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Antibacterial modification of polyolefin veneers

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Abstract: *Antibacterial modification of polyolefin veneers*. For application of plastic veneers, which are frequently used for furniture production for hospital and medical centers interiors, the anti-bacterial pre-treatment is necessary. The modification method using cold plasma seem to be attractive, ecological, and efficient with increasing interest. An increase in resistance to infections can be achieved by treating of polymer surfaces with substances containing antibacterial groups such as triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) and chlorhexidine (1,1'-hexamethylenebis[5-(4-chlorophenyl) biguanide]). This work has examined the impact of selected antibacterial substances immobilized on low-density polyethylene (PE) by low-temperature barrier discharge plasma. The anti-bacterially modified PE veneer surface led to inhibition of *Escherichia coli* and *Staphylococcus aureus* adhesion; the first causes intestinal disease, peritonitis, mastitis, pneumonia, septicemia, the latter is the reason for wound and urinary tract infections.

Keywords: antibacterial modification, polyolefin foil, surface properties, glutaraldehyde, radio-frequency plasma.

INTRODUCTION

PE is widely used in many applications including veneers production for furniture surface finishing (***Zhang et al. 2008, Kuzuya et al. 2003***). but infections resulting from application of this polymer represent the main clinical complication (***Zhang et al. 2006***). Cold plasma can be suggested as the appropriate procedure for the hydrophilization of the surface. Due to the cold plasma treatment surface the free energy is increased as a result of introduction of polar functional groups on the treated surface, thus making the surface of PE veneers more hydrophilic (***Costa 2011, Goddard and Hotchkiss 2008***). Antibacterial surface modification has several advantages, because it does not influence the bulk properties of the polymer, antibacterial agents are not released from the polymer volume, and the technique is relative simple and effective. In the first step, formation of functional groups on the polymer surface is necessary via the plasma species and in the second step end-functionalized polymer brushes are formed on polymer surface via radical graft polymerization of acrylic acid (AA), which is anchored on the plasma treated surface. Finally biomolecules are immobilized on plasma pre-treated surface PE veneers and carboxyl groups of AA are activated and they are ready to provide the immobilization sites.

EXPERIMENTAL

Chemicals

PE veneers made from low-density PE BRALEN FB 2-17 (Slovnaft-Mol, Slovakia), containing no processing additives, density = 0.918 $g \cdot cm^{-3}$, mass flow rate = 2 $g.10\ min^{-1}$ (190 °C, 2.16 kg). Acrylic acid (AA, Prop-2-enoic acid): $C_3H_4O_2$, colorless liquid (Acros Organics, Belgium), EDAC (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) (Fluka, USA), purum, assay = 98.0%, M_r = 191.70 $g \cdot mol^{-1}$, T_m = 110–115 °C.

Plasma Pre-treatment

The PE veneers were first cleaned with dichloromethane to remove impurities. Then the PE veneer activation was carried out under dynamic conditions at atmospheric pressure and room temperature with the DCSBD equipment developed at Comenius University, Faculty of Mathematics, Physics and Informatics in Bratislava.

Grafting by PAA

Immediately after plasma treatment the PE 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 PE foil. This solution contained also 0.1 wt. % sodium metabisulfite as a relevant reductant to inhibit AA homopolymerization.

Antibacterial Immobilization

The PE veneer pre-prepared by such way was then immersed into solution of triclosan and chlorhexidine. The first 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 samples were thoroughly washed and then dried for 24 h at room temperature to constant weight.

RESULTS AND DISCUSSION

Surface properties

The changes of contact angles of testing liquids caused by antibacterial treatment are shown in Figure 1. The water contact angle (θ_w) of untreated PE veneer (Sample 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 Sample 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, Sample 3) which corresponds to its hydrophilic character. Also triclosan (Sample 4) and chlorhexidine (Sample 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 Lifhitz-Van der Walls interaction and AB refers to the acid-base or electron-acceptor/electron donor interaction according to Lewis [33]. PE belongs to group of low-energy polymeric materials and therefore γ^{tot} of Sample 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 PE veneer, when γ^{tot} can significantly increases as in the case of Sample 2. The largest increase of γ^{tot} and γ^{AB} was observed for Sample 3 due to highest polarity in comparison with other samples as a result of polar oxygen group's presence. Sample 4 and 5 showed similar increases of surface free energy values, thereby confirming the increase in wettability.

Adhesion

The results of peel strength measurements of adhesive joints PE veneer to poly(acrylate) are shown in Figure 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). However, adhesion depend not only chemical composition and the chemical nature of the surface, but also on surface morphology (roughness). The rougher is the surface the higher 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 Sample 3 even though the surface energy reaches its highest value the peel strength is less than for Sample 4 and 5. Cross-linking occurred in Sample 5 (via glutaraldehyde) is another factor that contributes to the increase in the adhesion strength.

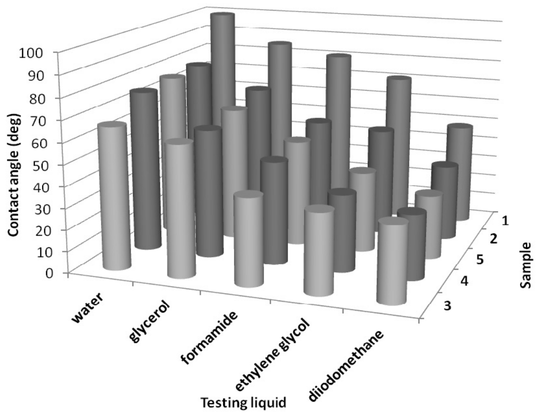

Fig. 1 Contact angle *vs.* surface treatment and *vs.* testing liquid; 1 - untreated PE veneer; 2 - plasma-treated PE veneer; 3 - AA grafted; 4 - triclosan coated; 5 – chlorhexidine coated

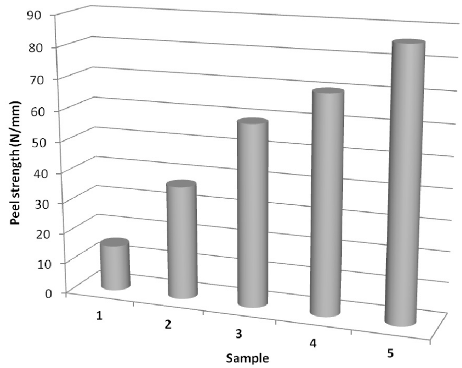

Fig. 2 Peel strength *vs.* surface treatment; 1 - untreated PE veneer; 2 - plasma-treated PE veneer; 3 - AA grafted; 4 - triclosan coated; 5 - chlorhexidine coated.

Antibacterial Activity Assessment

Table 1 shows inhibition zone area results. The inhibition zone area was calculated as the sample surface area deducted from the total area of the inhibition zone. The results show that untreated PE veneer (Sample 1), plasma-treated PE veneer (Sample 2) as well as acrylic-acid grafted PE veneer (Sample 3) do not display any antibacterial activity against both *Escherichia coli* and *Staphylococcus aureus* strains. The PE veneer coated with triclosan (Sample 4) does meet the expected antibacterial requirements. The average inhibition zone for the Gram-negative *Escherichia coli* strain is of 109 mm^2 and for the Gram-positive *Staphylococcus aureus* 486 mm^2. These values prove the antibacterial activity of the prepared layers as well as confirm XPS measurements. Similar results were obtained for chlorhexidine coated PE veneer (Sample 5). The average inhibition zone value of 43 mm^2 was calculated for *Escherichia coli* and 288 mm^2 for *Staphylococcus aureus* strain. It is worth mentioning, that both antibacterial agents are more active against Gram-positive bacteria. Finally, triclosan coated PE veneer show better results among the two antibacterial substances used.

Tab. 1 Inhibition zone area measurement

PE	Inhibition zone (mm^2)			Average value (mm^2)
	1	**2**	**3**	
Escherichia coli				
Sample 1	0	0	0	0
Sample 2	0	0	0	0
Sample 3	0	0	0	0
Sample 4	106	118	103	109
Sample 5	42	44	43	43

PE	Inhibition zone (mm^2)			Average value (mm^2)
	1	**2**	**3**	
Staphylococcus aureus				
Sample 1	0	0	0	0
Sample 2	0	0	0	0
Sample 3	0	0	0	0
Sample 4	475	497	486	486
Sample 5	288	278	298	288

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

CONCLUSION

This contribution was aimed at examining the impact of selected antibacterial agents, namely triclosan and chlorhexidine bound to the surface of PE veneers. DCSBD plasma treatment leads to increased surface free energy and surface wettability of PE veneer by introducing characteristic oxygen groups. A DCSBD plasma generator was used as activator of the PE veneers surface for efficient binding of acrylic acid and for its transformation to polymeric form by radical polymerization. Thus the bound acrylic acid created polymer brushes on the polymer surface that provided physical forces to bind antibacterial agents in an effective manner. The presence of triclosan and chlorhexidine was confirmed by different surface analysis techniques. Moreover the antibacterial effect of such treated PE veneer was proven by *in vitro* bacterial tests against *E. coli* and *S. aureus* when adhesion of bacteria to polymer was effective diminished.

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Streszczenie: *Antybakteryjna modyfikacja fornirów poliolefinowych*. Stosując okleiny z tworzyw sztucznych wykorzystywanych w produkcji mebli medycznych dla szpitali, konieczna jest antybakteryjna obróbka wstępna tych materiałów. Metoda modyfikacji zimną plazmą wydaje się być atrakcyjnym rozwiązaniem z ekologicznego i wydajnościowego punktu widzenia i cieszy się rosnącym zainteresowaniem. Zwiększenie odporności na infekcje może być osiągnięte przez obróbkę powierzchni polimerowych substancjami zawierającymi grupy przeciwbakteryjne takie jak triklosan oraz chloroheksydyny. W pracy zbadano biobójczy wpływ wybranych substancji antybakteryjnych umieszczonych na polietylenie małej gęstości (PE) w procesie plazmowania (zimną plazmą). Zmodyfikowana antybakteryjnie powierzchnia polietylenu (PE) zahamowała rozwój groźnych bakterii Escherichia coli i Staphylococcus aureus wywołujących chorobę jelit, zapalenie otrzewnej, zapalenie płuc, posocznicę, a ta z kolei jest przyczyną zakażenia ran i dróg oddechowych.

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