JOURNAL OF Materials CHEMISTRY

Low surface energy polysiloxane complexes

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Received 1st June 2000, Accepted 14th July 2000
First published as an Advance Article on the web 13th December 2000

Complexes of a commercially available amino-functionalized polysiloxane and perfluorinated dodecanoic acid were prepared to form smooth surfaces which were highly oil- and water-repellent. The surfaces of the complexes were found to be highly enriched with CF_3 groups, resulting in critical surface tensions as low as $6\,\mathrm{mN\,m^{-1}}$. A saturation of the surfaces with CF_3 groups was reached when the degree of complexation (the ratio of acid to amino functions) was 50%. The characterization of the surfaces of the complexes was carried out using contact angle and ESCA measurements. Temperature dependent mechanical measurements of the complexes in the bulk material show that no catalyst was necessary for the cross-linking of the complexes to rubber-like materials. The complexes were proposed for the development of non-toxic anti-fouling coatings.

Introduction

Surfaces with oil- and water-repellent properties are needed for many technical applications. Only fluorinated organic compounds combine both properties, but their use is restricted due to their poor solubility, as well as difficulties in forming coatings and their high costs. Therefore, fluorinated molecules were produced that stratify on the surface in the wet coating, resulting in excellent surface properties of fluoropolymers at low total fluorine levels. Recently, a survey of these coating systems which were based on well-established paints of the urethane- and acrylic-type was given by Anton.[1] A further strategy to reduce the surface energy effectively is the fluorination of siloxanes. Critical surface energies of about $15\,\mathrm{mN\,m^{-1}}$ were found[2] and in a number of patents the preparation of oil-repellent materials using perfluoroalkyl groups covalently bonded to the polysiloxane backbone was described.[3–11] Such polymers have many applications ranging from textiles to non-toxic, anti-fouling coatings. At present toxic anti-fouling systems are in use, but in situations where the use of biocides is restricted, silicone elastomeric coatings are accepted as a viable alternative to traditional anti-fouling treatment.[12,13] For political reasons,[14] effective non-toxic anti-fouling coatings will play a technological key role in the near future, especially for the protection of ship hulls. An important factor, which influences the performance and effectiveness of such silicone coatings, is their surface energy. For example, measurements of barnacle adhesiveness indicate that coatings with a surface free energy lower than $12\,\mathrm{mN\,m^{-1}}$ are required to prevent attachment.[15] This value is very much lower than that found for standard low energy surfaces produced by polytetrafluorethylene ($19\,\mathrm{mN\,m^{-1}}$)[16] or high molecular weight polysiloxanes ($24\,\mathrm{mN\,m^{-1}}$).[17] Only surfaces highly enriched with CF_3 groups can have surface energies much lower than that of polytetrafluorethylene. Recently, we reported on a strategy for preparing polyelectrolyte–surfactant complexes with fluorinated surfactants on the basis of self-organization.[18–21] The self-organizing concept has been established for solid-state polyelectrolyte–surfactant complexes with a high content of surfactant and polymers with a carbon backbone.[22,23] The purpose of this article is to show that the self-assembly concept can be expanded to functionalized polysiloxanes. Further, materials result that show extremely low surface energies and easy processing when complexed with fluorinated surfactants, such that they have a potential use as non-toxic anti-fouling materials.

Experimental

Perfluorododecanoic acid (98%, Fluka), hexane (HPLC grade, Aldrich), butan-1-ol (HPLC grade, Aldrich), butan-2-ol (99.5%, water-free, Aldrich) were used as received. The polysiloxane containing an amount of 0.6 mol% aminoethyl aminopropyl functions, (WR1100, Wacker Chemie, Germany) was used as delivered by the supplier. The viscosity was $5000\,\mathrm{mm^2\,s^{-1}}$, corresponding to a polymerization degree of about 1500. For complexation one equivalent of silicone oil (20.83 g) was dissolved in 100 ml hexane and 0.5 equivalent of perfluorododecanoic acid (1.0 g) was dissolved in 50 ml butan-2-ol and 0.5 ml methanol. While stirring, the surfactant solution was added in drops to the silicone oil, resulting in a transparent complex solution. Films were prepared by solvent casting as described earlier[24] and cross-linking was performed at temperatures in the range from 120 to 200 °C in the presence of air. Contact angle measurements were performed on a Krüss G10 contact angle goniometer; the angles reported here are the average of five measurements. The advancing contact angle was read by injecting a 5 μL liquid drop. Linear alkanes, diiodomethane and water (Millipore) were used as test liquids. ESCA data were collected in both survey and high-resolution mode on an ESCALAB 200 X system (VG Instruments, UK) equipped with an Al anode. Typical areas of analysis were 3.5 × 3.5 mm. The data were recorded at 20° collection angle, resulting in an analysis depth of about 5 nm. A Bohlin CVO-50 rheometer with a plate–plate geometry (20 mm diameter) was used for dynamic–mechanical measurements. The polysiloxane complexes were cast from solution as prepared to produce a homogeneous film on the lower plate. Measurements were carried out at a constant temperature of 125 °C at a shear rate of 1 Hz, loading with a constant shear stress of 50 Pa.

DOI: 10.1039/b004405i

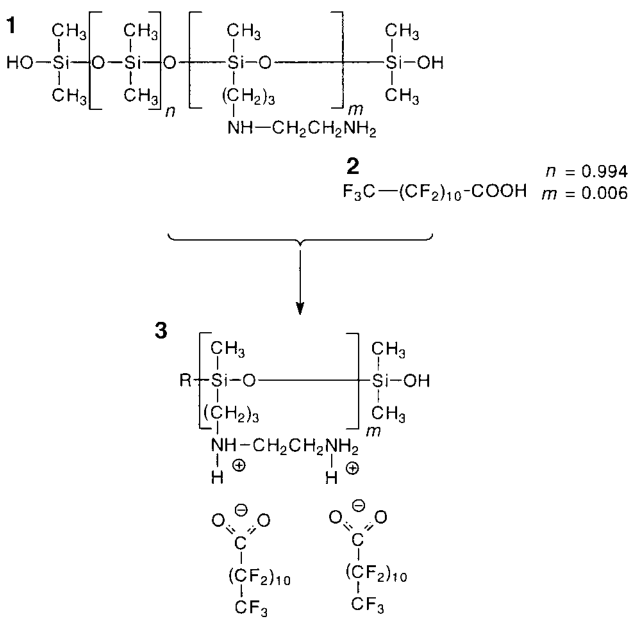

Fig. 1 Sketch of complex formation: **1**, amino-functionalized polysiloxane with hydroxy end groups. 0.6 mol% of the monomers contain aminoethyl aminopropyl groups; **2**, perfluorododecanoic acid; **3**, stoichiometric polysiloxane–surfactant complex.

Results and discussion

Surface energies

From the work of Zisman and co-workers it is known that perfluorododecanoic acid **2**, adsorbed as a monolayer on platinum surfaces, shows a critical surface tension of about 6 mN m^{-1},[25] which is the lowest value ever observed. However, such monolayers are not useful as a coating because they are readily attacked and destroyed when in contact with water. To prepare more water-resistant ultra-low energy surfaces using **2** we selected an amino-functionalized polydimethylsiloxane **1** for complexation (see Fig. 1). **1** is a commercially available silicone oil, which is widely used to give textile fabrics a softer feel.[26] For a good adhesion of **1** on a textile fabric about 0.6 to 2.4 mol% of its monomer units are functionalized with aminoethyl aminopropyl groups. The polysiloxane is end capped with hydroxy functions by which it can be condensed. For complexation perfluorododecanoic acid dissolved in a butan-2-ol–methanol mixture was added to **1**, which resulted in a transparent complex solution. To reduce the viscosity of the polysiloxane and for homogeneity of the mixture **1** was diluted with hexane. After removing the solvent under vacuum highly viscous films with smooth surfaces were formed. At elevated temperatures, in the range from 120 °C to 200 °C, the films were cross-linked. To be sure that all traces of weakly bound acid were removed the films were immersed in large baths of stirring water for 24 h. Then the dynamic contact angles, θ, of the test liquids with different surface tensions were measured by means of the sessile drop method.[27] Data of the advancing angles are given for complexation degrees of 100, 50 and 0%, corresponding to ratios of amino to carboxylic acid groups of 1 : 1, 1 : 0.5 and 1 : 0 (see Table 1). Surfaces of the pure polysiloxane are hydrophobic ($\theta = 98°$) but not oleophobic. For example decane and dodecane spread on the polysiloxane surface. By contrast the complex **3** surfaces became more hydrophobic with increasing fluorine content and reached a maximum of water- and oil-repellency at a complexation degree of about 50%. It can be seen that the contact angles of water are 130° for a complexation degree of 50% and 131° for 100%. The corresponding values of hexadecane are 84° and 85°; those for decane are 75° and 78°. For an adsorbed monolayer of perfluorododecanoic acid Zisman reported values of 105° for water (which is erratic because of dissolution), 78° for hexadecane and 70° for decane. Obviously, the contact angles of the different liquids on complex surfaces are larger than on the corresponding monolayer surfaces. But the use of contact angles for the calculation of surface energies is only reliable for homogeneous and smooth surfaces. On some rough surfaces abnormally high contact angles can be found. For example, contact angles of water in the range of 150 to 170° on biological surfaces of many plant leaves were reported.[28] Because this phenomenon is very strong for the Lotus flower, it is called the Lotus effect.[29] There, the high water-repellency is caused by different microstructures on a micrometre scale. The Lotus-effect can be mimicked artificially to produce anti-adhesive surfaces characterized by a structured surface consisting of elevations and depressions, where the distance between the elevations ranges from 5 to 200 μm and the height of the elevations ranges from 5 to 100 μm.[30] A second reason for the observation of extremely high contact angles can be a fractal structure of a surface, as demonstrated by a surface produced by an alkylketene dimer[31] and by surfaces of anodically oxidized aluminium fluorinated with 1H,1H,2H,2H-perfluorododecyl phosphate.[32] Then the contact angle is given as a function of the fractal dimension, the range of the fractal behavior, and the contacting ratio of the surface. To be sure that the high contact angles found for complex **3** surfaces are not due to roughness, the surfaces were investigated by scanning electron microscopy. It was found that surfaces of all polysiloxane complexes are very smooth on length scales in the range from several millimetres down to values lower than a micron. Therefore, it can be excluded that roughness is responsible for the high contact angles of the complex surfaces, and dynamic contact angles can be used as a measure of the surface energy in different ways. First, the surface energies were calculated using the equation of state approach derived by Neumann and Li[33] (see Table 1). It was found that the values calculated for the different test liquids range from 6.8 to 9.9 mN m^{-1} for a complexation degree of 50 and 100%, which is very much lower than that of the non-

Table 1 Static contact angles of different test liquids (θ) and surface energies (γ_s) of WR1100-C12 films cured for 12 h at 125 °C. The film thicknesses are 1 mm. The ratios of amino functions to carboxylic groups are 1 : 0, 1 : 0.5 and 1 : 1[a]

Complexation degree (%)		0	50				100
Fluorine content (% w/w)		0	4.58				8.76
Storage condition		Water	Water	SDS	Methanol	NaCl	Water
Test liquid	γ_l/mN m^{-1}	θ/° (γ_s/mN m^{-1})	θ/° (γ_s/mN m^{-1})	θ/° (γ_s/mN m^{-1})	θ/° (γ_s/mN m^{-1})	θ/° (γ_s/mN m^{-1})	θ°/ (γ_s/mN m^{-1})
Decane	23.9	0	75 (9.9)	70 (11.2)	61 (13.5)	69 (11.2)	78 (9.2)
Dodecane	25.4	0	79 (9.6)	75 (10.6)	69 (12.2)	73 (11.2)	82 (8.8)
Hexadecane	27.6	19 (26.3)	84 (9.2)	83 (9.4)	80 (10.2)	76 (11.4)	85 (8.9)
CH_2I_2	50.0	71 (25.5)	115 (6.7)	107 (9.4)	103 (11.0)	107 (9.4)	114 (7.0)
Water	72.7	98 (24.3)	130 (6.8)	127 (8.1)	122 (10.5)	125 (9.1)	131 (6.4)
Dispersive surface component γ_s^d/mN m^{-1}		—	9.0±0.3	9.9±0.5	11.5±0.9	10.8±0.1	8.4±0.1

[a] The error of measurement for the advancing contact angles θ is about 1°. The surface energies γ_s were calculated from the advancing contact angles using the equation of state derived by Neumann and Li.[33]

complexed polysiloxane (24.3 to 26.3 mN m^{-1}). Second, the most traditional way of estimating the surface energy of fluorinated surfaces is to calculate the critical surface tension γ_c, introduced by Zisman.[34] γ_c is still widely used, *e.g.* for the characterization of self-organizing fluorinated ionenes.[35] Using this procedure we obtained extremely low critical surface tensions of about 6 mN m^{-1} for a complexation degree of 50% as well as for 100%. These values were determined after an immersion time of 24 h in water to be sure that any slightly adsorbed acid was removed. Because of its empirical character it must be stressed that the critical surface tension does not have a physical meaning. Therefore, a third quantity was determined, which was theoretically justified and has been used by other authors:[36,37] the dispersion force component of the surface energy, γ_s^d, according to the Girifalco–Good–Fowkes–Young equation[38,39] ($\cos\theta = -1 + 2(\gamma_s^d)^{1/2}\gamma_l^{-+/-}$). γ_s^d is given by the slope of a plot of cos θ against the reciprocal square root of the surface tensions of non-polar liquids. Nearly identical low values were determined for complexation degrees of 50% ($\gamma_s^d = 9.0$ mN m^{-1}) and for 100% (8.4 mN m^{-1}). This may be interpreted as the saturation of the complex surface in CF_3 groups already at a complexation degree of 50%. As a test of the complex stability, the complex surfaces were immersed, while stirring for 24 h, in different solvents of practical relevance: 1% aqueous surfactant solution (sodium dodecyl sulfate), in methanol and in 3% aqueous sodium chloride solution. The latter has an ionic strength about that found in the Atlantic Ocean. As seen in Table 1, the contact angles after immersion in surfactant and salt solution, are only slightly reduced compared to that of the pristine surfaces. For the complex surfaces immersed in methanol a larger reduction of contact angles was found. But compared with the non-complexed silicone the contact angles are strongly enhanced. The surface energies using the equation of state are in the range of 8.1 to 13.5 mN m^{-1} (see Table 1). Values of γ_s^d range from 9.9 to 11.5 mN m^{-1}. From the low surface energy values we conclude that the complex surfaces are still highly enriched in CF_3 groups after immersion. Neither surfactant nor salt solution removes the perfluorododecanoic acid from the complex. Methanol is able to detach minor amounts of the fluorinated acid (see Fig. 2). This relatively good stability in solvents is an important advantage of the complex compared to surfaces of perfluorododecanoic acid on platinum. In contact with water, films of non-complexed perfluorododecanoic acid were dissolved readily,[40] whereas its complex is stable enough to withstand even polar solvents.

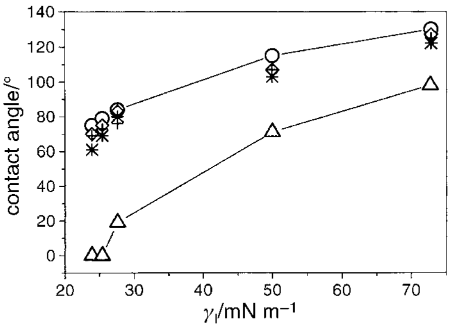

Fig. 2 Advancing contact angles of various kinds of liquid on cross-linked polysiloxane surfaces plotted against the surface tension γ_l of the liquids. From left to right, the points are values obtained with (1) decane, $\gamma_l = 23.9$ mN m^{-1}; (2) dodecane, $\gamma_l = 25.4$ mN m^{-1}; (3) hexadecane, $\gamma_l = 27.6$ mN m^{-1}; (4) methylene iodide, $\gamma_l = 50.0$ mN m^{-1}; (5) water, $\gamma_l = 72.7$ mN m^{-1}. Contact angles are shown for a cross-linked complex with a complexation degree of 50% after immersion in water (circles), sodium dodecyl sulfate solution (diamonds), sodium chloride solution (crosses) and methanol (stars). For comparison, the values of the non-complexed polysiloxane are given (triangles).

Elemental composition near the surface

The sensitivity of contact angles to the chemical composition extends only a few atomic layers below the surface, where polar liquids show a greater sensing depth than non-polar liquids.[41,42] In order to measure the elemental composition near the surface, X-ray photoelectron spectroscopic measurements (ESCA) were carried out. The analysis depth of this method was less than 5 nm for a low take-off angle (20°). It was found that the elemental composition within this near-surface region deviates considerably from the average composition of the complex. A remarkable excess of fluorine at the surface was detected with a relative atomic content of 32.4%, which is 5.2 times the bulk level (6.2%). Similar high fluorine enrichments at polymer surfaces were recently reported for carbon backbone containing polymers.[43] Because the depth of ESCA analysis is larger than the length of the fluorinated chain (*ca.* 1.5 nm) nitrogen and silicon will be found even for a theoretical dense-packed perfluorododecanoate monolayer at the surface. The atomic concentrations of nitrogen and silicon near the surface are 2.0% and 11.4%, respectively, whereas the corresponding values for the bulk composition are 0.5% and 22.1%. The higher nitrogen content found in the near-surface region is consistent with the complex structure, *i.e.*, the migration of fluorinated chains to the surface is accompanied by the movement of an equimolar amount of ammonium carboxylate ion pairs. Obviously, the predominant part of the ions is not located directly on the surface, otherwise much lower contact angles than the ones observed would have been found. As expected, the enrichment in fluorine at the surface is accompanied by a decrease of silicon.

Cross-linking

The cross-linking of the complexes to films with rubber-like properties was performed without catalysts. It was found qualitatively that the cross-linking of the complex could be achieved at a temperature where no significant cross-linking was observed for the pure polysiloxane (125 °C). Furthermore, non-stoichiometric complexes still having free amino functions cross-linked faster than stoichiometric or over-complexed ones. From this it can be concluded that cross-linking is not only due to the addition of acid. An optimum amount of perfluorododecanoic acid for a high reaction rate of cross-linking was

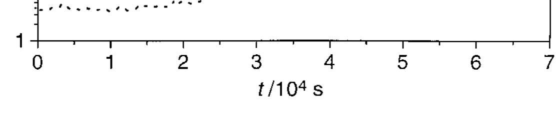

Fig. 3 Time-dependent isochronal shear modulus of amino-functionalized polysiloxane at $T = 125$ °C. The moduli rise due to cross-linking reactions. A non-complexed amino-functionalized polysiloxane (lower curve, dotted) rises slowly. At the end of the experimental time (7×10^4 s), no plateau was reached. The modulus of a complexed polysiloxane with a complexation degree of 50% (solid line), increases steeply within 10^4 s and reaches a constant value of 1.2×10^5 Pa at about 4×10^4 s. For comparison of the cross-linking rate, an effective cross-linking catalyst, dibutyltin dilaurate (2% w/w), was used for the non-complexed polysiloxane. The modulus increased steeply within 0.5×10^4 s and reached a constant value of 1.4×10^5 Pa at about 2×10^5 s (dashed curve). The frequency of measurements was 1 Hz.

found to be at a complexation degree of about 50%. In order to determine quantitatively the reaction rate of cross-linking, time-dependent isochronal dynamic–mechanical measurements at constant temperatures were carried out. As shown in Fig. 3 (dotted line), the shear modulus of the non-complexed polysiloxane increases only slowly at 125 °C. After 7×10^4 s, the value of the shear modulus is as low as 3×10^3 Pa. In contrast to that in the presence of 2% dibutyltin dilaurate, an effective cross-linking catalyst, the modulus increases steeply within the first 0.5×10^4 s due to a high cross-linking rate (Fig. 3, dashed line). A constant modulus of 1.4×10^5 Pa was reached within about 2×10^4 s. The modulus of the complexed polysiloxanes shows a similar high cross-linking reaction rate to that found for the heavy metal catalyst (Fig. 3, solid line). The modulus of the complex increases steeply within the first 10^4 s, it then levels off and reaches a constant value of about 1.2×10^5 Pa within 3×10^4 s. Although not as good as heavy metal compounds, the ammonium perfluorododecanoate moieties can be considered as effective catalytic entities for cross-linking.

Conclusions

In conclusion it was shown that a commercially available polysiloxane can be successfully complexed with perfluorododecanoic acid, resulting in a rubber-like material with surface energies as low as the lowest values encountered to date. Furthermore, the cross-linking of the complex is highly enhanced without the need of an additional catalyst. It was proposed that such complexes could be promising for the formation of a new kind of ultra-low surface energy material which would be useful, for example, as non-toxic anti-fouling coatings.

Acknowledgement

The authors wish to thank J. Conrad for helpful discussion, Wacker Chemie for providing the polysiloxane, W. Unger for ESCA analysis and T. Blankenburg for dynamic–mechanical measurements. The financial support of the German Science Foundation (DFG-Schwerpunkt "Polyelektrolyte mit definierter Molekülarchitektur", Grant Lo418/7-1) and the Max Planck Society is greatfully acknowledged.

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