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Evaluation of the quality of cyanoacrylate adhesive joints using the example of poly(methyl methacrylate) and polycarbonate

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Abstract

Adhesive bonding is one of the simplest and most common methods used for joining materials. It is applied in both production and repair works. The most commonly used adhesives are cyanoacrylates, due to the possibility of combining various materials and short curing time. One of the ways to assess the quality of the adhesive used is testing the shear strength of bonded joints. Three adhesives commonly available on the Polish market, from various manufacturers and with different prices per gram of product were tested. The polymer materials bonded were poly(methyl methacrylate) and polycarbonate, since they are broadly used in the automotive industry and household equipment. The study revealed significant differences in bonding strength, reaching as much as 38%. The adhesive's price was not commensurate with the quality of the product tested in all cases.

1. Introduction

One of the oldest techniques of joining is adhesive bonding (CAGLE CH. V. 1977, BROCKMAN W. and all 2009]. This technology is used not only in industrial solutions but also by households. The latter use all-purpose adhesives reasonably priced per gram of product. These include cyanoacrylate adhesives, commonly referred to as 'one-second adhesives' due to their very short curing time. The introduction of adhesives to the market brought multiple benefits, both in industrial and household uses. Adhesives do not damage the surface of materials to be joined (CZAPLICKI J., ET AL. 1987, RUDAWSKA A. and all 2016, PILAWKA R. ET AL. 2003, PORĘBSKA M., SKORUPA A. 1993).

For the study, cyanoacrylate adhesives from three manufacturers were used (two made in Germany, adhesives A and B, and one in the Netherlands, adhesive C), commonly available on the domestic market, with different unit prices per gram of product. Two thermoplastic polymers were chosen for the study: poly(methyl methacrylate) with improved impact resistance (so-called organic glass), and polycarbonate - because of the prevalence of these polymers in products of the automotive industry and in household items. Both polymers selected are materials with an amorphous

structure. All three manufacturers state their suitability for bonding these two polymers (ADAMS R. D., WAKE W.C. 1984, JÓZWIK J., KUCZMASZEWSKI J. 2000, RUDAWSKA A. 2013).

Cyanoacrylate adhesives are a special group of adhesives. They are solvent-free and, more importantly, mostly transparent. They differ in terms of consistency, from thin liquids to thick and gelatinous compounds. These are single-component products, based on methyl, ethyl and alkoxy groups, which quickly solidify. They are designed for bonding different pairs of materials (rubber, metal, wood, ceramics, plastics and materials difficult to bond, e.g. Teflon, polyolefins). They are used for bonding tight-fit components with gaps of up to 0.15 mm. Cyanoacrylate adhesives are polymerised by the catalytic activity of moisture in the air. Optimum results are achieved at room temperature and relative humidity of 40-60%. They are characterised by a very short curing time. Therefore, they are referred to as 'one-second adhesives'. Temperature resistance for most of them is -55°C to +95°C. Cyanoacrylate adhesives provide strong joints with steel, aluminum, plastics (e.g. PMMA, ABS, polystyrene, hard PVC and, after using a special primer, even to such difficult surfaces as polyethylene PE and polypropylene PP), elastomers (NBR Butyl, EPDM, SBR), leather and

wood. A drawback of these adhesives is the sometimes pungent odour sensed particularly at reduced air humidity (SOLANA A.G. and all 2010, CAGLE CH. V. 1977, ÖCHSNER A., GEGNER J. 2004). Currently, manufacturers continue to develop newer generations of adhesives, which enable the joining of elements with worse fit and larger gaps, without causing traces on the bonded joints. The joints are resistant to oils and fuels, and less resistant to moisture, particularly at elevated temperatures (WAKE W.C. 1988). However, they play an important role in the industry due to the simplicity and short time needed to achieve full bonding strength - within a few seconds or tens of seconds (www.mirexnr.com.pl). Cyanoacrylates (chemical name droplet adhesives) were discovered in 1942 in the search for new materials, a transparent polymer for the production of sights for the arms industry. A team of scientists led by Harry Wesley Coover Jr found a formulation that bonded to anything it made contact with (www.kleje-przemyslowe.pl). For this reason, cyanoacrylates were quickly rejected by US researchers. In 1951 cyanoacrylates were rediscovered by the Eastman Kodak scientists Harry Coover and Fred Joyner. In their discovery they saw the versatility of this type of adhesives, and hence their enormous commercial potential. The cyanoacrylate adhesive was first sold commercially in 1958 as 'Eastman # 910' (www.e-kleje.pl, BALDAN A 2012, BROCKMANN W., ET AL. 2009, CHOUPANI N. 2009).

Specific features of cyanoacrylate adhesives (www.kleje-przemyslowe.pl) include:

- very high shear and tensile strength;
- very fast curing;
- minimum consumption;
- multi-purpose use on various materials;
- fatigue resistance;
- simultaneous sealing action;
- easy application and installation;
- no toxic properties when cured, as proved by the National Hygiene Institute certificates approving use in drinking water plumbing;
- storage for 6 to 12 months at + 5 to +28°C (ÖCHSNER A., GEGNER J. 2004. KUCZMASZEWSKI J. 1988, SOLANA A.G. ET AL. 2010, KUCZMASZEWSKI J. 1988).

2. Methodology of research

Specimens were cut out of plates (see Table 1 for dimensions). They were prepared for bonding as recommended by the manufacturers of the adhesives, i.e. cleaned and degreased. Also, before degreasing the surface was treated by sanding to achieve roughness R_a 0.63-0.40 μm . A layer of adhesive was then applied with a small paintbrush. The adhesive was applied only on one of the surfaces to be bonded. The thinner the adhesive layer, the shorter the curing time and the greater the strength of the joint. After complete curing, the bonded specimens were subjected to shear strength tests in normal conditions, using an analogue FB dynamometer, with a measuring range of 0-5000 N and tolerance of $\pm 1\%$ of the range. 10 tests were performed for each of the

adhesives tested and materials bonded. The adhesion area of every specimen was measured after the shear test.

Table 1. Actual dimensions of bonded joints tested

Material	Layer thickness [mm]	Specimen width [mm]	Adhesive joint length [mm]	Total length of specimens bonded [mm]
PMMA	3.3 ± 0.02	5.9 ± 0.02	10 ± 1	100 ± 2
PC	3.5 ± 0.02	4.8 ± 0.02	10 ± 1	100 ± 2

Source: own study

3. Material, results and discussion

Poly(methyl methacrylate) (PMMA) is obtained from free-radical methyl methacrylate polymerization, where an atactic, syndiotactic or isotactic polymer can form depending on the process conditions (KOSZKUL J. 1999, PIELICHOWSKI J., ET AL. 1998, SZLEZYNGIER W. 1998, ŻUCHOWSKA D. 2000). The last is a polymer with a high degree of crystallinity and is characterized by higher mechanical properties (KOSZKUL J. 1999).

Industrial obtaining methods concern only the production of atactic PMMA, obtained in a mass, suspension, emulsion and in a solution in the presence of radical initiators (KOSZKUL J. 1999, PIELICHOWSKI J., et al 1998, SAECHTLING H. 2007, SZLEZYNGIER W. 1998, ŻUCHOWSKA D. 2000).

Poly(methyl methacrylate), as the so-called organic glass, is distinguished among other polymer materials by its very good optical properties, especially its high visible light (ca. 92%) and ultraviolet radiation transmittance (50-70%). Moreover, it shows a high weather resistance (including low temperature) and is also characterized by a very low water absorptiveness. Poly(methyl methacrylate) has good mechanical properties and displays a high chemical resistance. Compared to 96% silica glass, poly(methyl methacrylate) is much lighter and much more break-resistant and is characterized by a higher plasticity. However, it shows a lower stiffness and surface scratch resistance. Poly(methyl methacrylate) is a low synthetic material. Compared to other thermoplastics, its properties are generally good, except for a small elongation at break and a low impact strength, especially when it is notched (ACHARYA S., ET AL. 2013, SZLEZYNGIER W. 1998, SIKORA T., ET AL. 2008, WU H., ET AL. 2004).

PMMA is often used in many branches of industry: aviation, automotive, optical, electrotechnical, electronic and luxury goods industries as well as in construction. PMMA panels are used as the material for cabin housings, glazing and fairings in aircraft, helicopters and gliders. It is also widely used for the production of dashboards, housings of navigational and measuring apparatus and retro-reflecting devices, for the manufacture of prisms and lenses, buttons, tableware, watch glasses, windowpanes, fluorescent lamp housings and lampshades (OSIECKA E. 2005, SZLEZYNGIER W. 1998).

Polycarbonate (PC) is obtained from condensation polymerization of bifunctional alcohols or phenols with

phosgene or carbonic acid esters. The reaction can be carried out at the phase boundary or in a solvent. Depending on the structure of a carbohydrate part of the chain, PC can be aliphatic or aromatic. To date, only aromatic PC have gained engineering significance (KOSZKUL J. 1999, PIELICHOWSKI J., et al 1998, SAECHTLING H. 2007, SZLEZYNGIER W. 1998, ŻUCHOWSKA D. 2000, MAZUR P. 2014).

Polycarbonates have an amorphous structure, but due to a certain symmetry of the particle, they may crystallize under specific conditions. The flowing temperature of amorphous polymer is 220÷230°C, and the melting point of crystalline polymer is 260÷270°C. Its glass transition temperature is 150°C (KOSZKUL J. 1999, ŻUCHOWSKA D. 2000).

PC is distinguished by a particularly high impact strength and transparency accompanied by high stiffness. Products made of this material can work at temperatures ranging from -40 to 130°C, are creep- and hydrolysis-resistant, have low water absorptiveness, good heat stability and are physiologically neutral (can be sterilized and applied in medicine). This material is also used to produce composites (KOSZKUL J. 1999, PIELICHOWSKI J., et al 1998, SZLEZYNGIER W. 1998, ŻUCHOWSKA D. 2000).

PC is resistant to substances of neutral and acid pH, except for concentrated acids. Alkali cause decomposition of the polymer, while pyridine, chloroform and methyl chloride dissolve the material. They are also resistant to ethyl alcohol and toluene (KOSZKUL J. 1999, PIELICHOWSKI J., et al 1998, SAECHTLING H. 2007, SZLEZYNGIER W. 1998, ŻUCHOWSKA D. 2000).

Polycarbonates are a relatively expensive material, but they are often used, mainly due to their high impact strength and broad range of working temperatures, mostly in electrical engineering, machine building industry and for the production of household items (KOSZKUL J. 1999, OSIECKA E. 2005, SZLEZYNGIER W. 1998, MAZUR P. 2014.).

Table 2 shows the results of measurements of mean force values (from 10 tests) at which the bonded joint was broken. The parameters for PMMA is present graphically in Fig.1, and for PC in Fig. 2.

Table 2. Mean shear force values at which the bonded joint failed

Material \ Adhesive	A	B	C
PMMA	333 [N]	408 [N]	312 [N]
PC	292 [N]	300 [N]	218 [N]

Source: own study

Table 3 presents mean shear strength values. The shear strength for PMMA is present graphically in Fig.3, and for PC in Fig. 4.

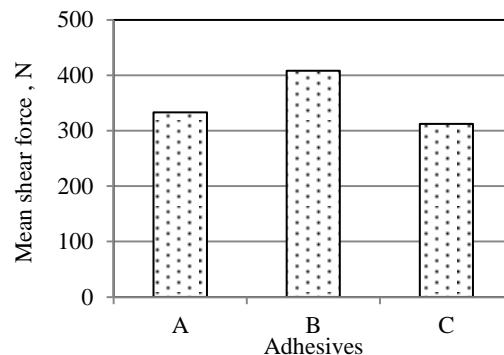


Fig. 1. Mean shear force values PMMA joints using three adhesives (A,B,C)

Source: own study.

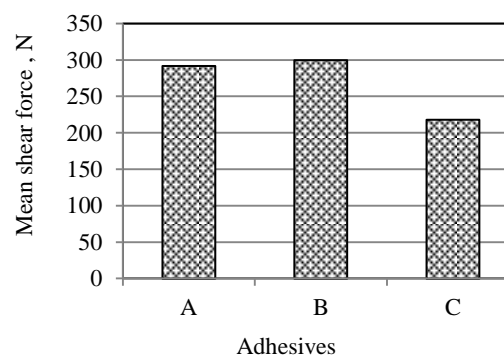


Fig. 2. Mean shear force values PC joints using three adhesives (A,B,C)

Source: own study

Table 3. Shear strength of bonded joints

Material \ Adhesive	A [MPa]	B [MPa]	C [MPa]
PMMA	5.64	6.92	5.29
PC	6.08	6.25	4.54

Source: own study

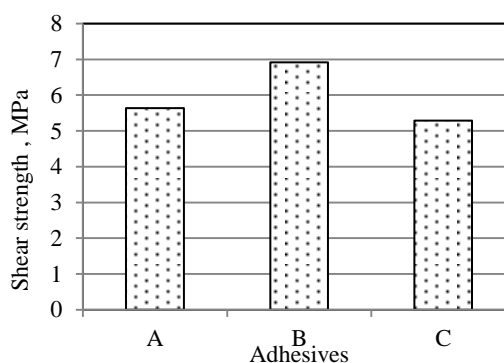


Fig. 3. Shear strength of bonded PMMA joints using three adhesives (A,B,C)

Source: own study

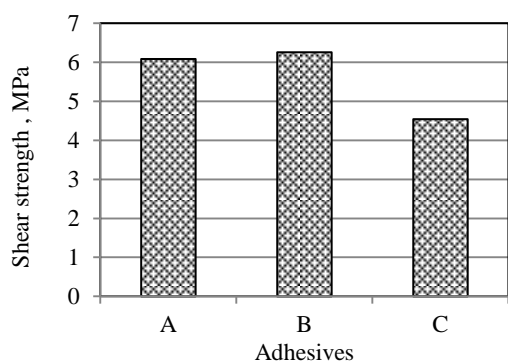


Fig. 4. Shear strength of bonded PC joints using three adhesives (A,B,C)

Source: own study

The highest mean shear force 408 N and almost 7 MPa shear strength obtained for B adhesives poly(methyl methacrylate). The lowest mean shear force 218 N and almost 4.54 MPa shear strength obtained for C adhesives poly(methyl methacrylate).

4. Summary and conclusion

The results obtained differed within up to 31% in the case of bonding PMMA, and up to 38% for PC, and were not always commensurate with the adhesive's price. The best results were obtained using the most expensive adhesive (B). For PMMA bonding the shear strength of adhesive B was 31% higher than that of adhesive C and 23% higher than that of adhesive A (the cheapest adhesive used). Similar results were achieved for bonding PC. The shear strength of adhesive B was 38% higher than that of adhesive C and only 3% higher than for adhesive A. According to the tests, the adhesive's price was not commensurate with quality of the product tested in all cases.

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使用聚（甲基丙烯酸甲酯） 和聚碳酸酯的實施例評價氰基丙烯酸酯粘劑接頭的質量

關鍵詞
瞬乾膠
聚合物
剪切強度

摘要

粘劑粘合是用於連接材料的最簡單和最常用的方法之一。它適用於生產和維修工程。最常用的粘劑是氰基丙烯酸酯，因為可能結合各種材料和短的固化時間。評估所用粘劑的質量的方法之一是測試粘劑接頭的剪切強度。在波蘭市場上通常可獲得的，來自各種製造商並且每克產品具有不同價格的三種粘劑被測試。所粘合的聚合物材料是聚（甲基丙烯酸甲酯）和聚碳酸酯，因為它們廣泛地用於汽車工業和家用設備。