly zero, and was not changed. Advancing contact angle of wetting is characterizing mainly the parts of the surface of a low surface free energy, receding contact angle is more affected by high energy parts. It can be seen from the data shown in Table I and Figure 1 that the hysteresis of the contact angles (i.e., the difference between advancing and receding contact angles) for water has a decreasing trend with the increasing treatment time for PE and PC samples. Different pattern was obtained for PP, where it was increased from 19° to ~45°. The general requirement for hysteresis is the existence of a large number of metastable states that differ slightly in

energy and which are separated from each other by small energy barriers.[15] These meta-stable states are generally attributed to either the roughness of the solid surface, or its chemical heterogeneity, or both. With respect to our data, longer plasma treatment times trigger lower hysteresis for PE and PC, what can be attributed to the creation of more homogeneous surfaces from the chemical composition point of view. This conclusion is supported also by observed increased surface roughness by SEM measurements (see next section). The latter trend was not observed for PP, where the hysteresis was two times higher after 1 min of plasma treatment, which indicated strong changes of the roughness and chemical composition heterogeneity of the treated surface. From the obtained data, the components of surface energy were calculated by means of Young–Dupré equation.[19] For all studied polymers, the increase of their surface energy was found, mainly of its polar component after applied plasma treatment. For example, in the case of PC, a polar component of surface energy was increased
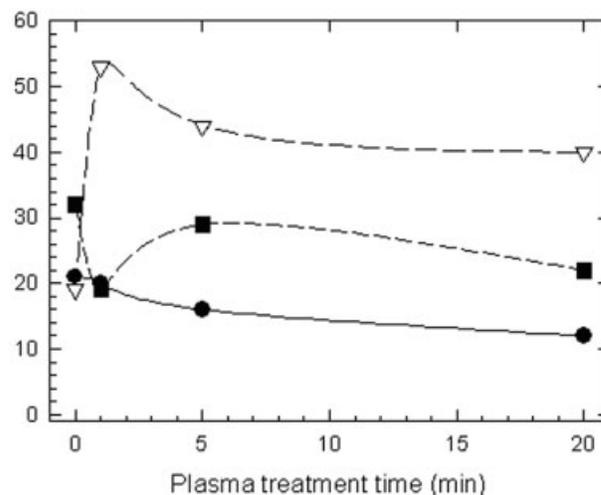
Figure 1 Plasma treatment time dependence of water contact angle hysteresis: PE (●), PP (▽), and PC (■).

TABLE II
Microhardness of the Studied PE and PP after Different Treatment Times by Air rfGD Plasma

| Plasma treatment time (min) | Microhardness (N/mm^2) | | | | | |
| | PE | | | PP | | |
	*	**	***	*	**	***
0	76	76	76	77	77	77
1	91	84	80	92	87	82
5	92	87	85	94	90	86
20	89	89	88	92	91	91

* Flow rate 7.7 cm^3/min.
** Flow rate 45.6 cm^3/min.
*** Flow rate 122.7 cm^3/min.

Figure 2 SEM images of the studied synthetic polymer surfaces (PE, PP, and PC) as obtained for different air plasma treatment times. Dimension of SEM illustrations is 1 × 1 μm^2, magnification ×30,000, bias 15 kV.

from 19.3 to 73.1 mJ/m^2, while a disperse component was decreased from 9.7 to 1.1 mJ/m^2. This is due to the creation of the carboxylic, carbonyl, and peroxide groups at the interface[20] as also found in our previous studies.[16–18,21–23] The latter species were generated in the system due to the presence of oxygen in the applied air plasma.

Microhardness measurements

Microhardness was measured for PE, PP, and PC samples treated by rfGD plasma for 0, 1, 5, and 20 min at three different plasma gas (air) flow rates (7.7, 45.6, and 122.7 cm^3/min). In the case of both PE and PP, a strong increase of the microhardness was obtained (approximately 15%), which was possible to follow also for the short treatment times. For treatment times ranging between 0 and 5 min, obtained microhardness was dependent on the applied plasma gas flow rate. For lower flow rates, more vigorous increase and faster the maximum hardness was settled. In contrary to that, for faster flow rates, a gradual increase of the surface microhardness was found. After 10, respectively, 20 min of plasma treatment the obtained microhardness was independent on plasma gas flow rate. In the case of PC, no changes of the surface microhardness were found. Results are shown in the following Table II.

Scanning electron microscopy

From SEM images shown in Figure 2, a clearly visible increase of the surface roughness was obtained after different plasma treatment times for all studied samples (PE, PP, and PC). A topology and the roughness of the originally smooth surfaces of the virgin substrates were dramatically changed and the surface roughness was vigorously increased after plasma treatment. The latter structures were clearly visible also in the different parts of the sample surface studied that reflects high reproducibility and homogeneity
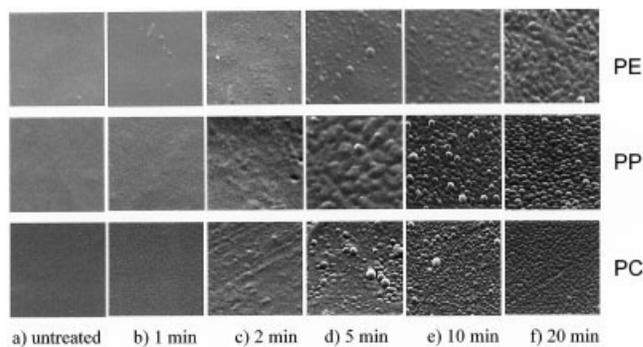
of the applied plasma treatment. From the latter data that followed, the equilibrium plasma etching was obtained after 20 min of treatment. It was then followed by pyrolysis and sublimation of the top layer of the interface and its subsequent substitution with a new layer having the same physicochemical properties. This resulted in constant velocity of observed changes of the polymeric body thickness at the coordinate in which the low temperature plasma etching was applied. For that reasons, in the next parts of this article the main interest of our studies will be focused on 20-min treatment time interval.

Adhesion joint tensile strength determination

From the measured data of joints prepared by Alkaprén 50 adhesive (see Fig. 3), it follows that in the case of the bonded PE, PP, and PC joints, plasma treatment
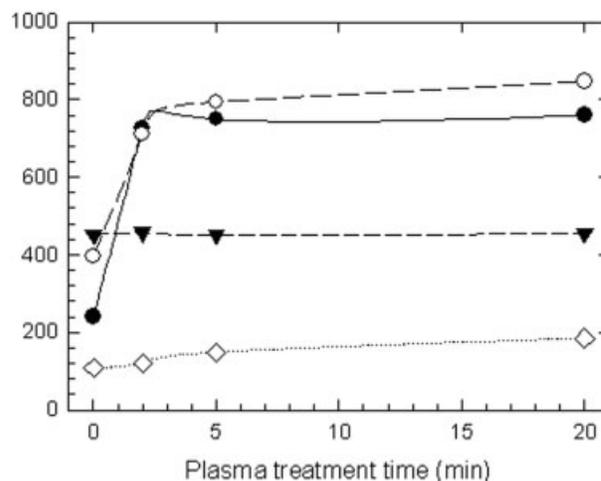
Figure 3 Effect of the plasma treatment time on maximum loading of the tested Alkapren 50 adhesive joints: PE (●), PP (○), PC (▼), and PC Helmicar 17 027 joint (◇). Testing was performed in the pull configuration.
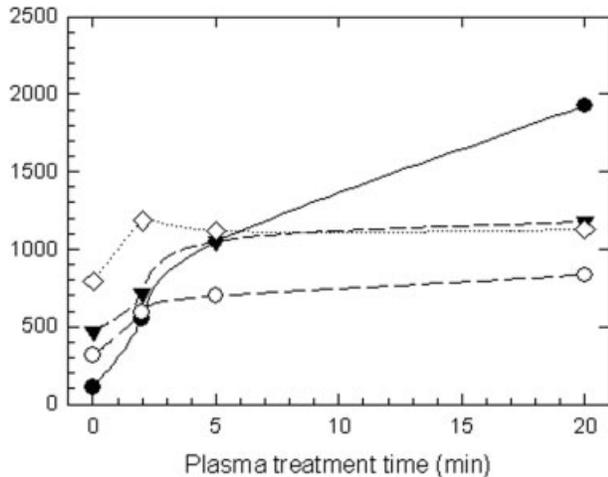
Figure 4 Effect of the plasma treatment time on maximum loading of the tested Loctite E 406 adhesive joints: PE (●), PP (○), PE + activator Loctite 770 (▼), PP + activator Loctite 770 (◇). Testing was performed in the pull configuration.
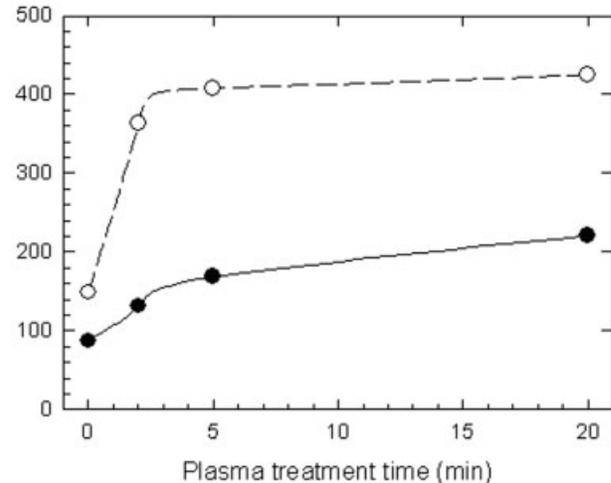
Figure 5 Effect of the plasma treatment time on maximum loading of the tested Loctite E 406 adhesive joints after accelerated ageing: PE (●), PP (○). Testing was performed in the pull configuration.

has the strongest effect on the PE joint, where the tensile strength was increased approximately three times followed by PP (approximately two-fold increase). In the case of PC, no dramatic changes in the values of maximum loading were found. This behavior can be explained by the fact that PC has markedly higher thermodynamic constants; hence, it is more resistant to the surface reactions induced by plasma treatment or can be explained by chemical incompatibility of the applied adhesive and the substrate. For exclusion of the latter factor, new set of tests were performed with application of different adhesive (Helmicar 17 027) as shown in Figure 3. Based on these experiments, it can be concluded that Alkaprén 50 is more effective adhesive for PC joints.

Next, results were measured for PE and PP with Loctite E 406 adhesive used with/without activator Loctite 770 (Fig. 4) and the applied accelerated climate cyclic ageing (Fig. 5). From these experiments follow the fact that the plasma surface treatment of the substrate surfaces prior to the adhesive application vigorously increases obtained values of the tensile strength of the adhesive joints in the case of PE 20-fold and in the case of PP three-fold increase. Application of the primer activator Loctite 770 has influence only on the untreated substrates. In the case of plasma-treated substrates, it is not affecting obtained mechanical properties of the joints, in the case of PE, it even decreases tensile strength of the joint (see Figs. 4 and 5). Results obtained for samples after accelerated cyclic ageing show much worth mechanical properties of the constructed adhesive joints. Any relations between maximum loading and the plasma treatment time after the accelerated ageing was not found. Similar results were also obtained for tensile testing in push arrangement (Fig. 6).

CONCLUSIONS

It was found in this study that air rfGD plasma treatment is a very efficient tool for increasing surface roughness and enhancing wettability of studied synthetic polymers (PP, PE, and PC). The latter effects were strongly dependent on flow rate of applied plasma gas. As an addition, the increased surface microhardness in the case of PP, PE was found after 20-min treatment times. Equilibrium values of the measured microhardness were obtained more rapidly at lower plasma gas flow rates than at higher flow rates. In the case of PC, air rfGD plasma treatment has no effect on obtained surface microhardness.

Results indicate that rfGD plasma treatment is a very effective tool for improvement of adhesive prop-
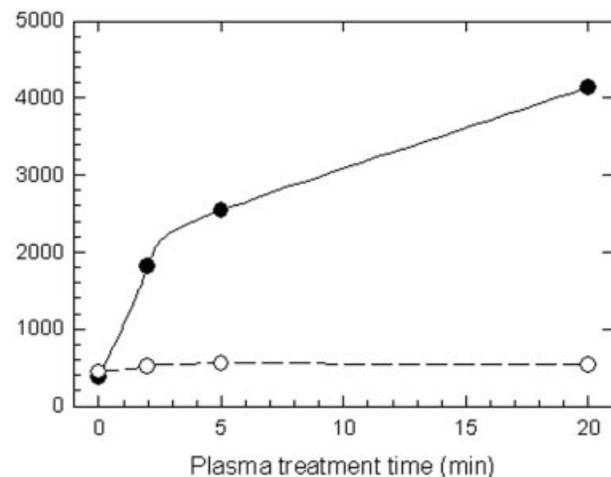
Figure 6 Effect of the plasma treatment time on maximum loading of the tested Loctite E 406 adhesive joints: PP (●), PC (○). Testing was performed in the push configuration.

erties of studied polymers. The value of maximum load raised from 107 to 1926 N (approximately 18-fold increase) for 20-min-treated PE and from 314 to 834 N (approximately three-fold increase) for PP. Artificial accelerated cyclic ageing rapidly decreased the quality of adhesive joint that can be demonstrated on 20-min-treated polyethylene sample. The value of maximum load decreased from 1926 to 221 N (approximately nine-fold decrease). This result indicates that the ageing of the adhesive joint of plasma-treated polymers can be a limitation factor in the possible application range of the final component or assembly because of the extremely high loss of its initially-enhanced mechanical properties. However, the strength of the thus prepared joints was higher in comparison to the plasma nontreated virgin samples.

References

1. Schindel-Bidinelli, E. H.; Gutherz, W. Konstruktives Kleben. Ein Lehrgang; VCH Publishers: Weinheim, 1988.
2. Mazumdar, S. K. Composites Manufacturing: Materials, Product, and Process Engineering; CRC Press: Boca Raton, FL, 2002.
3. Schönhorn, H. In Adhesion in Cellulosic and Wood-Based Composites; Oliver J. F., Ed.; Plenum : New York, 1981. NATO Conference Series, Series VI: Materials Science, Vol. 3, p 91.
4. Lehocký, M.; Lapčík, L., Jr.; Dlabaja, R.; Rachůnek, L.; Stoch, J. Czech J Phys 2004, 54 (Suppl C), 533.
5. Lee, L.-H. Fundamentals of Adhesion; Plenum: New York, 1991.
6. Royvanz, G. I. N.; Olhoff, N. Topology Optimization of Structures and Composite Continua; Kluwer: Dordrecht, 2000.
7. Liston, E. M.; Martinu, L.; Wertheimer, M. R. In: Plasma Surface Modification of Polymers: Relevance to Adhesion; Strobel, M.; Lyons, C. S.; Mittal, K. L., Eds; VSP: Utrecht, 1994; p 3.
8. Tervoort, T. A.; Visjager, J.; Smith, P. Macromolecules 2002, 35, 8467.
9. Nguyen, T. P.; Le Rendu, P., Long, P. D.; De Voss, S. A. Surf Coat Technol 2004, 180/181, 646.
10. Pijpers, A. P.; Meier, R. J. J Electron Spectrosc Relat Phenom 2001, 121, 299.
11. Molinie, P. J Electrostatics 1999, 45, 265.
12. Prat, R.; Koh, Y. J.; Babukutty, Y.; Kogoma, M.; Okazaki, S.; Kodama, M. Polymer 2000, 41, 7355.
13. Lopez, G. P.; Ratner, B. D.; Tidwell, C. D. J Biomed Mater Res 1992, 26, 415.
14. van Ooij, W. J.; Anderson, H. R., Jr, Eds. First International Congress on Adhesion Science and Technology—-Invited Papers; VSP: Utrecht, 1998.
15. Hiemenz, P. C. Principles of Colloid and Surface Chemistry; Marcel Dekker: New York, 1986.
16. Peterková, P.; Lapčík, L., Jr. J Polym Mater 2003, 20, 67.
17. Drnovská, H.; Lapčík, L., Jr.; Buršíková, V.; Zemek, J.; Barros-Timmons, A. M. Colloid Polym Sci 2003, 281, 1025.
18. Lehocký, M.; Drnovská, H.; Lapčíková, B.; Barros-Timmons, A. M.; Trindade, T.; Zembala, M.; Lapčík, L., Jr. Colloids Surf A 2003, 222, 125.
19. van Oss, C. J.; Chaudhury, M. K.; Good, R. J. Chem Rev 1988, 88, 927.
20. Wu, S. Polymer Interfaces and Adhesion; Marcel Dekker: New York, 1982.
21. Peterková, P. Ph.D. Dissertation, Brno University of Technology, Brno, 2002.
22. Drnovská, H. Ph.D. Dissertation, Brno University of Technology, Brno, 2003.
23. Dlabaja, R. Ph.D. Dissertation, Tomas Bata University in Zlín, Zlín, 2004.