

Antibacterial modification of polymer veneers

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Abstract: *Antibacterial modification of polymer veneers.* The increase of the resistance to infections can be achieved by plastic veneers, e.g. produced from low-density polyethylene (LDPE), surface treatment by substances containing antibacterial groups such as triclosan and chlorhexidine. This research has examined the impact of selected antibacterial substances immobilized on LDPE via poly acrylic acid (PAA) grafted on LDPE by low-temperature barrier discharge plasma. This surface treatment led to inhibition of *Escherichia coli* and *Staphylococcus aureus* adhesion; the former is causing intestinal disease, peritonitis, pneumonia and septicemia.

Keywords: adhesion, antibacterial compounds, contact angle, discharge plasma, low-density polyethylene, surface free energy, formaldehyde free

INTRODUCTION

LDPE is widely used in many useful applications, e.g. in packaging industry. It is used e.g. in furniture industry as plastic veneers, and also in human medicine for catheters production in coronary angioplasty as well as in pharmaceutical industry [1, 2]. Many kinds of infection resulting from application of this medical polymer represent main clinical complication [3-5]. Antibacterial surface modification is controlled by physical-chemical interactions between bacteria and polymer surface. This treatment has several advantages, because it does not influence the bulk properties of polymer, antibacterial agents are not released from polymer volume, and the technique is relative simple and effective.

EXPERIMENTAL

Materials

LDPE BRALEN FB 2-17 veneers: Slovnaft MOL (Slovakia, density = 0.918 g·cm⁻³, the product complies with Food Contact Regulations and the grade is suitable for manufacturing of pharmaceutical packing-product.

Triclosan (5-Chloro-2-(2,4dichlorophenoxy)phenol): Irgasan, C₁₂H₇Cl₃O₂, Fluka Analytical (Italy), white powder, melting point = 56-58 °C. Chlorhexidine (N',N''''-hexane-1,6-diylbis[N-(4-chlorophenyl):imidodicarbonimidic diamide, C₂₂H₃₀Cl₂N₁₀, Aldrich Chemistry (Spain), white powder, melting point = 134 °C. Acrylic acid (propenoic acid): C₃H₄O₂, Acros Organics (Belgium), Assay = 99.5 %, extra pure.

Treatment by DCSBD plasma

The LDPE veneer activation was carried out by DCSBD equipment developed at Comenius University in Bratislava under dynamic conditions at atmospheric pressure and room temperature. The treatment was performed at following settings: power supply = 200 W, plasma treatment time = 15 s, in air atmosphere and all samples were treated on both sides.

Grafting by PAA

Immediately after plasma treatment the LDPE veneer was immersed into 10 volume % aqueous solution of AA for 24 h at 30 °C in order to initiate of radical graft polymerization of AA onto activated surface of LDPE foil.

Antibacterial immobilization

LDPE veneer grafted by PAA was immersed into solution of triclosan and chlorhexidine. The former solution was prepared as 2 w/v % solution of triclosan in absolute ethanol and the latter as 2 w/v % solution of chlorhexidine in 70 v/v % isopropanol aqueous solution for 24 h at 30 °C in an oven. The antibacterial treated veneers were thoroughly washed and then dried for 24 h at room temperature to constant weight.

Methods of surface measurements

The wettability of LDPE veneer treated by multistep process via PAA plasma grafted and Antibacterials immobilization were carried out by the measurement of contact angle using sessile drop technique using Surface Energy Evaluation system (SEE system with CCD camera, Advex Instruments, Czech Republic). The adhesive properties, namely peel strength (force per unit width) of adhesive joint of antibacterial treated LDPE by triclosan and chlorhexidine via DCSBD to poly(2-ethylhexyl acrylate) deposited onto polypropylene foil (with 15 mm width), were carried out by measurements of 90° peel test at a rate of peel 10 mm per minute using 100 N universal INSTRON 4301 dynamometer (England). In Vitro bacterial adhesion and biofilm experiments were performed using gram-positive (*S. aureus* 3953) and gram-negative (*E. coli* 3954). The circular shape specimens ($d \approx 8\text{mm}$) were cut from the pristine and modified LDPE veneers. So called agar diffusion plate (inhibition) test was performed for antibacterial activity evaluation of tested substrates. The substrates were placed on agar plate inoculated by bacterial suspension. The bacterial suspension volume was 100 μl for all samples. Bacteria concentration was 10^7 units· ml^{-1} and incubation time was 24 h at the temperature 37 °C. After that, inhibition zone diameter was measured in 5 directions and average value was calculated.

RESULTS AND DISCUSSION

The changes of contact angles of testing liquids caused by antibacterial treatment are shown in Fig. 1. The water contact angle (θ_w) of untreated LDPE (veneer 1) achieves the highest values from the all samples because it is polymer with hydrophobic and chemical inert surface. θ_w significantly decreased after plasma effect of the veneer 2 when different functional groups were introduced on to the surface formed from plasma species and therefore the treated surface acquired more polar or hydrophilic character. The highest decrease of the contact angle was observed in case of surface covered by polyacrylic acid (PAA) (veneer 3) which corresponds to its hydrophilic character. Also Triclosan (veneer 4) and chlorhexidine (veneer 5) immobilization led to θ_w decrease. For investigation of other physicochemical parameters of the treated surface Lifshitz-Van der Waals/acid-base (LW/AB) theory was used, which allows to obtain γ^{tot} and its components such as non-polar LW (γ^{LW}) and polar AB (γ^{AB}) components. LW indicates the total dispersive Lifshitz-Van der Walls interaction and AB refers to the acid-base or electron-acceptor/electron donor interaction according to Lewis. LDPE belongs to group of low-energy polymeric materials and therefore γ^{tot} of veneer 1 achieves very low values which correspond with difficulties during processing, such as dyeing, printing and bonding (low adhesion). This can be removed by plasma treatment of LDPE when γ^{tot} can significantly increases as in the case of veneer 2. The largest increase of γ^{tot} and γ^{AB} was observed for veneer 3 due to highest polarity in comparison with other

samples as a result of polar oxygen groups presence. Veneer 4 and 5 showed the similar increase of surface free energy values thereby confirming the increase in wettability.

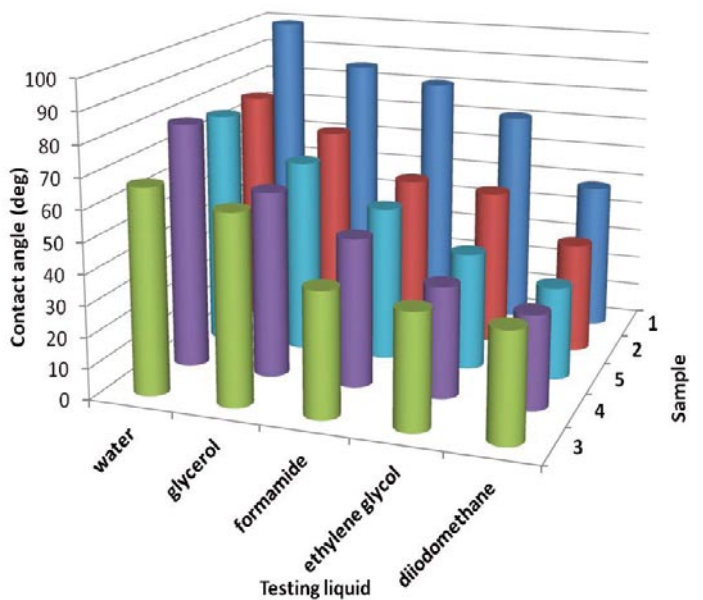


Figure 1. Contact angle vs. surface treatment and vs. testing liquid; 1 - untreated LDPE veneer; 2 - plasma-treated veneer; 3 - AA grafted veneer; 4 - triclosan coated veneer; 5 - chlorhexidine coated veneer.

The results of peel strength measurements of adhesive joint to poly(acrylate) are shown in Fig. 2. Surface free energy changes are closely related to adhesion between two materials in contact. Therefore, the increased wettability resulted in an increase of adhesion strength of adhesive joint to more polar poly(acrylate). But adhesion depends not only on chemical composition and chemical nature of the surface but also on surface morphology (roughness). The rougher is the surface the lower is the adhesion and vice versa. Thus, adhesion is a complex parameter consisting of several related chemical and physicochemical properties. Therefore, in the case of veneer 3 even though the surface energy reaches its highest value the peel strength is less than for veneer 4 and 5. Cross-linking occurred in veneer 5 (via glutaraldehyde) is another factor that contributes to the increase in the adhesion strength.

Table 1 shows inhibition zone area results. The inhibition zone area was calculated as veneer surface area deducted from total area of inhibition zone. The results show that untreated (veneer 1), plasma treated (veneer 2) as well as acrylic-acid grafted sample (veneer 3) does not report any antibacterial activity against both *Escherichia coli* and *Staphylococcus aureus* strains. The sample coated with triclosan (veneer 4) does meet expected antibacterial requirements. The average inhibition zone for gram – negative *Escherichia coli* strain is of 115.1 mm² and for gram – positive *Staphylococcus aureus* 493.1 mm². These values prove antibacterial activity of prepared layers. Similar results were obtained for chlorhexidine coated veneers (veneer 5). The average inhibition zone value of 42.2 mm² was calculated for *Escherichia coli* and 288.1 mm² for *Staphylococcus aureus* strain. It is worth mentioning, that

both antibacterial agents are more active against gram – positive bacteria. Finally, triclosan coated veneers show better results among both antibacterial substances used.

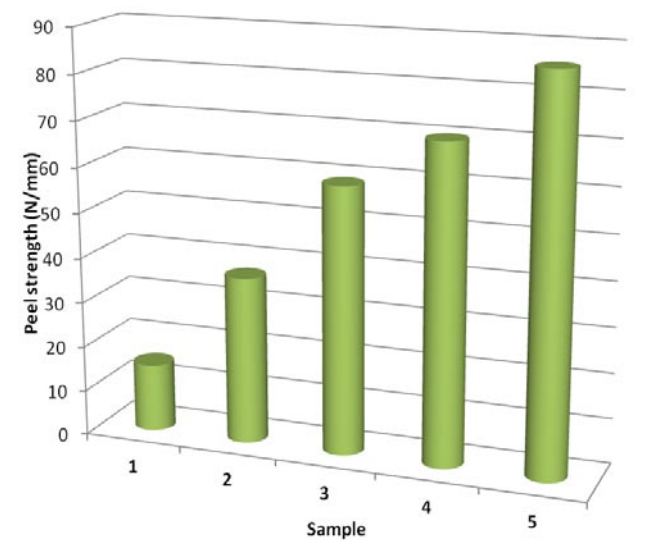


Figure 2. Peel strength vs. surface treatment; 1- untreated LDPE veneer; 2 - plasma-treated veneer; 3 - AA grafted veneer; 4 - triclosan coated veneer; 5 - chlorhexidine coated veneer.

Table 1. Inhibition zone area measurement on surface of LDPE veneers

LDPE veneer*	Inhibition zone (mm ²)			Average value (mm ²)
	1	2	3	
Escherichia coli				
veneer 1	0	0	0	0
veneer 2	0	0	0	0
veneer 3	0	0	0	0
veneer 4	105.8	118.3	121.2	115.1
veneer 5	40.2	43.8	42.5	42.2
Staphylococcus aureus				
veneer 1	0	0	0	0
veneer 2	0	0	0	0
veneer 3	0	0	0	0
veneer 4	475.0	496.3	507.9	493.1
veneer 5	286.4	279.3	298.5	288.1

*veneer: 1-untreated LDPE; veneer 2-plasma-treated; veneer 3-AA grafted; veneer 4-triclosan coated; veneer 5-chlorhexidine coated.

CONCLUSIONS

DCSBD plasma leads to an increase of the surface free energy by introducing characteristic oxygen groups to LDPE veneer surface. DCSBD plasma source as activator of

LDPE veneer surface was used for efficient binding of acrylic acid and for its transformation to polymeric form by radical polymerization. Thus bounded acrylic acid created polymer brushes on the polymer surface, that was capable of physical forces bind antibacterial agent's effective manner. The presence of triclosan and chlorhexidine was confirmed by different surface analysis techniques. Moreover the antibacterial effect of such treated LDPE film was proven by in vitro bacterial tests against *E. coli* and *S. aureus* when adhesion of bacteria was effective diminished.

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Streszczenie: Antybakteryjna modyfikacja fornirów polimerowych. Podwyższenie właściwości antybakteryjnych można osiągnąć poprzez zastosowanie fornirów wykonanych np. z polietylenu o niskiej gęstości (LDPE), powierzchniowemu naniesieniu substancji zawierających grupy przeciwbakteryjne, takie jak triklosan oraz chloroheksadyna. Badania miały na celu określenie wpływu wybranych substancji antybakteryjnych, osadzonych na LDPE poprzez zastosowanie kwasu akrylowego (PAA) przy wykorzystaniu niskotemperaturowej plazmy. Powierzchniowa aplikacja substancji antybakteryjnych prowadzi do zahamowania rozwoju *Escherichia coli* i *Staphylococcus aureus*, które mogą być przyczyną choroby jelit, zapalenia płuc, zapalenia otrzewnej i posocznicy.

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