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Nano-adsorbents control surface properties of polyurethane

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Abstract

Additives are minor but critical components that polymers need for processing and applications. However, these additives may also have adverse effects, e.g. for polymeric biomaterials, leaching additives can change surface properties, and may lead to poor biocompatibility. How to use additives yet keep them from detrimental behaviors is a challenging issue. Diffusion barriers may be used to slow down the additive migration but difficult to stop it. In this paper, we introduce the concept of ''nano-adsorbents'' in polymers. These nano-adsorbents confined the additives within the polymers by thermodynamically interacting with them. While the additives are still present in polymers to provide intended functions, they are thermodynamically constrained from free migration to the surface. Nano sized-fillers were selected due to their high surface to volume ratio. This new usage of nano-fillers for polymers was demonstrated with a biomedical polyurethane and a surface coated nanoclay that thermodynamically attracts the additive in the polyurethane.

Keywords: Biomaterials; Nanocomposites; Surface

1. Introduction

Functional additives, low molecular weight oligomers, and some degradation products are present in almost all polymer materials. They are not problematic for most commodity applications. However, for biomedical and other sophisticated applications, they can cause concerns. For example, the biocompatibility of polymers can be compromised by leaching mobile components into the implantation host even though the polymers themselves are biocompatible. For this reason, a big portion of the biocompatibility evaluation of biomaterials is to test leachables (ISO-10993). Because reliability requirements of biomaterials are extremely high, even minor components of them can determine whether they are suitable for biomedical applications. Accumulation of such species in the polymer surface can also significantly change its surface properties such as adhesion and water contact angles. Unfortunately, the presence of such components is almost unavoidable. For example, processing additives are necessary for polymers to be made into useful shapes. As such, purification is not even an option to solve the problem. Diffusion barriers may be used to delay the accumulation processes, but they cannot completely stop the diffusion to eliminate the problems.

In this paper, we introduce a ''nano-adsorbent'' approach in which we do not try to remove these components from the polymers. Instead, we introduce selected nanostructures in the polymers and use these nanostructures to confine most of these minor components inside the polymers with nano-scale dispersion. Therefore, while these necessary components still remain available for their intended functions, they do not accumulate outside the surfaces to cause adverse physical effects. Nanostructures have a high surface to volume ratio so they are expected to have high efficiency and nano-scale homogeneity. These nanostructures are referred to as nano-adsorbents.

We demonstrated this nano-adsorbent idea with a hydrophilic poly(etherurethane) that is one of the most broadly

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used polymers in implantable biomedical devices such as artificial hearts, cardiac pacemakers, and structural tissue replacements [1,2]. This polyurethane is microphase separated into hard and soft domains that allow it to be made into products ranging from flexible elastomers to rigid plastics. However, in order for polyurethane to be processed into useful devices, a hydrophobic additive, *N*,*N*′-ethylenebisstearamide (EBS-$(C_{17}H_{35}\text{-}CONHCH_2)_2$) has to be included in the materials at a low level for good metal release properties. This additive, while making processing possible, tends to accumulate at the polyurethane surface and lead to surface compositions very different from that of the bulk. For example (see Section 4), based on X-ray photoelectron spectroscopy (XPS) analysis, pure polyurethane has 77, 5, and 18 atomic % of carbon, nitrogen, and oxygen, respectively. EBS has 92, 4, and 4 atomic % of C, N, and O, respectively. However, when only 0.25 wt% of hydrophobic EBS was compounded in the hydrophilic polyurethane, followed by annealing the specimens at 50 °C for 4 h, there were 91, 4, and 5 atomic % of C, N, and O, respectively, observed on the surface as revealed by XPS. This composition was significantly different from that of the pure polyurethane, but very close to that of EBS, indicating that the polymer surface was almost completely covered by EBS. The above EBS amount and annealing process are typical for biomedical polyurethanes. However, when such material is implanted into patients, the host tissues see the hydrophobic EBS as opposed to the hydrophilic polyurethane.

Because the EBS and polyurethane have similar % of N, the % of C is chosen to measure how much EBS are in polymers' surfaces. We assume the percentage of surface covered by EBS to be a linear function of atomic % of C, with 92% of C indicating 100% EBS coverage at materials' surfaces and 77% of C indicating pure polyurethane surface.

2. Nano-adsorbent concept

The idea to use nano-adsorbents to reduce the accumulation of EBS molecules at the samples' surfaces is based on the following simple rationales. The hydrophobic EBS molecules tend to migrate to and accumulate at polymers' surfaces (or air interface) because this lowers their energies. If nano-adsorbents have stronger attractive interactions with the EBS molecules, the energy is further lowered when the EBS molecules reside near the nano-adsorbents, and hence the EBS molecules re-partition themselves among the polymer surfaces, bulk, and nano-adsorbents. The overall accumulation at surfaces will be reduced (Fig. 1). Also, due to reduction in bulk concentration, the migration rate of EBS molecules would be reduced.

The nano-adsorbents chosen in the present paper are nanoclay fillers. There are extensive literatures about surface coated nanoclay [3–14]. Based on that, we chose a nanoclay filler that is surface coated with a hydrophobic compound, dimethyl, benzyl, hydrogenated tallow quaternary ammonium (Closite 10A. See Table 1 for structure). There are more than 20 CH_2 and CH_3 groups and a benzene ring in each coating molecule. Polyurethane has a high concentration of polar groups such as urethane and ether (about 0.4 urethane groups and 0.6 ether groups for every four CH_2. See Section 3). Therefore, it is expected that the coated clay surface has stronger attractive interactions with EBS molecules (36 CH_2 and 2 amide groups) than the hydrophilic polyurethane matrix.

This interaction difference might be described more clearly by the solubility parameters of these materials. The solubility parameters of the clay 10A coating, EBS, and polyurethane were estimated to be 16.3, 17.5, and 22.7 $(\mathrm{J/cm^3})^{0.5}$, respectively [15]. The Flory–Huggins interaction parameters (χ) between the clay coating and the EBS was estimated to be 0.35, and that between the EBS and the polyurethane to be 6.5 (see Section 3). The concentration of the EBS confined in regions near the clay coating can be higher than that of the free EBS in the polyurethane matrix by a factor of $e^{\Delta\chi} \sim e^{6.5-0.35} \sim 400$. Because the EBS molecules that accumulate at the polymer surface are in equilibrium with the free EBS in the bulk, the surface concentration is expected to reduce accordingly. It should be pointed out that this simple estimation is only a qualitative measure.

Surface coated clay platelets are about 2–3 nm thick and 10–100 nm wide and therefore they have a high surface to volume ratio [6,7]. A small amount of filler can have a significant confinement effect on the EBS molecules, while its effect on the bulk properties of the polyurethane are negligible.

3. Experimental

3.1. Sample preparation

The polyurethane used in the present study is a duplicate of Pellethane 2363-75D (Dow Chemical, MI). It was prepared through a condensation reaction among 4,4′-methylene bisphenyl diisocyanate (MDI), polytetramethylene oxide (PTMO, 650 g/mol), and 1,4-butanediol (BDO). The hard segments are made from MDI and BDO and the soft segments from MDI and PTMO. The molar ratio of PTMO to BDO is 1:3.5, which is equivalent to a composition of 47 wt% of soft segments and 53 wt% of hard segments. The glass transition temperature of this material is 35 °C (measured with a Pyris 1 DSC, Perkin–Elmer, at a temperature increase rate of 40 °C/min). The molecular weight and polydispersity index are 59 kg/mol and 1.5, respectively (Agilent 1100 HPLC coupled with a Wyatt Dawn EOS 18 angle light scattering unit, Phenogel 5 μm columns, and tetrahydrofuran mobile phase). The material absorbs up to 1.5 wt% of water after saturation at room temperature. Therefore, this polymer is rather hydrophilic.

All the clay fillers were purchased from Southern Clay Products Inc (TX). The organic coatings of these clay samples are listed in Table 1. More detailed information about density, platelet *d*-spacing, and coating amount can be found at www.nanoclay.com. Polymer and clay samples were dried down to less than 100 ppm moisture and melt-blended with a twin-screw extruder ($L/D = 24$, $D = 25$ mm, Haake, German). Mixing was done at 150 rpm and 205 °C melt temperature. EBS was compounded with polyurethane either during polymer preparation or together with clays. The composites

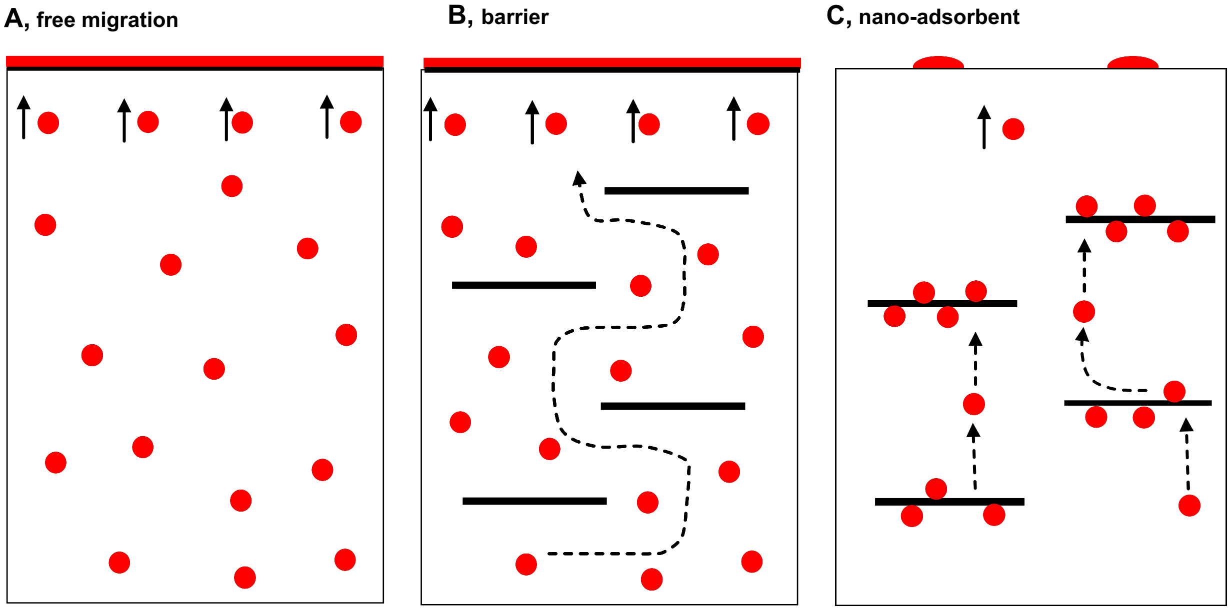

Fig. 1. Barrier and nano-adsorbents. A, hydrophobic additives dispersed in a hydrophilic polymer. The additive molecules have a lower energy if they accumulate at surface. Therefore, the polymer surface can be masked. B, nano-platelets dispersed in a polymer. The barrier properties of the platelets can slow down the migration of the additive molecules to the surfaces. But eventually the polymer surface is masked because the same energy level will be achieved. C, nano-adsorbents. Nano-platelets are surface coated with hydrophobic compounds that have strong attractive interactions with the hydrophobic additive molecules. Then, the additive molecules stay near the platelet surfaces (adsorption). This re-partition reduces the additive concentration in polymer matrix, and as a result, reduces their accumulation at the materials' surface. The migration rate of additives is also reduced.

were injection molded into testing specimens (at 215 °C) followed by being thermally annealed at 50 °C for 4 h to eliminate residual stress.

3.2. Characterization

Surface composition of the samples was measured using a Physical Electronics Quantum 2000 Scanning XPS (MN). The monochromatic Al Kα X-ray source was operated at 15 kV with a power of 50 W. The analysis was done at a 45° take-off angle. Low energy electron and Ar^+ ion floods were used for charge compensation. The area of analysis was $300 \times 1000\ \mu m^2$. Morphology of clay dispersion was observed with transmission electron microscopy (TEM) (Jeol 1210, Japan) on microtomed slices (50 nm thick). Tensile testing was performed with a MTS instrument (MN). Adhesion test samples were made by applying a layer of triacetoxysilane terminated silicone adhesive (Med2000, Nusil Inc. CA) on straight polyurethane specimens ($76 \times 12.7 \times 6.4\ mm^3$) and curing at 50% relative humidity and 37 °C for 24 h. Ninty degrees peeling tests were performed with the MTS at a peeling rate of 2.54 mm/min. Water contact angle was measured at room temperature. Each data point of the above measurements represented an average of two to five repeats.

Solubility parameters (δ) were estimated with the Hoftyzer–Van Krevelen methods. The molar volumes (ν) were estimated with the Fedors' method. These methods are described in Ref. [15]. The urethane group was approximated as a combined ester and secondary amine group because there is no urethane listed in the original reference. Flory–Huggins parameters were estimated at 50 °C (the annealing temperature) based on the equation $\chi = (\delta_1 - \delta_2)^2 \nu' / (kT)$ where ν' is the average molar volume and k is Boltzmann constant. Ammonium and negative counter ions in the clay coating molecules were not included in the estimation because they are attached or next to the clay surfaces and should not involve in the interactions with EBS.

Table 1
Surface coatings of different clay. General formula is $N^+R_1R_2R_3R_4Y^-$

	NA	30B	10A	25A	93A	15A
R_1	NO	Methyl	Methyl	Methyl	Methyl	Methyl
R_2	NO	T*	Methyl	Methyl	HT	Methyl
R_3	NO	Hydroxyethyl	Methyl benzyl	HT	HT	HT
R_4	NO	Hydroxyethyl	HT*	2-Ethylhexyl	H	HT
	Hydrophilic	*Hydrophilic*	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic
Solubility parameter of coating $(J/cm^3)^{0.5}$		19.1	16.3	15.4	16.1	15.9
Y^-		Cl^-	Cl^-	$CH_3SO_4^-$	HSO_4^-	Cl^-

[*] T is tallow, a mixture of about 65% C18, 30% C16, and 5% C14 hydrocarbons. HT is hydrogenated tallow. H is hydrogen.

4. Results and discussion

We compounded various amounts of surface coated 10A clay into polyurethane that contains 0.25 wt% of EBS. We annealed specimens at 50 °C for 4 h. The XPS analysis showed that without the 10A clay the sample had 91% C at the surface (pure polyurethane has 77%), indicating that about 93% of the polymer surface was covered by EBS (Fig. 2). However, as little as 0.5 wt% of surface coated 10A clay dramatically reduced the surface carbon from 91 to 82% (33% polyurethane surface is covered by EBS). This shows that 0.5 wt% clay (nano-adsorbents) reduced the surface EBS by about 65%.

The EBS molecules at the polyurethane surface are at equilibrium with those in bulk and near coated clay platelets. So the surface EBS concentration cannot reach zero regardless of how much coated clay is added. But the theoretical minimal amount of coated clay that can adsorb all the EBS molecules based on geometry limits may be estimated. It is assumed that the coated clay platelets are well exfoliated. The EBS molecules adsorbed to the coated clay surface align perpendicular to the surface and form packed self-assembled monolayers. The maximum layer thickness is about the length of its hydrophobic segments ($C_{17}H_{35}CONHCH_2$), about 20 times the CH_2 size (0.3 nm, based on the density of EBS ~ 1 g/cm^3) or 6 nm. The thickness of coated clay platelet is about 2 nm. Then the volume ratio of the EBS to the coated clay (two surfaces) is about 6:1. The minimal amount of coated clay needed for 0.25 wt% EBS is about $0.25/6 \times 2 = 0.08$ wt%. The factor of 2 is due to the density difference between the EBS and the coated clay (~ 2 g/cm^3). If we assume that the EBS layer thickness is about its molecular diameter (0.3 nm), then the minimal amount of coated clay would be about 1.5 wt%. The observed 0.5 wt% is in between the values of these two ideal cases.

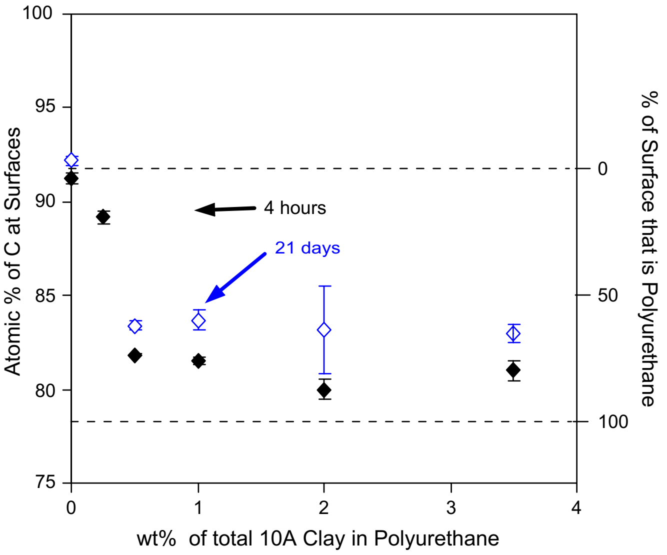

Fig. 2. Reduction of surface EBS by nano-adsorbents. Surface chemical composition of polyurethane samples that contained 0.25 wt% EBS and various amounts of surface coated nanoclay (10A) after annealing at 50 °C for 4 h (solid diamond). The upper and low dashed lines in the figure indicate the carbon atomic % of pure EBS and polyurethane, respectively. Without the nanoclay, the surface of the polyurethane is almost identical to that of EBS. However, even 0.5 wt% of coated nanoclay made the surface composition closer to pure polyurethane than to EBS. This composition did not change significantly after 21 days of annealing at 50 °C.

Clay has previously been used to produce barrier properties in polymers [4,16–23]. How much reduction of surface EBS observed here was due to the barrier properties of the 10A clay? To answer this question, we further annealed some of the samples at 50 °C for 21 days. The surface chemical analysis gave very similar results as before (Fig. 2), even though the annealing time was almost 100 times longer. Assuming the barrier mechanism works, the maximum permeation reduction could be estimated based on the following equation [4,20,21],

$$P_0/P_c = \left(1 + \mu\alpha^2\phi^2\right) \tag{1}$$

where P_0 and P_c are permeability of pure polymer and the polymer with added clay, respectively, α is particle aspect ratio (10–100. See TEMs in Fig. 3), ϕ is clay volume fraction, and μ is a geometric factor $= \pi^2/(16 \ln^2\alpha)$. Substituting the values yields $P_0/P_c < 2$ (less than 1.3 was observed in Ref. [4]). This is much less effective than the above observations. Therefore, the barrier mechanism cannot be responsible for such a significant reduction in the EBS accumulation at surface.

To further confirm the adsorption mechanism, we selected another five types of different clay fillers that have both hydrophilic and hydrophobic coatings (Table 1). Hydrophilic coatings should have weaker attractive interactions with the hydrophobic EBS molecules and were expected to have less or no effects on EBS migration. As shown in Fig. 4, all the clays with hydrophobic coatings significantly reduced the surface EBS. In contrast, the two hydrophilic clays, NA that is a natural clay without coating and 30B that is hydrophilic coated clay, had much less effect in preventing the EBS molecules from migrating as indicated by the high carbon contents in the samples' surfaces. The exfoliation of all the coated clays, both hydrophobic and hydrophilic, was similar (TEMs in Fig. 3. The NA clay is not coated and did not exfoliate). These results strongly support the profound nano-adsorbent mechanism.

The solubility parameter of the 30B clay coating molecules is close to that of the EBS (Table 1). It may be expected the 30B clay would have a stronger effect in confining the EBS than observed. The observed weaker effect may be due to the possible hydrogen bonding or polar–polar interactions between the urethane groups in the polymer chains and the hydroxyl groups of the 30B clay coating molecules. These attractive interactions may lead to the abundant polyurethane matrix molecules competing with the minor EBS to bind the clay coating molecules. As a result, this clay filler may not be a good nano-adsorbent for the EBS molecules. This yields a supplementary rule in selecting nano-adsorbent molecules. That is the nano-adsorbent compounds should not have too strong attractive interactions with the polymer matrix.

One of the biggest gains from the reduction of polyurethane surface EBS is that the polyurethane surface composition reverted to polyurethane rather than EBS. There are some

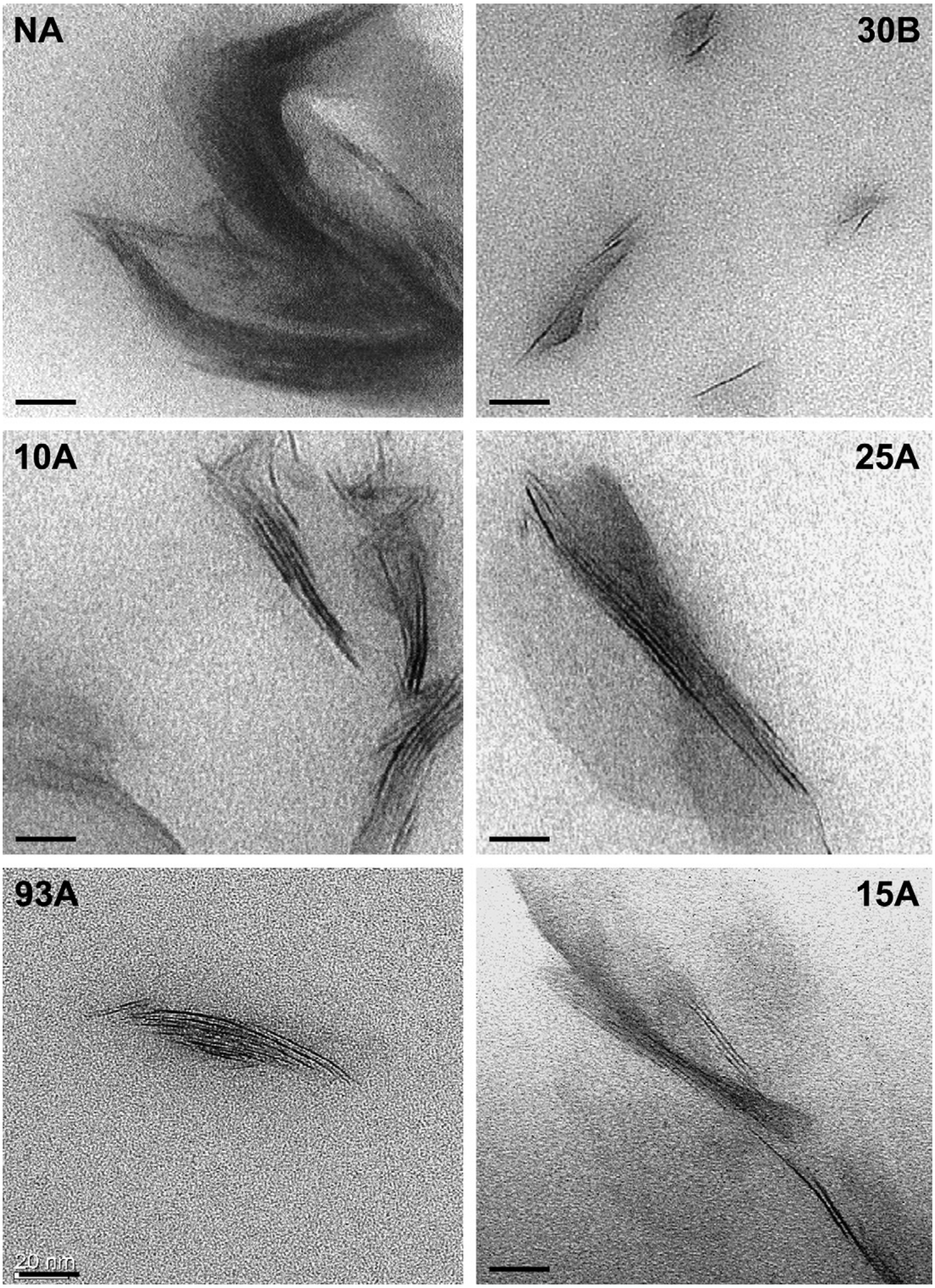

Fig. 3. TEMs of polyurethane filled with 2 wt% of different clay fillers. It appears that the clays surface coated with hydrophobic compounds (10A, 25A, 93A, and 15A) have similar exfoliation. The natural clay (NA) that does not have a surface coating was much less exfoliated. The 30B clay has a relatively hydrophilic coating and seems to have slightly better exfoliation as evidenced in some single layer fragments in the composite TEM. The aspect ratios are about 10–100 for most of the clays except NA. Scale bars represent 20 nm.

benefits. For example, the adhesion of these composites to a biomedical grade silicone adhesive was measured (Section 3). As shown in Fig. 5A, the specimens with lower surface carbon contents (more polyurethane), achieved with the hydrophobic clay, had almost one order of magnitude higher adhesion strength to the silicone adhesive than those with higher surface carbon contents (specimens either without clay or with hydrophilic clay such as 30B and NA). The water contact angles of these samples were also quite different: the surfaces with lower carbon contents (more PU) had lower

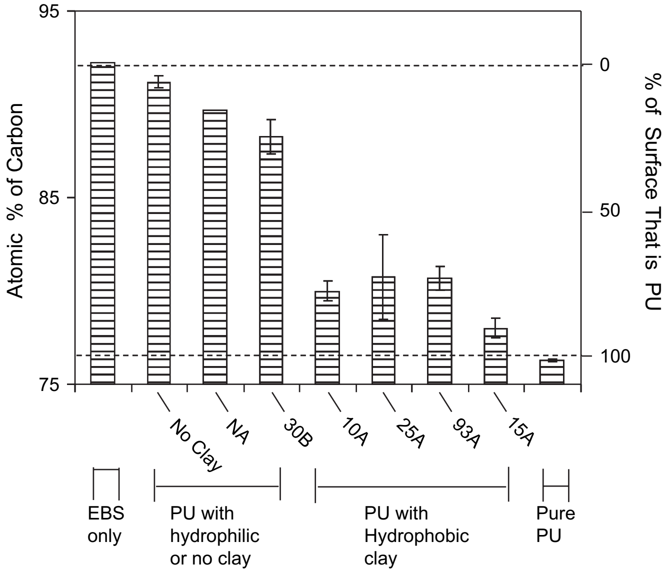

Fig. 4. Surface carbon on polyurethane with various nano-adsorbents. Surface composition of the polyurethane samples that contained 0.25 wt% of EBS and 2 wt% of clay with various surface coatings. The hydrophobic EBS was effectively confined to the bulk by the hydrophobic clay coatings (10A, 25A, 93A, and 15A) but not by the hydrophilic ones (NA and 30B). This further supports that the hydrophobic surfacecoated clay are adsorbents for the EBS molecules.

water contact angle (Fig. 5B), meaning that they were more hydrophilic.

This same nano-adsorbent mechanism can be applied to other biomedical applications where minor functional components are needed in materials. As the concentration of these nano-adsorbent components in the polymer is very low, their effects on the bulk properties of materials are expected to be negligible. In the present paper, the mechanical properties of the polyurethane with various clay fillers (2 wt%) were within 10% of the pure polyurethane. Also, even though most of the EBS molecules were confined inside the polymers by the added nano-adsorbents, the remaining low concentration of EBS in the polymer surface still allowed all the materials to process equally well as the polymer without clay. This may bring up a question “why not just reduce the surface EBS by adding much less EBS initially?” While the approach will theoretically work, practically it is very difficult to control the reproducibility and homogeneity of the dispersion if very small amounts of additives are used. These reproducibility and dispersion homogeneity, however, are fundamentally important for biomedical applications.

An interesting observation is that the surface EBS concentration did not significantly depend on the 10A clay concentration (Fig. 2). It has been noticed in the literature that some intended functions (e.g. barrier) of the nanoclays did not increase as would be expected with increasing loading levels [4]. This was explained in terms of greater layer aggregation at higher clay loadings. This explanation probably applies to our cases. The layer aggregation reduced the surface area of clay fillers that would be available for the EBS molecules to adsorb otherwise.

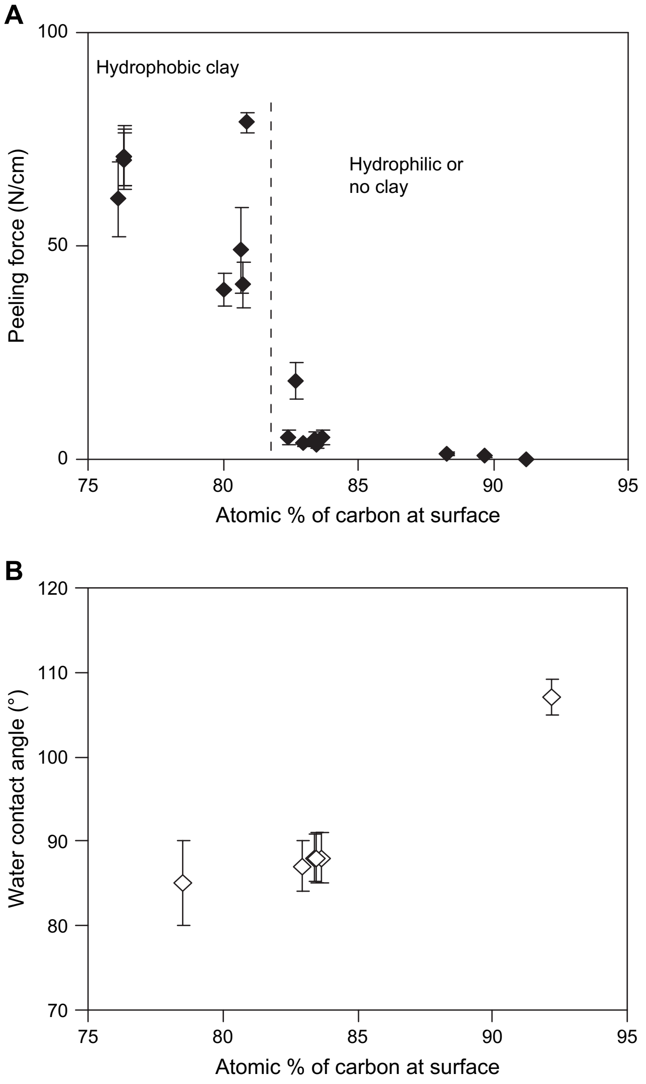

Fig. 5. Surface properties changed by EBS. Adhesion between the polyurethane and a biomedical silicone adhesive (A) and water contact angle (B) as functions of surface carbon percentage of samples. There were strong correlations between these two properties and the surface carbon content.

Acknowledgements

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