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Surface properties of polyamides modified with reactive polydimethylsiloxane oligomers and copolymers

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Abstract

Surface modification of polyamide-6 (PA-6) was investigated by melt blending with silicone–urea copolymers or organofunctionally terminated polydimethylsiloxane oligomers. Blends were prepared in a laboratory scale high-shear melt mixer. Surface characteristics of the blends were determined by static water contact angle measurements and X-ray photoelectron spectroscopy. Effect of the type, composition, average molecular weight and amount of the silicone additive in the blends, on the surface properties were determined. Influence of the thermal history of the samples on the surface properties was also investigated. All of the blends showed formation of silicone rich surfaces. Surface modification was permanent due to either the formation of chemical bonds between additive and polyamide and/or very strong hydrogen bonding between urea and amide groups.

Keywords: Polydimethylsiloxane; Polyamide; Surface modification

1. Introduction

Polyamides are one of the most versatile classes of engineering polymers. Depending on their chemical nature (e.g. aliphatic or aromatic) and backbone structures, they display a wide range of properties. Aliphatic polyamide fibers and films, such as polyamide-6 (PA-6) and polyamide-66 (PA-66) are widely utilized in many industrial and textile applications due to their high mechanical strength and durability. For many applications surface properties of the finished products (e.g. film, fiber or molded article) play important roles. In textile or carpeting applications surface finish, gloss, water repellency, dye reception, abrasion and stain resistance of the fibers are of critical importance. For film and other industrial applications, adhesion, printability, surface release and lubricity and coefficient of friction mainly determine the end use and the performance. As a result, especially in fibers, the surfaces are modified by different techniques, generally, after the spinning process. In films and products obtained by molding techniques specialty surface modifying additives are usually blended with the polyamide resin before processing. These additives include silicones and their copolymers, fluorine containing polymers and low molecular weight polyolefin waxes [1].

The use of polydimethylsiloxane (PDMS) or silicone containing copolymers in the permanent surface modification of various organic polymeric resins through blending has been an active field of research [2–6]. However, almost all of the organic polymers modified and reported in open literature, were amorphous in nature. These studies have shown that due to their very low surface energies (20–22 mN/m) and low solubility parameters [7], when copolymerized or blended with other organic polymers, PDMS tends to phase separate in bulk and also migrate to the air–polymer interface. In order to have permanent surface modification using this approach, the organic component of the silicone copolymer chosen must have good compatibility with the base polymer [8]. The surface compositions and properties of the final systems depend on the amount and the block length of silicone in the copolymer or blend, type and nature of the base resin (e.g. amorphous or crystalline morphologies), method of sample preparation and annealing conditions. In most investigations, organic resins used are amorphous in nature and the films of blends

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are prepared by solution casting [4,5,8]. This usually leads to the formation of surfaces which are an order of magnitude or more richer in silicone concentration than the bulk composition. During the sample preparation from solution, where the solvent is slowly evaporated, siloxane segments have ample time to phase separate in bulk [9] and also move to the air–polymer interface to form lowest energy surfaces as dictated by thermodynamics. However, if the organic component is semi-crystalline, such as PA-6 or poly(ethylene terephthalate) (PET) and the samples are prepared by melt processing, the bulk and surface morphologies of the systems strongly depend on the processing conditions and thermal history and mainly on the rate of cooling from melt and the annealing conditions [3,10,11]. This is a direct result of the competition between the rate of crystallization (or in general the rate of solidification) of the base polymer and the rate of phase separation and migration of the additive to the air polymer interface.

Surface modified polyamides can also be obtained through copolymerization of amide and silicone monomers. Preparation of silicone-amide (PDMS-PA) block or segmented copolymers are usually achieved by two different reaction techniques [4,12]. Diblock (AB) copolymers or triblock (ABA) copolymers with PDMS middle blocks can be prepared by the ring-opening polymerization of ε-caprolactam, where a mono- or difunctionally terminated PDMS oligomer is used as an initiator [13–15]. Amine, anhydride or *N*-acyllactam terminated PDMS oligomers are capable of initiating the anionic polymerization of ε-caprolactam in bulk or in solution, usually under the catalytic action of trace amounts of alkali hydrides. Block lengths of PDMS can be varied over a wide range. Block lengths of polyamide segments are determined by the initial stoichiometric ratio of the polymerization mixture. Multiblock PDMS-PA copolymers are prepared by the reaction of α,ω-amine terminated PDMS oligomers and difunctional carboxylic acids or their derivatives. In such reactions diamines can be used as chain extenders [16–18]. Although these types of silicone-amide copolymers exhibit good mechanical properties and may perform as thermoplastic elastomers [4,12] the main interest of this study is in their surface activities. Particular interest is in their use as surface modifying additives for PA-6.

In this study three different approaches were investigated for producing permanently water repellent polyamides through surface modification with PDMS containing additives. These additives were (i) silicone–urea copolymers with high PDMS content, (ii) telechelic organoamine terminated PDMS oligomers and (iii) telechelic organoepoxy terminated PDMS oligomers with different molecular weights. Surface properties of the blends were investigated by water contact angle measurements and XPS (ESCA). Effects of the type, composition and amount of silicone additive in the blends and the thermal history of the samples on the surface properties were determined. Surface modification was obtained without affecting the bulk properties of the base resins.

2. Experimental part

2.1. Materials

Polyamide-6 resin was obtained from Allied-Signal Fibers, Petersburg, VA. Aminopropyl (PDMS-NH2), *N*-methylaminopropyl (PDMS-NH) and glycidoxypropyl (PDMS-E) terminated PDMS oligomers, with various molecular weights were either obtained from Th. Goldschmidt AG, Essen, Germany or prepared in our laboratories, through well-known equilibration reactions [4]. Bis(4-isocyanatocyclohexyl)methane (HMDI) with a purity better than 99.5% was obtained from Bayer, Germany. 2-Methyl-1,5-diaminopentane (Dytek A) was kindly provided by DuPont Chemicals, Wilmington, DE. Reagent grade tetrahydrofuran (THF), isopropanol (IPA) and methylene chloride were purchased form Aldrich and used as received. Fig. 1 gives the chemical structures of PDMS oligomers and copolymers used in this study. Table 1 provides various characteristics of these oligomers.

2.2. Preparation of PDMS copolymers

Silicone–urea copolymers were synthesized by the solution polymerization of HMDI, PDMS-NH2 oligomers and Dytek A. PDMS-NH2-7K and PDMS-NH2-3K were used as the soft segments and Dytek A as the chain extender.

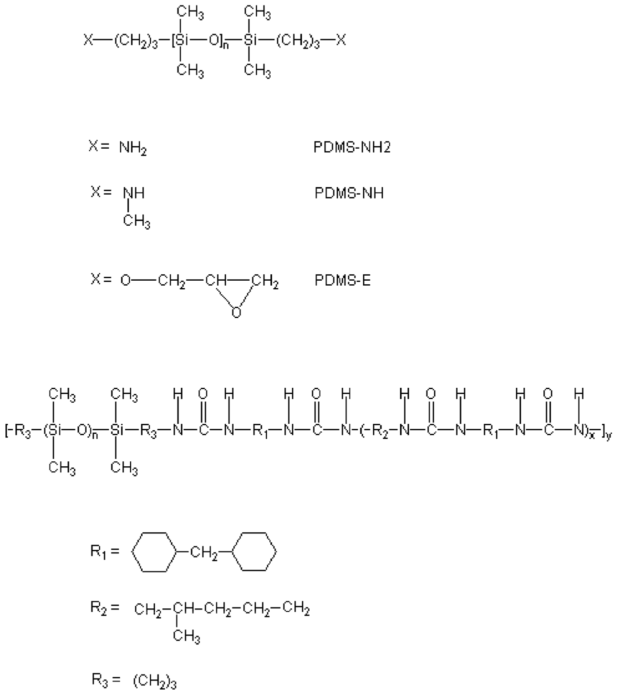


Fig. 1. Chemical structures of telechelic, organofunctionally terminated PDMS oligomers and silicone–urea copolymer.

Table 1
Characteristics of α,ω-organofunctionally terminated PDMS oligomers

Sample code	No of PDMS repeat units	Mn (g/mol)	T_g (°C)
PDMS-NH2-1K	9	800	−117
PDMS-NH2-3K	32	2500	−123
PDMS-NH2-7K	93	7000	−123
PDMS-NH-1K	10	900	−120
PDMS-NH-3K	32	2500	−121
PDMS-NH-7K	92	7000	−123
PDMS-E-1K	10	900	−119
PDMS-E-3K	31	2500	−123
PDMS-E-7K	92	7000	−123

Soft segment content of the copolymers were kept constant at 75% by weight. Reactions were carried out in THF/IPA mixture at room temperature, in a three-neck, round bottom flask fitted with an overhead stirrer, nitrogen inlet and addition funnel. A two-step procedure, which is known as the prepolymer method was used during the synthesis. Calculated amounts of HMDI and PDMS-NH2 oligomer were weighed into separate flasks and were dissolved in THF. HMDI solution was introduced into the reactor. PDMS-NH2 solution was introduced into the addition funnel and added onto HMDI solution into the reactor dropwise. After this step the prepolymer formed was chain extended with stoichiometric amount of Dytek A solution in IPA, which was also added dropwise into the reaction mixture. Completion of the reactions was monitored by the disappearance of the strong isocyanate peak at 2260 cm^{-1} using an FT-IR spectrometer. Silicone–urea copolymers obtained were recovered by coagulating the polymer in methanol/water (80/20) mixture. Copolymers were later dried in a vacuum oven at 50 °C, until constant weight and kept in a desiccator until further use. The yields were quantitative. Table 2 gives the compositions and various characteristics of silicone–urea copolymers synthesized. Intrinsic viscosities, determined in IPA at 25 °C using Ubbelohde viscometers, show the formation of high molecular weight silicone–urea copolymers.

2.3. Preparation of silicone modified polyamides

Blends were prepared in a laboratory scale, Haake, twin-screw, high-shear melt mixer. Total capacity of the system was about 40 g. Temperature and screw speeds were precisely controlled during melt blending. Prior to blending PA-6 resin was dried in an air oven at 110 °C for 4 h.

Table 2
Chemical compositions of silicone–urea copolymer additives

Code	Siloxane oligomer				
	Mn (g/mol)	Amount (wt%)	HMDI (wt%)	Dytek A (wt%)	[η] (dl/g)
PSU-1	2500	75.0	19.7	5.3	0.43
PSU-2	7000	75.0	18.2	6.8	0.49

To prepare the blends the mixer was heated under dry nitrogen atmosphere to about 240 °C, polyamide resin was added into the chamber and completely melted. Desired amounts of the additives were then added into the system and the mixtures were processed for up to 15 min. Samples were taken out of the melt system periodically for characterization. Under these conditions optimum processing time was found to be around 3 min. Blend samples were cooled down to room temperature and were kept in a sealed polyethylene bag until further testing. At these temperatures and blending times no appreciable transamidation is expected to take place [19,20]. Amide exchange reactions in melt is shown to be effective above 250 °C [21, 22].

2.4. Characterization techniques

Infrared (FT-IR) spectra were obtained on a Nicolet Impact 400D spectrometer. Thin films of the materials were cast on KBr discs and scanned at a resolution of 2 cm^{-1}.

Thermal analyses of the products were obtained on a Rheometrics PL-DSC Plus instrument, under nitrogen atmosphere with a heating rate of 10 °C/min. Temperature and enthalpy calibration of DSC was obtained by using indium, lead and tin standards. A Shimadzu TGA-50H was used to determine the thermal stabilities of products. Experiments were carried out under dry air at a flow rate of 30 ml/min and a heating rate of 20 °C/min up to 1000 °C.

Blend films with smooth surfaces (for contact angle measurements) were prepared by compression molding at 275 °C between stainless steel sheets. Before molding stainless sheets were cleaned by successive washings with methylene chloride, THF, DMF and deionized water. Films were quench cooled in water after compression molding, dried and kept in sealed polyethylene bags until annealing.

2.5. Water contact angle measurements

Water contact angles of starting materials and the blends were determined by using a Kruss G-10 goniometer and deionized, triple distilled water. Contact angles of PA-6, silicone–urea copolymers and the blends were determined on compression molded films. Water contact angles of PDMS oligomers were determined on thin films cast on a glass substrate. Volume of each water droplet was about 20 microliter. Each contact angle value given in the tables represent an average of 8–10 readings. Contact angles of the blends were determined under three different conditions: (i) contact angles of compression molded, quench cooled films, (ii) contact angles of films after annealing at 110 °C for 2 h, and (iii) contact angles of annealed films after extraction with methylene chloride, a good solvent for PDMS oligomers and for silicone–urea copolymer.

2.6. X-ray photoelectron spectroscopy (XPS or ESCA)

XPS spectra of virgin and modified films (obtained by direct melting of virgin materials and blends on metal probes) were recorded on a Kratos ES 300 electron spectrometer using MgK X-rays at 1253.6 eV. The films were inserted into the vacuum system with a base pressure of less than 10^{-8} mbar and were analyzed directly.

3. Results and discussion

Telechelic, organofunctionally terminated PDMS oligomers and silicone–urea copolymers were used as surface-modifying additives for PA-6. The ultimate aim of the study was to provide permanently water repellant, silicone-rich, hydrophobic surface properties to polyamide fibers or films, without affecting their bulk properties. This was achieved by blending PA-6 resin with small amounts of silicone additives before processing. In order to provide permanent surface modification to the system, the additives must either react or form strong hydrogen bonding interaction with the polyamide resin. Amine and epoxy terminated PDMS oligomers, which are used as modifiers, are capable of reacting with amine or carboxylic acid end-groups of polyamides. As for the silicone–urea copolymers, urea groups in the hard segments can form very strong hydrogen bonding with the amide groups of the base polymer. In other words, the urea groups act as 'anchoring groups' to the base polymer, whereas the siloxane segments phase separate and migrate to the polymer–air interface.

Polymer surface modification through the use of silicone copolymers or oligomers show that various factors have strong influences on the surface formation, surface compositions and surface properties of the final systems [23–26]. These are; (i) amount of the additive used, (ii) type and nature (structure) of the additive, (iii) block copolymer architecture, (iv) block length of the silicone oligomer, (v) type and nature of the base resin (e.g. amorphous or crystalline morphologies) and (vi) method of sample preparation and annealing conditions.

3.1. Water contact angles

Before investigating the surface behavior of modified systems, static water contact angles of starting materials, virgin PA-6 and oligomeric and copolymeric PDMS additives have been determined. The results are provided in Table 3. As expected, PA-6 has a fairly polar surface and shows a water contact angle of 69.3 ± 2.1°. Upon annealing at 110 °C for 2 h the contact angle shows a small shift to 72.4 ± 1.7°. Silicone–urea copolymers display very hydrophobic surfaces with contact angles around 103–104°, which do not show any change upon annealing at 110 °C for 2 h. Organofunctionally terminated silicone oligomers, which have end groups of different polarities and very hydrophobic backbones show very interesting water contact angle behavior. As can be seen in Table 3, for PDMS-NH2 series contact angles depend on the chain length. For the shortest oligomer with Mn, 800 g/mol, contact angle is 43.8 ± 3.5°. As the oligomer molecular weight increases to 2500 and 7000 g/mol, water contact angles also increase to 51.5 ± 2.3 and 73.0 ± 1.1°, respectively. These water contact angles seem to be unusually low for PDMS oligomers. However, this is due to the presence of fairly polar primary amine end-groups, which can reorient themselves upon contact with water, in order to minimize the interfacial tension [27,28]. The influence of end group type on the water contact angle can also be clearly seen when oligomers with similar molecular weights but with different end groups are compared. For PDMS oligomers with Mn, 2500 g/mol, the contact angles for amine, *N*-methylamine and epoxy terminated systems were determined to be 51.5 ± 2.3, 54.6 ± 1.2 and 55.3 ± 2.0°, respectively. For oligomers with Mn, 7000 g/mol water contact angles for amine, *N*-methylamine and epoxy terminated systems are 73.0 ± 1.1, 76.2 ± 2.4 and 78.1 ± 1.8°, respectively. As discussed in the following paragraph, when reacted with PA-6, due to the absence of end group effects, these oligomers provide much higher water contact angles for the blends.

Table 3
Water contact angles of PA-6 and silicone modifiers before and after annealing

Sample code	Contact angle (°) (Before annealing)	Contact angle (°) (After annealing)
PA-6	69.3 ± 2.1	72.4 ± 1.7
PSU-1	103.9 ± 2.5	104.0 ± 3.1
PSU-2	104.4 ± 3.3	105.7 ± 2.1
PDMS-NH2-1K	–	43.8 ± 3.5
PDMS-NH2-3K	–	51.5 ± 2.3
PDMS-NH2-7K	–	73.0 ± 1.1
PDMS-NH-3K	–	54.6 ± 1.2
PDMS-NH-7K	–	76.2 ± 2.4
PDMS-E-3K	–	55.3 ± 2.0
PDMS-E-7K	–	78.1 ± 1.8

Table 4 provides water contact angle data on PA-6 modified with various telechelic organofunctional PDMS oligomers before and after annealing. As discussed before, influence of oligomer molecular weight, amount of additive and annealing on the surface behavior can clearly be seen in Table 4. First of all annealed samples all show dramatic enrichment of silicone on the surface as indicated by substantial increase in the water contact angles. Secondly, as expected, increasing the amount of silicone additive in the blend gives rise to higher water contact angles. Thirdly, as the molecular weight of the additive goes up from 2500 to 7000 g/mol water contact angles also increase for blends containing equal amounts of additive. Results in Table 4 clearly shows that PDMS oligomers with Mn, 7000 g/mol

Table 4
Water contact angles of PA-6 films modified with organofunctional PDMS oligomers (before and after annealing)

Sample code	PDMS additive		Average contact angle (°)	
	Type	Amount (%)	Before annealing	After annealing
PA-PDMS-1	NH2-3K	0.5	70.5	79.2
PA-PDMS-2	NH2-3K	1.0	73.8	85.6
PA-PDMS-3	NH2-3K	2.5	73.5	91.3
PA-PDMS-4	NH2-3K	5.0	76.7	99.8
PA-PDMS-5	NH-3K	0.5	68.5	79.0
PA-PDMS-6	NH-3K	1.0	71.4	85.2
PA-PDMS-7	NH-3K	5.0	75.8	95.3
PA-PDMS-8	E-3K	1.0	62.5	74.1
PA-PDMS-9	E-3K	3.0	77.8	81.5
PA-PDMS-10	E-3K	5.0	88.0	99.2
PA-PDMS-11	NH2-7K	0.5	75.5	99.2
PA-PDMS-12	NH2-7K	1.0	77.8	95.2
PA-PDMS-13	NH2-7K	5.0	87.8	105.3
PA-PDMS-14	E-7K	0.25	–	60.5
PA-PDMS-15	E-7K	0.5	–	93.5
PA-PDMS-16	E-7K	1.0	–	97.5
PA-PDMS-17	E-7K	2.0	–	99.3
PA-PDMS-18	E-7K	5.0	–	101.2

are very effective surface modifiers for polyamide-6. Even at an additive level of 0.5% by weight blend surfaces show water contact angles above 90°, clearly indicating the formation of silicone rich surfaces. Type of the end group does not seem to influence the extent of surface modification. As discussed before, this is an expected behavior assuming that the end groups have reacted with the polyamide backbone. When results provided in Tables 3 and 4 are compared, it is interesting to observe that all of the annealed samples show higher water contact angles than the pure oligomeric PDMS additives.

Table 5 gives water contact angle data on polyamides modified with silicone–urea copolymers, PSU-1 and PSU-2, which have PDMS contents of 75% by weight but PDMS soft segment molecular weights of 2500 and 7000 g/mol, respectively. Similar to the PDMS oligomers, both of these additives can effectively modify the surface properties of PA-6 at very low additive levels. As the amount of silicone–urea copolymer in the blend is increased, as expected, water contact angles also increase for both additives. Interestingly, when compared with blends containing similar amounts of reactive PDMS oligomers, silicone–urea copolymers seem to be more effective in surface modification. This can be seen in Tables 4 and 5 by comparing blends containing equivalent amounts of additives, where silicone–urea copolymer containing blends give higher water contact angles than those of PDMS oligomers. Influence of annealing on the extent of surface modification can clearly be seen in Fig. 2, where water contact angles before and after annealing for PSU-1 modified PA-6 are plotted against the amount of additive. For semi-crystalline polymers with high Tg and Tm migration rate of the additive to the film surface will be competing with the rate of polymer solidification [24,25]. For quenched systems, such as the samples prepared in our investigations, usually the additives are trapped in the bulk before they can phase separate and migrate to air surface. In such cases it will be necessary to anneal the system in order to promote/accelerate migration to the surface.

Table 5
Water contact angles of PA-6 films modified with silicone–urea copolymers (Before and after annealing)

Sample code	Additive		Average contact angle (°)	
	Type	Amount (%)	Before annealing	After annealing
PA-PSU1-1	PSU-1	0.5	71.7	93.1
PA-PSU1-2	PSU-1	1.0	72.8	97.8
PA-PSU1-3	PSU-1	2.0	76.8	102.7
PA-PSU1-4	PSU-1	5.0	77.5	102.4
PA-PSU2-1	PSU-2	0.5	76.5	95.1
PA-PSU2-2	PSU-2	1.0	75.5	101.7
PA-PSU2-3	PSU-2	2.0	95.2	103.7
PA-PSU2-4	PSU-2	5.0	97.5	108.3

In order to demonstrate that surface modification of PA-6 films through the use of reactive, telechelic PDMS oligomers or silicone–urea copolymers was permanent, modified films were subjected to extraction with methylene chloride for 5 h. After extraction the films were vacuum dried at 50 °C overnight. No detectable weight loss was observed in the films before and after extraction. Table 6 gives water contact angles for various blends before and after methylene chloride extraction. Results clearly show that extraction with methylene chloride, a good solvent for silicones, does not change the surface properties as evidenced by water contact angles of the blends. These results also indicate that both PDMS oligomers and silicone–urea copolymers are permanently incorporated into polyamide resin through chemical bonding and/or strong hydrogen bonding, as a result, provide permanent surface modification to the system.

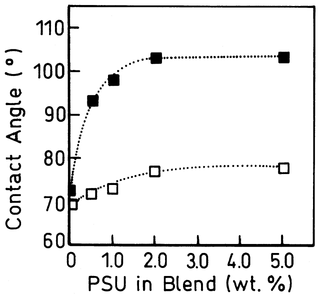


Fig. 2. Influence of annealing on the water contact angles of PA-PSU1 blends at various additive levels, before annealing (□) and after annealing (■).

Table 6
Influence of methylene chloride extraction on the water contact angles of PDMS modified PA-6 blends

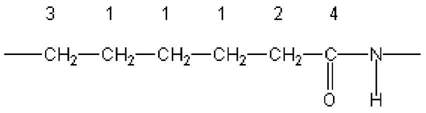
Sample code	Additive		Average contact angle (°)	
	Type	Amount (%)	Before extraction	After extraction
PA-PSU2-2	PSU2	1.0	101.7	100.2
PA-PSU2-4	PSU2	5.0	103.7	102.4
PA-PDMS-12	NH2-7K	1.0	95.2	96.1
PA-PDMS-13	NH2-7K	5.0	105.3	103.6
PA-PDMS-16	E-7K	1.0	97.5	98.2
PA-PDMS-17	E-7K	2.0	99.3	100.8

3.2. XPS studies

XPS, also known as ESCA, is one of the most sensitive and widely used techniques for the chemical analysis of material surfaces [5,8,29]. In this technique surfaces are bombarded with X-rays and the kinetic energy of the resulting photoelectrons are measured. From the energy difference between incident X-rays and the kinetic energy of the photoelectrons the binding energies and oxidation states of different atoms present in the system are determined. The angle between the outgoing electrons and the surface can be varied between approximately 10 and 90° and accordingly the depth of electron emission from the surface can be controlled. At 90° take-off angle the depth of emission is about 10 nm, whereas at around 30° it is about 5 nm. When chemical compositions of the surfaces obtained by XPS are compared with that of known bulk chemical compositions of the polymeric systems in many cases they may differ considerably.

Fig. 3 gives C1s, O1s, N1s and Si2p regions of the XPS spectra for PA-6, silicone–urea copolymer (PSU-2) and PA-6 modified with 1.0% by weight of PSU-2 (PA-PSU2-2). These XPS spectra were obtained with a 90° take-off angle on samples before annealing. When each region of the spectrum is closely examined detailed information on the nature of the chemical bonding in the system is obtained. C1s peak positions and the corresponding C atom compositions and the positions of O1s and N1s peaks in PA-6 backbone are provided in Table 7. In PSU-2, as expected O1s, N1s, Si2p and several C1s peaks are observed. In PSU-2 modified PA-6, in addition to typical C1s, O1s and N1s peaks, a fairly substantial Si2p peak is also observed, clearly indicating that in the top 10 nm of this modified film there is substantial amount of PDMS, although there is only 1.0% by weight of the additive in bulk. As shown in Fig. 4, when the samples are annealed, noticeable changes in the XPS spectra were observed when compared with samples that are not annealed. Also shown in Fig. 4 are the XPS spectra obtained for annealed PA-PSU2-2 at 30° take-off angle corresponding to reduced probe-depth. Table 8 provides comparative analytical data obtained from the XPS analysis of PA-6, PSU-2 and PA-PSU2 blends with different compositions. Also provided in Table 8 is the influence of annealing and the take-off angles (30 and 90°) on the XPS data obtained.

Table 7
Analysis of the XPS spectrum for PA-6 BR (peak positions and relative amounts of carbon in the backbone)



$$-\overset{3}{CH_2}-\overset{1}{CH_2}-\overset{1}{CH_2}-\overset{1}{CH_2}-\overset{2}{CH_2}-\underset{\underset{O}{\|}}{\overset{4}{C}}-\underset{\underset{H}{|}}{N}-$$

	C1s				O1s	N1s
	1	2	3	4		
BE (eV)	285.0	285.3	286.0	288.0	531.4	399.8
Rel. area	50	17	17	16		

XPS spectra were also obtained for modified PA-6 samples containing 2.0 and 5.0% by weight of PSU-2, before and after annealing. When XPS spectra of PSU-2 modified PA-6 samples with different amounts of additive were analyzed in terms of (Si), (C) and (N) atomic compositions, a very interesting phenomenon was observed. These results are tabulated in Table 8 and are also graphically shown in Fig. 5, where the Si/C atomic ratio obtained from XPS (indicating the surface concentration) is plotted against bulk PSU-2 concentrations. In pure PSU-2, which consists of 75% by weight of PDMS, XPS studies show a Si/C atomic ratio of 0.44 at 30° take-off angle and 0.42 at a take-off angle of 90°. It is interesting to note that for

Table 8
Analysis of XPS spectrum of PA-6 and PSU-2 modified PA-6 samples

		C1s		N1s	O1s	Si2p
	Angle (°)	CH	C=O			
BE (eV)		285.0	288.0	399.8	531.4	101.9
PA-6	90	82	18	11	19	–
	30	85	15	9	20	–
PA-PSU2-2	90	87	13	9	30	15
	30	88	12	6	34	19
PA-PSU2-2 (Annealed)	90	88	12	9	31	15
	30	90	10	5	29	14
PA-PSU2-3	90	89	11	7	45	30
	30	90	10	5	50	32
PA-PSU2-3 (Annealed)	90	90	10	6	45	30
	30	91	9	4	46	33
PA-PSU2-4	90	90	9	5	50	34
	30	91	8	3	54	40
PA-PSU2-4 (Annealed)	90	92	8	3	51	38
	30	93	7	2	54	40
PSU-2	90	93	7	2	55	42
	30	92	8	1	58	44

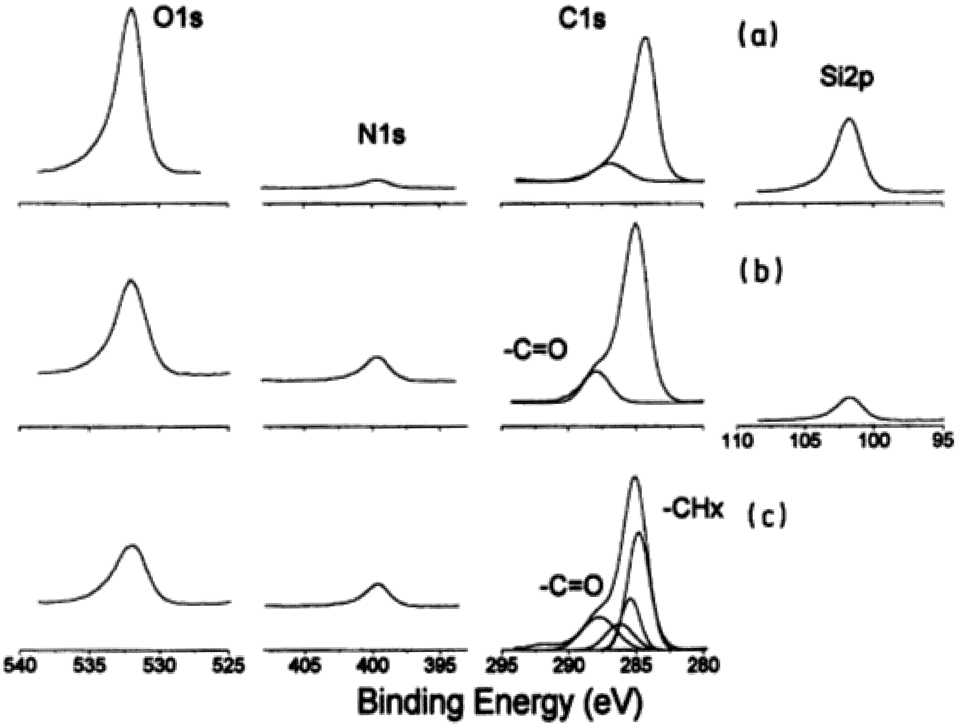


Fig. 3. Comparison of O1s, N1s, C1s and Si2p regions of XPS spectra at 90° take-off angle. (a) PSU-2, (b) PA-PSU-2, and (c) PA-6.

5.0% by weight PSU-2 containing PA-6 sample (PA-PSU2-4) (Si) peak obtained from XPS spectrum at 30° angle corresponds to ca 0.40 Si/C atomic ratio indicating almost the same surface composition as pure PSU-2. In 2.0% PSU-2 containing blend (PA-PSU2-3) Si/C atomic ratio 0.30 composition and for 1.0% PSU containing PA-6 (PA-PSU2-2) it is around 0.18. Very similar results are obtained for 90° take-off angle, as shown in Fig. 5.

All of these XPS results indicate substantial enrichment of PDMS at the surface of the modified films, and in fact almost complete saturation at about 5.0% by weight additive level. Results of the water contact angle measurements and

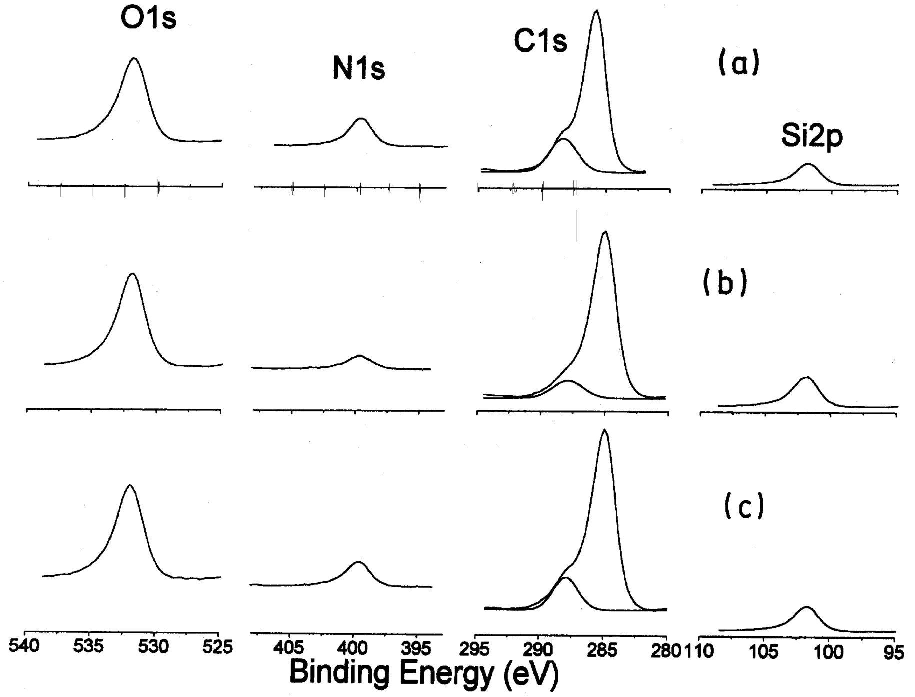


Fig. 4. Comparison of O1s, N1s, C1s and Si2p regions of XPS spectra of PA-PSU2-2 blend (a) 90° take-off angle before annealing, (b) 90° take-off angle after annealing, and (c) 30° take-off angle after annealing.

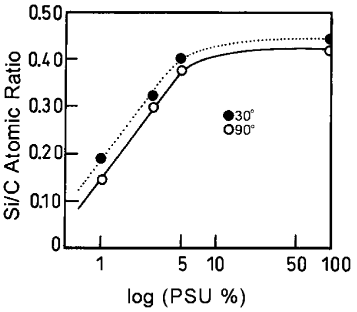


Fig. 5. Plots of surface Si/C atomic ratios determined by XPS against the amount of PSU-2 in bulk (●) 30° and (○) 90° take-off angles, after annealing.

XPS strongly support each other, both showing substantial enrichment of PDMS on the surface of modified polyamide films [5,24,30]. As indicated before, when the incident angle is 90°, XPS probes a depth of approximately 10 nm, much deeper than that probed by water-contact angle measurements, which usually shows one or two monolayers. However, from the angle-dependent XPS studies, it is evident that, in addition to the surface monolayer of PDMS, there is a reservoir of siloxane just beneath the surface, to a probed-depth of about 10 nm.

3.3. Thermal properties

DSC studies on PA-6 and the blends did not show any significant differences on the melting behavior of crystalline regions, even at 5% loadings of the PSU-2 copolymer. Fig. 6 shows the DSC melting endotherm for virgin PA-6 and the blend (PA-PSU2-4) which contains 5% by weight of silicone–urea copolymer. After compression molding and quenching in water at room temperature, both films were annealed at 110 °C for 4 h. As shown in Fig. 6 melting endotherms of the base PA-6 and the blend containing 5% by weight of PSU-2 (PA-PSU2-4) are almost identical. Both endotherms start at around 200 °C and show a slight shoulder. Peak minimum for the modified system is at 222.6 °C and for PA-6 it is at 223.1 °C, which are virtually the same. Melting is completed at 230 °C, for both. The area under the melting peaks, which give the enthalpy of fusion (ΔHfus) are also almost identical (within experimental error) for modified system (43.6 J/g) and virgin PA-6 (45.1 J/g). Similar behavior is observed for all blends. These DSC results are a good indication that thermal properties and crystallinity of the base PA-6 are not influenced by the addition of silicone–urea copolymers. Stress–strain tests on the blends have also shown that modulus and tensile strengths of the blends with low levels of additive are very similar to that of pure PA-6.

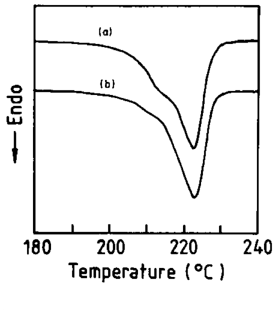


Fig. 6. Comparison of the DSC melting endotherms (a) PA-PSU2-4, and (b) PA-6.

4. Conclusions

Permanent surface hydrophobization of polyamide-6 has been demonstrated through melt blending with low levels of telechelic PDMS oligomers or silicone-urea copolymers. Influence of additive type, additive amount, average PDMS molecular weight and annealing conditions on the surface properties of the resultant films were investigated by static water contact angle measurements and XPS.

When telechelic PDMS oligomers were compared, additives with Mn, 7000 g/mol were more effective surface modifiers than those with Mn, 2500 g/mol. For high molecular weight PDMS additives water contact angles greater than 90° were obtained at additive levels of 0.5% by weight, whereas for Mn, 2500 g/mol PDMS more than 2.5% by weight additive was required to achieve similar contact angles. End group type of the oligomer (amine or epoxy) does not seem to have a strong influence on the surface properties. When compared with telechelic oligomers, at equal levels of incorporation, silicone–urea copolymers provided much better surface hydrophobization as indicated by higher water contact angles. Similar to the PDMS oligomers, silicone–urea copolymers based on Mn, 7000 g/mol PDMS were more effective than those based on Mn, 2500 g/mol.

Being a semi-crystalline polymer, there is a very strong thermal history effect on the development of surface properties in PA-6. As expected, quench cooled films showed very low contact angles, where very fast cooling resulted in immediate solidification of the polymer melt, trapping PDMS in the solid matrix before migrating to the polymer–air interface. After annealing at 110 °C for 4 h, a dramatic enrichment of siloxane on the surface was observed in all blends, which displayed water contact angles well above 90° and up to 108°. Incorporation of silicone additives does not influence the bulk properties of PA-6.

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