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Macromolecular anchoring layers for polymer grafting: comparative study

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Abstract

Comparative study of efficiency of macromolecular anchoring layers in the grafting of end-functionalized polymers to a surface was conducted. Poly(glycidyl methacrylate) (PGMA) and epoxydized polybutadienes (EPB) were utilized as the primary anchoring films. Amount of the epoxy moieties introduced to the surface was varied via thickness of the modifying polymer layer or amount of epoxy groups in the polymer backbone. Comparison between the grafting of polystyrene and poly(ethylene glycol) to the various macromolecular anchoring layers indicated that grafting ability of a layer was mostly governed by thickness of the interpenetration zone between the two polymers (anchoring and being grafted). In case of low level of the interpenetration, only functional groups at the periphery of the primary polymer layer were available for the grafting. Then, amount of grafted polymer did not increase with total number of epoxy groups in the anchoring film. However, as the thickness of the interpenetration zone increased, higher amount of the functional groups become available for the grafting.

Keywords: Polymer grafting; Epoxy containing polymer; Polymer anchoring

1. Introduction

Ultrathin polymers layers anchored to a substrate can be used to modulate various surface properties without altering general performance of a bulk material. Adhesion [1], lubrication [2], wettability [3,4], friction [5] and biocompatibility [6] can be tailored by the surface modification. Therefore the modification via polymer layers grafted to a surface has been the subject of intensive theoretical [7,8] and experimental [9–13] investigations.

Preparation of the anchored polymer layers can be readily achieved by the 'grafting to' method [9,10,14,15]. In the method, end-functionalized polymer chains react with complementary functional groups located on the surface of the substrate to form tethered chains. The advantage of the method is that the well-defined end-functionalized polymers can be employed for the grafting and, as a result, well-defined layers can be readily obtained. On the other hand, the technique has a disadvantage in terms of the maximum grafting that can be achieved, namely the grafting is self-limiting [16]. In fact, reactive end of a macromolecule to be grafted must diffuse through the layer of already grafted polymer chains to reach the reactive sites on the surface.

The density of the brush obtained by the 'grafting to' method can be increased if the attachment of macromolecules is conducted from a solution at Θ conditions [9] or from melt [10,12,13,17]. Grafting from melt in particular offers potential advantages due to screened excluded volume interactions [10]. Additional increase in grafting density for the attachment from the melt can be achieved when a macromolecular (primary) anchoring layer is used for the introduction of reactive group on a substrate surface. The primary polymer (mono) layer can be prepared from linear [18–20] or hyperbranched macromolecules [21–23].

The grafting from melt employing a macromolecular anchoring layer was reported in details in our previous communications [20,24,25]. Specifically, we reported attachment of end-functionalized polystyrene (PS) and poly(ethylene glycol) (PEG) from melt to a primary layer of poly(glycidyl methacrylate) (PGMA), anchored to silicon wafers. Comparison of the results for the PS grafting to the PGMA primary layer with published data [17] obtained for the epoxysilane monolayer suggested that there are many similarities between these grafting processes. The same key trends were observed. Nevertheless, the grafting to the macromolecular reactive layer was more effective. The epoxy groups situated in the loops/tails

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of the adsorbed PGMA macromolecule were more accessible when compared to epoxysilane with terminal epoxy groups located mainly at the monolayer surface. The higher efficiency of PGMA in the grafting reactions was, thus, related to the high mobility of the epoxy reactive groups and to the formation of an interpenetrating zone at the PS/PGMA interface.

Köthe et al. [19] reported surface modification of different substrates utilizing a macromolecular anchoring layer consisting of epoxidized polybutadiene (EPB). The polymer with different degrees of epoxidation (19, 47 and 96%) was employed. The reactive polymer was permanently adsorbed on the silicon oxide particles and substrates. Residual epoxy groups of the coating layer were used for covalent bonding of toluene diisocyanate and amino terminated polyethylene glycol. In general, the grafting efficiency of the layer was lower that the efficiency of the PGMA grafting layers. However, the polymer anchoring was conducted from a solution and not from a melt. The present article focuses on comparison between efficiency of PGMA and EPB reactive anchoring polymer layers for the grafting conducted from melt.

2. Experimental

Highly polished single-crystal silicon wafers of ⟨100⟩ orientation (Semiconductor Processing Co.) were used as a substrate. The wafers were first cleaned in an ultrasonic bath for 30 min, placed in a hot (80 °C) 'piranha' solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide; (caution: the cleaning solution is highly corrosive and extremely reactive with organic substances) for 1 h, and then rinsed several times with high purity water.

Poly(ethylene glycol) monomethyl ether ($M_n \approx 5000$ g/mol, degree of polymerization, $N = 114$) obtained from Aldrich was modified by succinic anhydride (Aldrich) to obtain carboxy end group derivative (PEG). Acylation was carried out by refluxing with large excess (ca. 20) of succinic anhydride in tetrahydrofurane (THF). PEG was purified by multiple precipitations from THF solution in diethyl ether. (FTIR spectra indicated that high degree of carboxilation was achieved). Carboxy terminated PS was synthesized by 'living' free radical polymerization ($M_n = 9600$ g/mol degree of polymerization, $N = 92$) in the Institute of Polymer Research Dresden, Germany by Dr J. Pionteck and Dr H. Malz.

Glycidyl methacrylate from Aldrich was polymerized radically to give PGMA, $M_w = 285{,}600$ g/mol, PDI = 3.4 (GPC). The polymerization was carried out in methyl ethyl ketone (MEK) from VWR at 60 °C. AIBN from Aldrich was used as an initiator. The polymer obtained was purified by multiple precipitations from MEK solution in diethyl ether.

Polybutadiene ($M_w = 424{,}540$ g/mol, PDI 2.93 (GPC)) from Aldrich was epoxidized in $CHCl_3$ solution in the presence of stoichiometric (to double bonds) amounts of formic acid and 30% hydrogen peroxide [26]. Reaction was carried at room temperature for different times. Degree of epoxidation was estimated from ^{1}H NMR [27]. Vinyl proton signal was used to monitor extent of the reaction. Epoxidation for 2, 4, 6 and 24 h yields EPBs with molar content of epoxy groups 26.7, 42.6, 53.2 and 72%, respectively, referred, in the text as EPB-2, EPB-4, EPB-6 and EPB-24, correspondingly.

The PGMA (EPB) was dissolved in MEK at different concentrations (0.05–0.5% w/v) and thin films were deposited on the substrate by dip coating (Mayer Feintechnik, model D-3400), dried overnight at ambient conditions and annealed for 20 min at 110 °C. The thickness of the deposited PGMA (EPB) films was controlled by varying the concentration of the PGMA (EPB) solution. The PEG powder was deposited onto the surface of clean glass slides and covered with silicon wafer modified by the primary layer. PS was dip coated from 0.7% MEK solution. The specimens were placed in a vacuum oven at elevated temperature (110 °C for PEG and 150 °C for PS) for 10–14 h to enable the end groups to anchor to the epoxy-modified substrate. At high temperatures, carboxylic groups are able to react with the epoxy groups of the primary layer. The temperatures chosen for the grafting were well above glass transition temperature for PS (100 °C) and melting temperature for PEG (62–76 °C) [28]. Unbound polymer was removed by multiple washing with toluene at 75 °C including washing in an ultrasonic bath (In a control experiment we attempted to graft un-functionalized PS and PEG (no carboxylic end groups) to the surface via the macromolecular anchoring layers. Practically no polymer attachment was observed).

Static contact angle measurements were made using a contact angle goniometer (Kruss, Model DSA10). Calculation of the contact angle was made using the tangent method. Contact angle measurements were made with water (pH 7.0), and a static time of 30 s before the angle measurement. Ellipsometry was performed with a COMPEL automatic ellipsometer (InOmTech, Inc.) at an angle of incidence of 70°. Reproducibility of the ellipsometry measurements was better than +/−10%. Original silicon wafers from the same batch and silicon wafers with PGMA layer were tested independently and used as reference samples for the analysis of grafted polymer layers. Refractive index for EPB was assumed to be $n = 1.5$, for PEG was obtained from supplier ($n = 1.465$, Aldrich); for PGMA ($n = 1.525$) and PS ($n = 1.59$) was calculated using group contribution method [28]. Atomic force microscopy (AFM) studies were performed on a Dimension 3100 (Digital Instruments, Inc.) microscope. We used the tapping to study the surface morphology of the modified substrates in ambient air. Silicon tips with spring constants of 50 N/m were used. Imaging was done at scan rates in the range 1–2 Hz. The root mean square roughness of our samples was evaluated from the AFM images recorded [29]. NMR was performed at 300 MHz (Bruker) with TMS as internal standard.

To characterize the polymer layers, several parameters have been evaluated [30]. The surface coverage (adsorbed amount), Γ (mg/m^2), was calculated from the ellipsometry thickness of the layer, h (nm) by the following equation:

$$\Gamma = h\rho \tag{1}$$

where ρ is density of attached (macro) molecules. The density of (1.05 g/cm^3) for PS was used in calculations and the density

of PGMA (1.08 g/cm^3) was assumed to be the same as for poly(propyl methacrylate) [28]. The density data for EPB (assumed to be the same as for PB (0.9 g/cm^3)) and PEG (1.09 g/cm^3) were provided by the supplier [31].

The chain density, σ (chain/nm^2), i.e., the inverse of the average area per adsorbed chain, was determined by:

$$\sigma = \frac{\Gamma N_A * 10^{-21}}{M_n} = \frac{(6.023\Gamma * 100)}{M_n} \quad (2)$$

where N_A is the Avogadro's number and M_n (g/mol) is the number-average molar mass of the grafted polymer.

The free energy of mixing (ΔG_M) for PEG(PS)/primary polymer pair was estimated from the Flory–Huggins equation [32]:

$$\frac{\Delta G_M}{V_0 KT} = \frac{v_1 v_2 \chi}{V_x} + \frac{v_1 \ln v_2}{V_1} + \frac{v_2 \ln v_2}{V_2} \quad (3)$$

where v_1 and v_2 are volume fractions of two components, V_1 and V_2 are molecular volumes of the components, K is the Boltzmann's constant, V_0 (volume occupied by N_0 number of cells in Flory–Huggins theory (taken as 1 cm^3), and V_x is given by:

$$\frac{1}{V_x} = \frac{\left(1 - \frac{2}{Z}\right)}{V_R} \quad (4)$$

where Z is the lattice coordination number ranging from 6 to 12 and V_R, volume occupied by monomer unit. In our calculations the geometrical mean of PEG (PS) and PGMA (EPB) monomer units volumes and $Z = 10$ were used.

The interaction parameter, χ for PEG(PS)/PGMA(EPB) pair was estimated by means of the following equation [32]:

$$\chi = \frac{V_r(\delta_1 - \delta_2)^2}{RT} \quad (5)$$

where V_r is molar volume of monomer unit of the polymer, δ_1 and δ_2 are solubility parameters of the polymers; R is the universal gas constant and T is the temperature in Kelvin. In our estimations, the geometrical mean of V_r for the PEG(PS) and PGMA(EPB) monomer units was used. The solubility parameters were estimated using the atomic increments approach proposed by Askadskii [33]. Calculated values of the solubility parameter were 22.01, 18.65, 15.3, 16.65 and 20.49 (J/cm^3)$^{1/2}$ for PEG, PS, PB, EPB (100% epoxidation) and PGMA, respectively.

The interphase thickness was approximated by substitution in the following equation [34]:

$$S_{th} = \frac{2a}{\sqrt{6\left(\chi - \left(\frac{1}{N_1} + \frac{1}{N_2}\right)2 \ln 2\right)}}, \quad (6)$$

where a is the statistical segment length and N_1 and N_2 are the degree of polymerization of two polymers. The statistical segment length for PGMA and EPB was assumed to be the same as for PS (~0.6 nm) [32]. The segment length for PEG (0.29 nm) was calculated from known end-to-end distance, L: $a = \sqrt{L^2/3N}$ [35,36]. In our calculations by Eq. (6), geometrical mean of the PEG(PS) and PGMA(EPB) segment lengths was used.

3. Results and discussion

3.1. Macromolecular anchoring layers

In our experiments EPB (with different content of epoxy groups) and PGMA macromolecular anchoring layers were placed on a silicon surface by dip coating from MEK solutions. To study attachment of the primary layers to the substrate, thin layers (9+/−2 nm) of PGMA and EPB-6 were deposited and aged at room temperature for different times. Next, unbounded polymer was extracted with MEK and amount of the polymer remaining on the substrate was monitored by ellipsometry. The thickness of the residual layer is presented in Fig. 1. Data obtained for both polymers indicated that after very short time (less than 10 min) 1–2 nm thick layer of reactive macromolecules was permanently attached to the surface.

The thickness of the polymer film (and, accordingly, surface coverage, Γ) increased with time and reached 7 nm and 3.5–4 nm for EPB-6 and PGMA, respectively. In general, EPB-6 demonstrated higher rate of attachment if compared to PGMA. Assuming similar reactivity of epoxy group in both polymers the higher rate can be attributed to the lower glass transition temperature of EPB-6 and, thus, increased mobility of the EPB macromolecules. ($T_g = -50$ °C for EPB was estimated from T_g of polybutadiene = −95 °C [obtained from the supplier [31]]

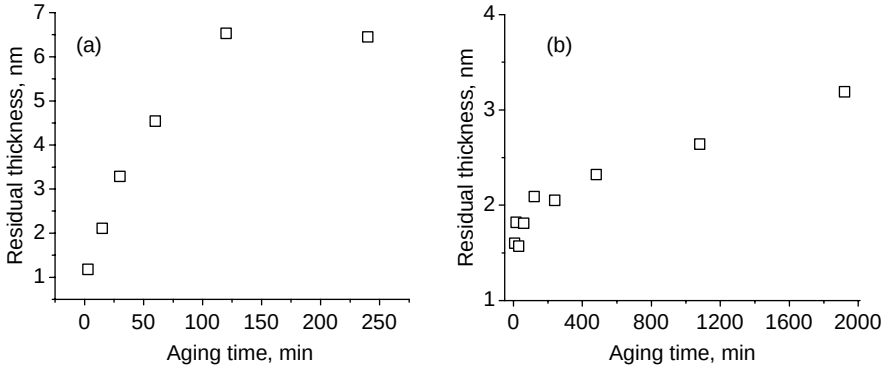

Fig. 1. Time dependence for attachment of (a) EPB-6 and (b) PGMA macromolecules to silicon substrate. Room temperature.

and T_g of 100% epoxidized PB 25 °C, calculated using Bicerano method [37]). T_g = 75 °C was measured by DSC for PGMA.) In most of our further investigations thickness of all anchoring layers was kept on the level of 1.4 +/− 0.2 nm. Additionally, the layers were annealed at 110 °C for 20 min. Our previous studies [24,25] showed that such an annealing stabilizes structure of the PGMA primary layer. Additionally, the annealing above T_g allowed increasing thickness of the PGMA layer permanently attached to the substrate above 4 nm attainable at room temperature. (It was difficult to produce uniform films with the thickness below 1 nm by the dip-coating technique reproducibly. On many occasions dewetting was observed for the thinner films. Thus, anchoring layers with the thickness below 1 nm were not investigated in the present work).

The substrates covered with the adsorbed PGMA and EPB films were rinsed vigorously by series of polar solvents including DMSO and THF. It was determined that the polymer chains could not be detached from the surface after the solvent treatment, indicating permanent bonding of the macromolecules to the surface. AFM studies of the layers revealed that the films were smooth and homogeneous. Fig. 2(a) demonstrates that PGMA layer uniformly covers entire substrate surface on micro-level. Morphology of the primary polymer layer on the nano-level is shown in Fig. 2(b). The layer was molecularly flat with RMS roughness less than 0.3 nm. AFM topography of the primary layer consisting of EPB-6 is shown in Fig. 2(c) and (d). RMS roughness of the layer was 0.3 and 0.15 nm on micro- and nano-level, correspondingly.

3.2. PEG grafting to anchoring macromolecular layer

Thickness of the primary layers deposited (~1.4 nm) corresponds to comparable initial number of 6.4 and 7.4 epoxy groups/nm^2 throughout PGMA and EPB-6 films, respectively. However, maximum amount of the end functionalized PEG that could be grafted via the layers was rather different. The thickness of the PEG layer grafted to the PGMA film was 9.4 nm (1.23 chains/nm^2). The grafting through EPB-6 resulted in PEG attachment of only 2 nm (0.25 chains/nm^2). Accordingly, the number of the functional groups in the layer, which were utilized for the grafting, was 19 and 3.4% for PGMA and EPB-6, respectively.

Fig. 3 demonstrates AFM topography images of the PEG grafted to PGMA and EPB-6 primary layers. The imaging revealed that the grafted layers covered entire surface of the substrate. However, different types of layer morphology were observed depending on the grafted layer thickness. Isolated domains (Fig. 3(a)) observed for low grafting density (attainable when PEG was grafted to EPB-6). We associate

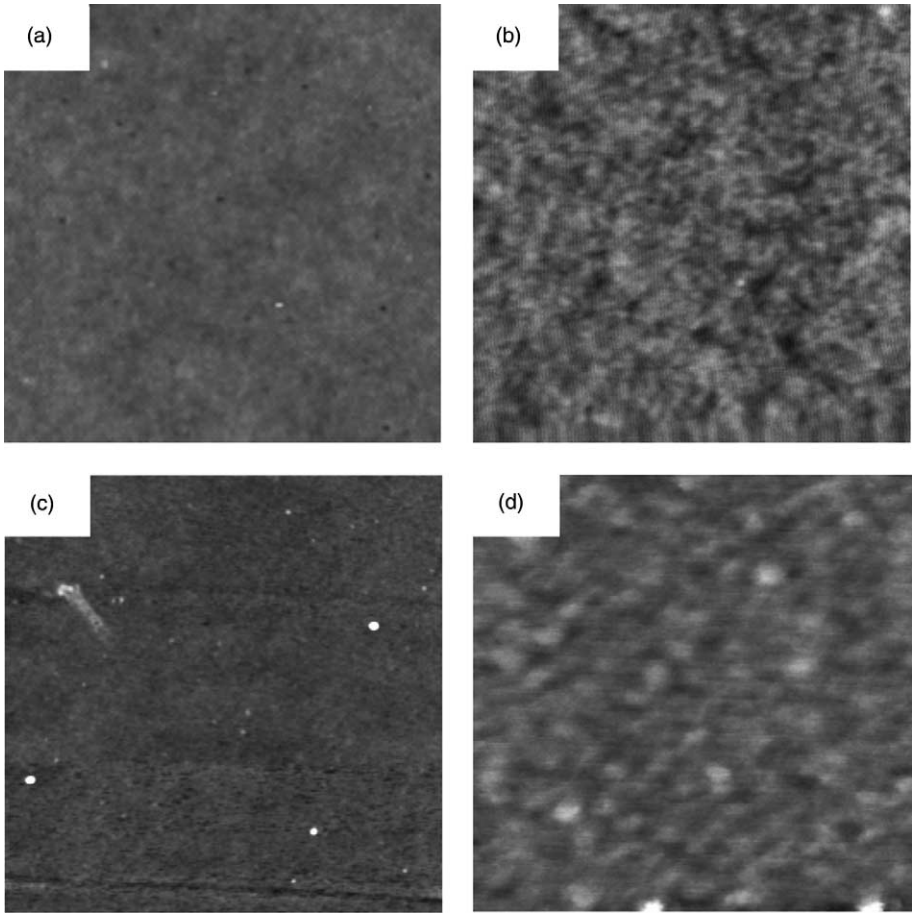

Fig. 2. AFM topography images of PGMA (a, b) and EPB-6 (c, d) primary monolayers. (a, c) 5×5 μm^2; (b, d) 1×1 μm^2. Vertical scale is: 10 nm for images (a) and (c); 4 nm for (b) and (d).

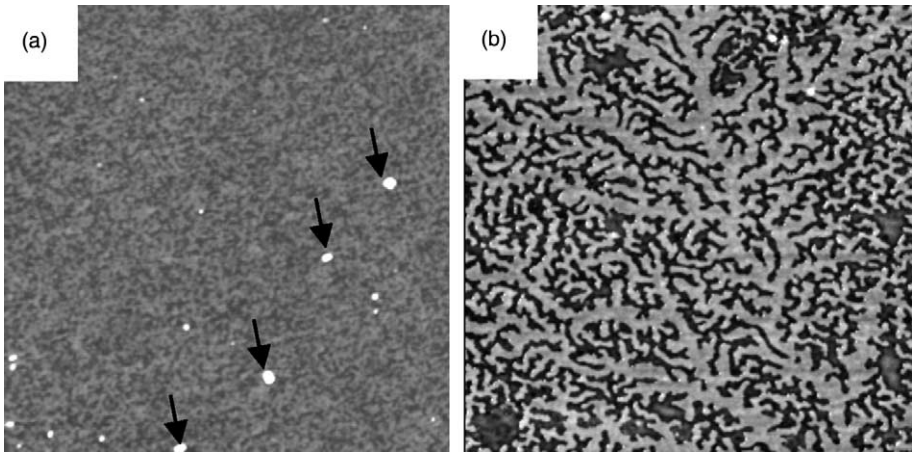

Fig. 3. AFM topography images of the PEG layer grafted to (a) EPB-6, (b) PGMA anchoring films. PEG domains are marked on image (a). Image size 5×5 μm^2, vertical scale 20 nm.

the domains with PEG crystals being formed by a fraction of the grafted macromolecules [38]. For thick PEG layers (grafted to PGMA) the crystalline formations uniformly covered the whole substrate surface (Fig. 3(b)). AFM RMS roughness was increased from 0.7 nm for the PEG layer grafted to the EPB-6 to 3.3 nm for the highly crystallized PEG layer grafted to PGMA.

When an end-functionalized polymer is grafted from melt to the surface modified with the anchoring reactive macromolecules the extent of polymer interface, involving two different polymers (anchoring and being grafted) may remain intact if the polymers are totally immiscible [39]. In that case the grafting polymer chains can reach only epoxy groups located at the surface of the PGMA (EPB) films (Fig. 4(b)). Opposite and more favorable for the grafting situation is when the polymer completely penetrates into PGMA (EPB) film (Fig. 4(c)). Then, virtually all epoxy groups are available for the reaction.

Miscibility between PEG and macromolecular layers (PGMA and EPB) was calculated using the Flory–Huggins equation (Eq. (3)). The estimations revealed that there is no thermodynamical miscibility predicted for the PGMA(EPB)/PEG pairs at the grafting temperatures used in the present study (110 °C). Therefore, the interdiffusion zone should be formed between PGMA(EPB) and PEG. Level of the interpenetration at the interface (or width of PEG/PGMA(EPB) interphase) is a function of the statistical segment length, degree of polymerization and interaction parameter χ. The interphase thickness can be estimated employing Eq. (6). Fig. 5 shows variation of the interphase thickness versus the temperature of the grafting. The thickness calculated by the Eq. (6) increases with the temperature and reaches approx. 0.45 and 1.65 nm at 110 °C (grafting temperature) for EPBs and PGMA, respectively. In this scenario, only certain amount of epoxy functional groups located inside the layer may be available for the grafting. According to the estimations PEG has to penetrate to a

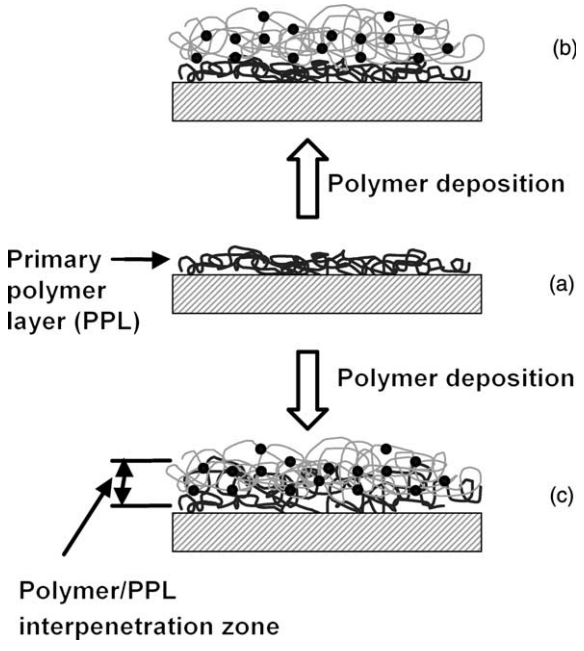

Fig. 4. Two boundary situations during polymer grafting to PGMA (EPB) layer. (b) No penetration of grafted chains into primary polymer layer. (c) Formation of polymer/PGMA(EPB) interpenetration zone.

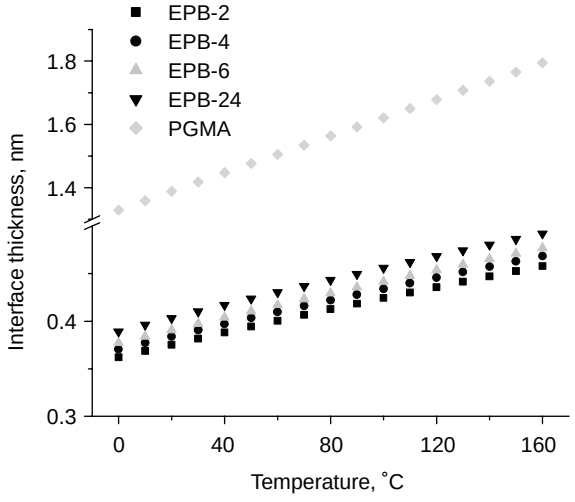

Fig. 5. Thickness of interface between PEG and primary polymer layers versus temperature.

significant extent inside the PGMA anchoring macromolecular layer possessing thickness of 1.4 nm. The number of the groups available in EPB-6 layer has to be sufficiently lower. In fact, the ratio of epoxy group utilization (19% for PGMA and 3.4% for EPB-6) was roughly proportional to the thickness of interface between PEG and primary polymer layer. The obtained result indicated that the total amount of the epoxy groups in primary layer is not a limiting factor for the grafting.

The grafting of PEG to substrates modified with EPBs possessing different amounts of epoxy groups supported the decisive role of the interface thickness. The epoxy content in the polybutadienes was varied from 26.7 to 72 mol%. The interface thickness calculated by Eq. (6) for these polymers and PEG was, however, very close and significantly lower than the thickness for PGMA (Fig. 5). Fig. 6 demonstrates how thickness and grafting density of the PEG grafted film change with the level of the epoxidation. Obtained data suggested that the grafting of the PEG to EPBs was virtually identical for the layers with different number of the functional moieties. Three times increase in the epoxy content did not cause corresponding increase in the grafting density.

3.3. PS grafting to anchoring macromolecular layer

Grafting of non-polar polymer, PS (with degree of polymerization very close to the degree of PEG) to the surface via the macromolecular anchoring layers was also studied. Thickness of the anchoring layers was ~1.4 nm (6.4 epoxy group/nm^2 for PGMA and 7.4 epoxy group/nm^2 for EPB-6). Maximum thickness of PS film grafted at 150 °C to the primary layers was 6.2 nm (0.38 chain/nm^2) and 5.7 nm (0.35 chain/nm^2) for PGMA and EPB-6, respectively. Namely, both primary layers demonstrated comparable ability to anchor PS macromolecules. AFM imaging revealed smooth and homogeneous morphology of the PS film grafted to both primary polymer layers (Fig. 7). RMS roughness was 0.24 and 0.67 nm for the PGMA and EPB-6 primary, layers respectively. The higher roughness for the EPB-6 anchoring layer may be connected to higher mobility of the layer at elevated temperatures causing higher level of segregation (on the nano-level) between PS and EPB chains.

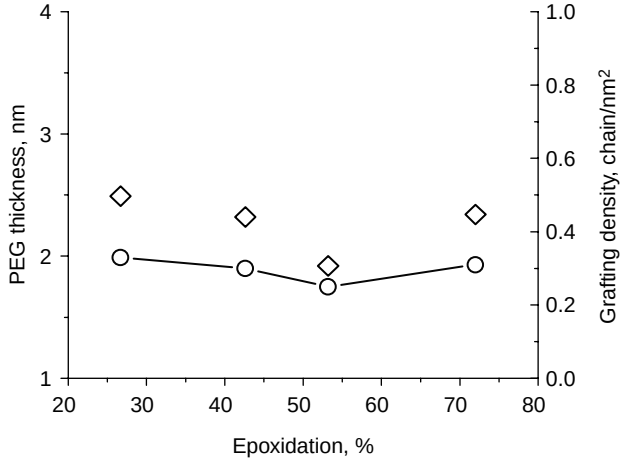

Fig. 6. PEG thickness (diamonds) and grafting density (circles) attached to different EPBs. Line is drawn for eye guide only.

The percentage of the functional groups in primary polymer layer that were utilized for grafting was close: 6 and 4.7% for PGMA and EPB-6, respectively. Such a low level of the epoxy groups' utilization indicated that number of epoxy groups in the anchoring layer does not limit the PS attachment as well. The extent of PS grafting ought to be connected with interfacial situation at PS/EPB and PS/PGMA boundaries. Thermodynamical calculations (Eq. (3)) revealed positive free energy of mixing for PS/EPB and PEG/PGMA polymer pairs. Thus, there is no thermodynamical miscibility predicted for the polymers in contact. Next, interface thickness between two polymers was calculated employing Eq. (6). Fig. 8 presents results of the estimations. It appeared that amount of PS grafted to both anchoring polymer layers can be related to the interphase thickness. In fact, the thickness at 150 °C (1.1 nm for PGMA and 0.9 nm for EPB) was very close for the both anchoring layers, and the comparable extend of PS chains penetration into the anchoring layers caused comparable attachment of the macromolecules.

3.4. Influence of thickness of anchoring layers on PEG grafting

One of the distinct advantages of the macromolecular anchoring layer approach to surface modification is the possibility of fabrication of relatively thick anchoring layers permanently attached to the boundary. The thicker layers allow: (i) introduction of a higher number of functional groups to the surface; (ii) possibility of modification of complex (rough) surfaces; (iii) improved durability and wear resistance of modified surface. Therefore, we have studied grafting of PEG to PGMA and EPB-6 layers possessing higher thickness. Fig. 9 presents how grafted amount of PEG depends on thickness of the primary polymer layer. As for the anchoring of PEG to the thinner layers a difference between PGMA and EPB-6 was observed. For the epoxydized polybutadiene increase in thickness caused certain decrease in PEG grafting amount, whereas for the glycidyl polymer the amount of PEG attached to the surface increased with thickness of the anchoring layer.

The obtained for EPB trend is somewhat surprising, since with increase in the layer thickness number of reactive epoxy groups in the film is increased. Additionally, for the thicker layers less monomeric units are in close proximity to the solid substrate, which restricts their motions. The increased amount of the reactive units and their enhanced mobility are supposed to offer better chance for the groups to react with carboxy functionalities of the polymer being grafted. However, the opposite tendency was observed experimentally. It appeared that the more unrestricted segments might better prevent interfacial interdigitation of the thermodynamically immiscible polymers. It should be mentioned as well that the real process of the polymer grafting is a dynamic process. Before the first chain is grafted the interface between the polymers (anchoring and being grafted), in fact, may be approximated by Eq. (6). In course of grafting the nature of the interface is changed. Instead

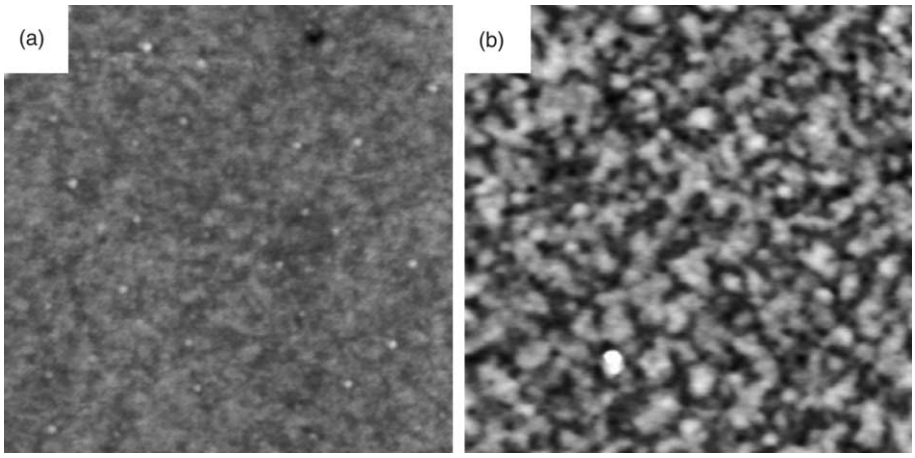

Fig. 7. AFM topography images of PS grafted to (a) PGMA, (b) EPB-6. Image size 1×1 μm^2, vertical scale 10 nm.

of the interface between the two homopolymers complex interface between the homopolymers and graft copolymer (PEG grafted to the anchoring macromolecule) is present. The new interface may be more or less extended than the original one, causing increase or decrease in polymer attachment.

Different behavior of EPB-6 and PGMA suggests that some initial degree of interpenetration may be necessary for enhanced homopolymer/copolymer interface and grafting, where the attachment become more efficient for the thicker anchoring films. It appeared that extremely thin initial interfacial zone between PEG/EPB-6 is not enough to improve miscibility as grafting proceeds. Then, instead of the improvement the first PEG chains attached to EPB macromolecules may be rejected by the anchoring layer and forced to the boundary preventing grafting of new chains. This rejection process become more pronounced when the thickness of the anchoring film (mobility of the monomeric units in the film) is increased.

Previous to drawing conclusions from the study presented it is worth to mention a factor that may additionally affect the grafting under consideration. Throughout the attachment of a functionalized polymer via the macromolecular anchoring layer at elevated temperature, beside reaction between the end groups and epoxy functionalities, self cross-linking of the macromolecules constituting anchoring film may occur [20,24] . The cross-linking side reactions may also affect the anchoring behavior of the reactive layers.

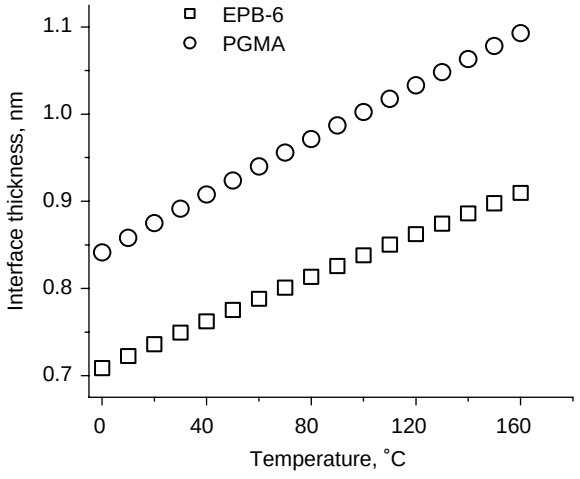

Fig. 8. Thickness of interface between PS and primary polymer layers as function of the grafting temperature.

4. Conclusions

Ultrathin polymer films consisting of macromolecules bearing different number of epoxy functional groups were successfully used for polymer anchoring (from melt) by the ‘grafting to’ approach. PGMA and epoxydized polybutadienes were utilized as the primary anchoring polymer layers. It was determined that the macromolecules could not be detached from the surface after the solvent treatment, indicating permanent bonding of the chains to the surface. Epoxy groups located in loops and tails of the attached primary layer were not connected to the substrate and served as reactive sites for the following polymer grafting of PS and PEG. Amount of the epoxy moieties introduced to the surface was tuned via thickness of modifying polymer layer or amount of epoxy groups in the backbone.

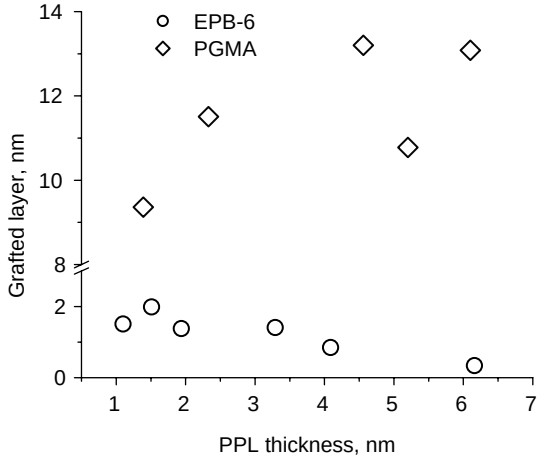

Fig. 9. Thickness of PEG grafted layer versus thickness of primary polymer layer. Grafting temperature −110 °C. Grafting time 12–14 h. (Grafting of PEG to thick PGMA film (4–7 nm) was done for 2 h).

Comparison between grafting of PEG and PS to the various macromolecular anchoring layers indicated that grafting ability of a layer was mostly governed by thickness of the interpenetration zone between the two polymers (anchoring and being grafted). In case of low level of the interpenetration, only functional groups at the periphery of the primary polymer layer were available for the grafting. Then, amount of grafted polymer did not increase with total number of epoxy groups in the anchoring film. However, as the thickness of the interpenetration zone increased, higher amount of the functional groups become available for the grafting. Therefore, grafting density increased with the primary polymer layer thickness.

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