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Surface and wear behavior of bis-(4-hydroxyphenyl) cyclohexane (bis-Z) polycarbonate/polycarbonate–polydimethylsiloxane block copolymer alloys

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Abstract

The utilization of block copolymers containing siloxane segments is well known to be of great interest for surface modifications. This paper focuses on the use of segmented bis-(4-hydroxyphenyl) cyclohexane (bis-Z) polycarbonate–polydimethylsiloxane copolymers as an additive to improve surface and wear properties of this non-crystallizable polycarbonate. The effects of chemical composition, block size, and casting solvent on surface and wear properties of the modified polycarbonate were elucidated by using angle-dependent X-ray photoelectron spectroscopy (XPS), tapping mode atomic force microscopy, and mechanical testing. XPS results showed that the siloxane segments were enriched on the surface even at bulk composition as low as 1 wt% siloxane, depending on siloxane block size and casting solvent. The friction coefficient was strongly dependent not only on the surface enrichment of siloxane but also on the molecular weight of siloxane block segment. The initial friction coefficient had a little influence on the overall wear resistance due to the rapid wear process of the uppermost surface. Instead, stress–strain behavior of the samples played a key role in the observed wear resistance. The latter first increased and then deteriorated with siloxane concentration. A modified Ratner model was successfully employed to interpret the results. © 2002 Published by Elsevier Science Ltd.

Keywords: Bis-(4-hydroxyphenyl) cyclohexane based polycarbonate; Block copolymer; Polydimethylsiloxane

1. Introduction

Polydimethylsiloxane (PDMS) block incorporation into copolymers contributes many benefits such as enhanced solubility and processability, thermal stability, hydrophobicity, improved impact resistance and biological inertness [1, 2]. One of the key properties is its low surface energy, which results in surface segregation of siloxane at the micro- or nano-level in most polymer blend systems. This attractive feature enables one to achieve a low energy surface when added even in small amounts to the corresponding homopolymeric system. Copolymers used for these types of blend systems wherein the other block structure is polycarbonate have been extensively investigated because of their high potential for end-use applications.

For last 30 years, several attempts have been made to synthesize polycarbonate–PDMS block copolymers. Vaughn et al. [3] synthesized polycarbonate–PDMS block copolymers by phosgenation of a mixture of bisphenol A and an α,ω -dichloro-terminated dimethylsiloxane oligomers in the presence of pyridine. The polycarbonate blocks were produced in situ and each block was randomly coupled. Tang et al. [4–8] have also made polycarbonate–PDMS block copolymers in an effort to form a perfectly alternating block architecture by the reaction of preformed reactive dimethyl silyl amino end group terminated polysiloxane oligomers with hydroxyl-terminated bisphenol A polycarbonate oligomers.

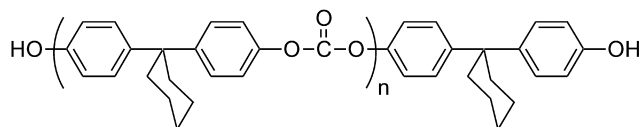
The surface properties of polymer blends containing siloxane block copolymer are influenced by several parameters such as the composition of the copolymer, the length of each block, the architecture of the copolymer, the casting solvent and annealing conditions. Dwight et al. [9–11] have shown that in siloxane-containing block copolymers and their blends with homopolymers, the surface siloxane concentration tended to enrich rapidly to

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Scheme 1. Chemical structure of PCZ-OH.

the typical values of the pure block copolymers, as the bulk siloxane content to about 1%. They also found that at equivalent siloxane content in the bulk, longer siloxane blocks further enhanced of surface segregation. Chen and Gardella [13] have observed that in a polysiloxane–poly(α -methylstyrene) copolymer modified poly(α -methylstyrene) system, the multi-block type copolymer had higher siloxane enrichment on its air contacting surface than the star block copolymer, when the molecular weight of poly(α -methylstyrene) homopolymer was comparable to that of siloxane segment in the copolymer. Gardella et al. [14,15] have further elucidated that casting solvent and annealing treatment played a significant role in influencing the surface compositions in PDMS incorporated block copolymers and their blends with homopolymers. On the basis of their results, the surface enrichment of siloxane would be enhanced by increasing the polymer–solvent interaction, the solvent evaporation rate and the annealing time.

The incorporation of siloxane also leads to significant change of the morphology, which is one of the most important factors imparting the physical and mechanical properties unique to those systems. Much attention has been given to the surface and bulk morphologies of siloxane block copolymers blended with homopolymers [10,16–21]. The literature showed that the surface and bulk morphologies containing siloxane block copolymer has its unique phase separated morphology caused by the migration of siloxane component to the interface and the morphology is dependent on the molecular weight of siloxane segment and the siloxane content as in other block copolymers.

However, relatively few systematic studies have been done on the important friction and wear properties of siloxane modified systems, even though it is a well known fact that siloxane modifiers are effective lubricants. Eiss et al. [22–24] have elucidated that the incorporation of trifluoropropylmethylsiloxane–PDMS block copolymer into an epoxy could reduce both the wear rate and the friction coefficient by roll formation of elastomeric domain structures. They concluded that an optimum domain size and composition were required to reduce the surface stresses and improve the wear resistance. Dieng et al. [25] have studied the friction behavior of siloxane modified polystyrene systems and found that polystyrene–PDMS block copolymers had a lubricating effect when more than 30 wt% of copolymer was added to the polystyrene system.

Thus, although these studies have suggested that the tribological properties could be related to siloxane concentration, it is still rather difficult to interpret the friction and

wear properties with the bulk concentration of siloxane, since the siloxane components are non-uniformly distributed due to its surface affinity. Furthermore, there is no general agreement about the relationship between wear resistance and material properties.

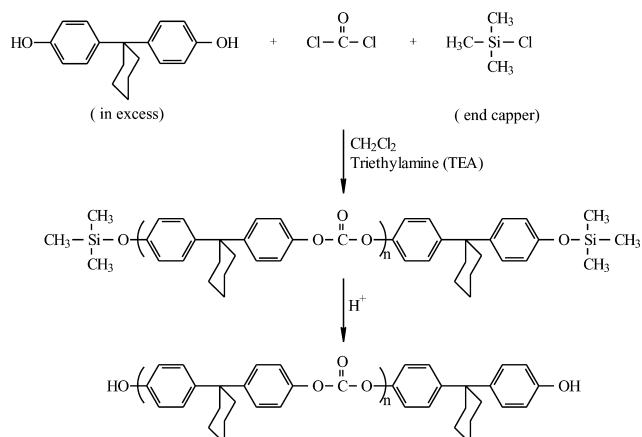
Investigation of the effects of siloxane-containing copolymer and casting solvent on improving friction and wear properties have been now done with the high volume bisphenol A polycarbonate engineering thermoplastic system. This has a number of desirable properties, such as high T_g , toughness, the ability to be coated as a film from solvents, good thermal stability, and transparency [26]. However, it is also known to slowly crystallize from solution, which sometimes causes undesirable behavior such as haze or embrittlement [9,27,28]. The main purpose of this study, therefore, was to investigate the effects of siloxane-containing copolymer and casting solvent for the effective modification of less studied non-crystallizing aromatic polycarbonate to improve friction and wear properties. In order to avoid unnecessary ambiguity caused by the crystallization, this study used a cyclohexyl containing bisphenol Z type polycarbonate (PCZ), which is also known by others as the polycarbonate derived from ‘bisphenol C’, since those systems will not undesirably crystallize from solution. An additional advantage of PCZ is its relatively high T_g (180 °C) compared with bisphenol A polycarbonate. The repeat unit shown with reactive end groups is shown in Scheme 1.

The PCZ–PDMS block copolymers were synthesized using similar methodologies to those described earlier [3,4], and surface properties of PCZ–PDMS copolymer modified PCZ polymeric films were evaluated. For quantifying surface enrichment of the siloxane component, the films were analyzed by angle-dependent X-ray photoelectron spectroscopy (XPS), and surface and bulk morphologies were characterized by tapping mode atomic force microscopy (AFM). Surface friction property and wear behavior were analyzed by the plate on plate geometry friction testing and the well-known Taber abraser, respectively. The relationship between material properties and wear behavior was established by the application of a modified Ratner model [29].

2. Experimental

2.1. Materials

Bisphenol Z (4,4'-cyclohexylidenebisphenol) was obtained from Tokyo Chemical Company. Chlorotrimethylsilane was purchased from Aldrich Chemical Company. Triethylamine and dry methylene chloride were also obtained from Aldrich Chemical Company. Phosgene stored in a 5 l cylinder was provided by Matheson. The low molecular weight bis(dimethylamino)polydimethylsiloxane end blocking oligomers were kindly supplied by Crompton



Corporation. The number average molecular weights of the functional PDMS oligomers synthesized for this research were 1.1 and 1.6 kg/mol calculated from the ^1H NMR end group analysis spectra. Chlorobenzene was provided by Fisher Chemical Company. Bisphenol Z polycarbonate (PCZ) homopolymer with $M_n = 33.7$ kg/mol was supplied by the Mitsubishi Gas Chemical Company. All of the above materials were of high purity and used without further purification.

2.2. Synthesis of hydroxyl-terminated PCZ

The hydroxyl-terminated bisphenol Z polycarbonate was prepared by condensation of bisphenol Z and phosgene in a nitrogen atmosphere as shown in Scheme 2. Triethylamine was used to scavenge the byproduct hydrogen chloride and chlorotrimethylsilane was used as a labile monofunctional endcapper to control the molecular weight of PCZ [30]. The chlorotrimethylsilane required for obtaining the oligomer with the desired molecular weight was calculated according to the modified Carothers equation [31].

The setup typically consisted of a 3 l 4-neck round-bottom flask equipped with mechanical stirrer, condenser, phosgene, bubbled through the reaction mixture and nitrogen inlet, a condenser with a gas outlet connected to a caustic trap to decompose any outlet phosgene and HCl. In a typical reaction for the preparation of a hydroxyl-terminated polycarbonate with $M_n = 7000$, 134.18 g (0.5000 mol) of bisphenol Z and 1300 ml of dry methylene chloride were placed into the reactor. Triethylamine, 106.25 g (1.050 mol) was added into the reactor while stirring. When the bisphenol Z was completely dissolved, 9.085 g (0.08373 mol) of chlorotrimethylsilane was slowly added into the reactor and the solution was kept stirring for 30 min. The pH value of the solution at this time was about 10. Then, phosgene was introduced into the reactor at a rate of about 200 ml/min. Initially, the solution temperature increased and reflux was observed due to the exothermic reaction. After about 15 min, the solution temperature began to decrease. In the meantime, the solution became cloudy

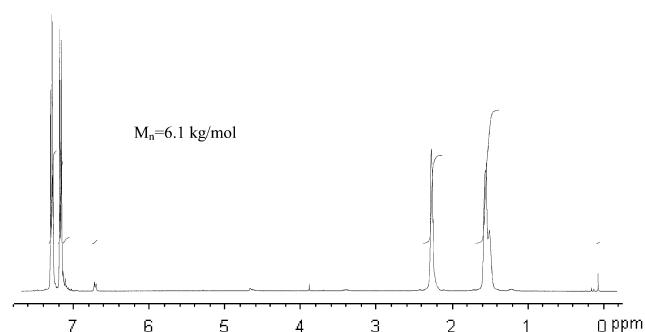
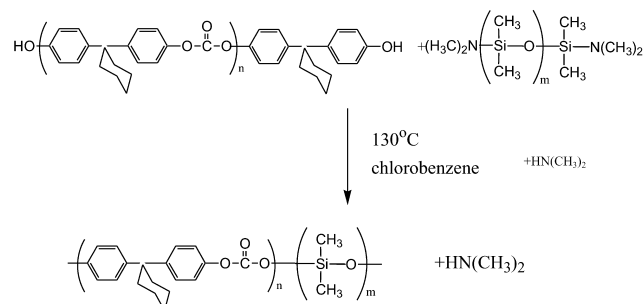


Fig. 1. 400 MHz ^1H NMR spectrum of PCZ-OH in CDCl_3 .

and some white precipitate was observed. After about 90 min, the pH value was also decreased to about 8. Phosgene was slowly and continuously introduced into the reactor for another 30 min. Finally, the solution was kept stirring for 120 min to complete the reaction and remove excess amounts of phosgene through nitrogen purging. Next, 800 ml of deionized water was slowly added into the reactor while vigorously stirring. Note that this should be done slowly, as it can produce a strongly exothermic reaction! The solution was kept without stirring for 2 min to allow the upper water layer to separate and be discarded. The lower organic solution layer was washed two times with dilute hydrochloric acid, and three times with deionized water. After 80 ml of methanol and 4 ml of concentrated HCl were added into the slightly cloudy solution, the solution became clear and was stirred for 2 h. It was again washed two times with deionized water. The bisphenol Z polycarbonate oligomer was isolated by precipitation in methanol, filtered, dried in a vacuum oven at 80°C for 24 h and was kept dry until further use. The number average molecular weight, M_n of the oligomer was determined by ^1H NMR peak integrals (Fig. 1) and gel permeation chromatography.

2.3. Synthesis of perfectly alternating PCZ-PDMS block copolymer

Earlier research showed that the block copolymers containing Si-O-C bond linkages were, in contrast to expectation, quite hydrolytically stable [32–34]. The silylamine-hydroxyl condensation reaction shown in Scheme 3 was used to synthesize perfectly alternating block copolymer in solution. The reactions were conducted in a 2 l, four-necked, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet, and a reverse Dean-Stark trap with a reflux condenser. In a typical reaction to produce a PCZ-PDMS block copolymer, 77 g (0.011 mol) of hydroxyl-terminated PCZ ($M_n = 7000$ g/mol) were placed in the reactor and 900 ml of chlorobenzene was used to dissolve the oligomer. The solution was heated to reflux (132°C) and approximately 100 ml of solvent was removed through the trap to dehydrate the system. Then 17 g (0.010 mol) of a dimethylamino-terminated PDMS liquid

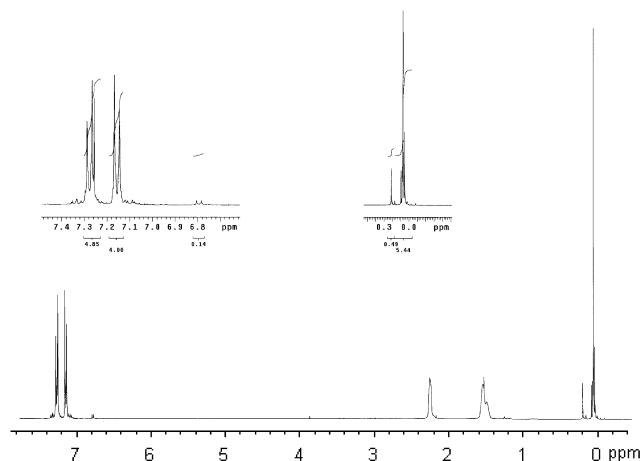


Scheme 3. Synthesis of perfectly alternating PCZ-PDMS copolymers.

with a $M_n = 1700$ g/mol was placed in an addition funnel and about half of the liquid was added dropwise to the hydroxyl-terminated polycarbonate solution over a period of 1 h. As the reaction proceeded, the evolution of dimethylamine was detected with the pH paper. After about 1 h, the rest of the liquid was added in the solution over as additional 1 h. As the stoichiometric point was approached, a noticeable increase in the viscosity of the reaction mixture was observed, as expected. The reaction was allowed to run overnight even though the evolution of dimethylamine was very slow after a few hours of reflux. Longer reaction times are important to further increase the molecular weight. The copolymer was precipitated in methanol, redissolved in methylene chloride, again precipitated in methanol, filtered, and dried in a vacuum oven at 80 °C for 24 h. Structural information of the copolymer was obtained from the ^1H NMR spectrum as shown in Fig. 2 and according to the appropriate integrals as shown in Table 1.

2.4. Preparation of PCZ/PCZ–PDMS alloys

The blend solutions of PCZ homopolymers and block copolymer with various weight ratios were prepared by solution-casting (15%, w/v) on a surface cleaned aluminum plate. To investigate solvent effects, ten reagent-grade casting solvents or tetrahydrofuran (THF) containing

Fig. 2. 400 MHz ^1H NMR spectrum of polycarbonate–PDMS copolymer (Copolymer2) in CDCl_3 .Table 1
Copolymer structural information

	Copoly1	Copoly2
Molecular weight, M_n (kg/mol)	22.7	20
Block length of polycarbonate (kg/mol)	10.2	6.1
Block length of PDMS (kg/mol)	1.1	1.6
PDMS (wt%)	10	20

solvent mixtures were selected and used as received. For XPS, TM-AFM, coefficient of friction (COF) and wear tests, the thin films were prepared by conventional dipping process. Then the thin films with thickness of about 25 μm were cast after drying at room temperature for 12 h, and further dried at 120 °C for 1 h. For tensile properties, films with thickness of about 250 μm were cast on glasses after drying at room temperature for 48 h, 80 °C for 1 h, and 120 °C for 1 h. All the samples were finally dried at 140 °C for 3 h under vacuum and then stored in a vacuum oven until the desired tests were performed. No solvent could be detected in the films, within the detection limits of ESCA. The sample code and formulation for this study are shown in Table 2.

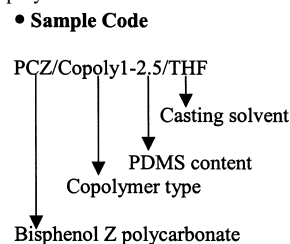
3. Measurements

3.1. Polymer characterization

Gel permeation chromatography (GPC). GPC measurements were performed to characterize the molecular weights and molecular weight distributions of the polymers. Chloroform was used as a mobile phase at room temperature. A

Table 2
Sample code and copolymer content

Sample code	PDMS content (wt%)	Copolymer content (wt%)
Control	0	0
PCZ/Copoly1-025	0.25	2.5
PCZ/Copoly1-05	0.5	5
PCZ/Copoly1-1	1	10
PCZ/Copoly1-2.5	2.5	25
PCZ/Copoly1-5	5	50
PCZ/Copoly2-025	0.25	1.25
PCZ/Copoly2-05	0.5	2.5
PCZ/Copoly2-1	1	5
PCZ/Copoly2-2.5	2.5	12.5
PCZ/Copoly2-5	5	25



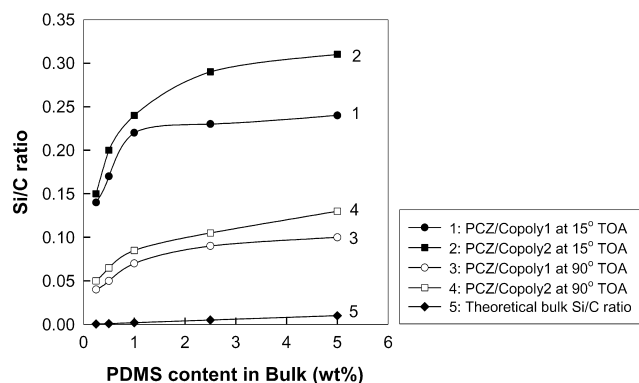


Fig. 3. Si/C atomic ratios of solvent-cast films of PCZ containing copolymer additives as a function of PDMS content.

Waters 2690 instrument, with a differential refractive index detector and a Viscotek differential viscometer in parallel, allowed the calculation of absolute molecular weights via the universal calibration technique.

NMR. ^1H NMR spectra of the polymers were obtained on a Varian Unity 400 spectrometer operating at 400 MHz, using deuterated chloroform as the solvent.

XPS. Siloxane compositions of the as-cast and worn surfaces of the modified films were measured on an angle-dependent XPS (Perkin–Elmer physical electronic model 5400) with a hemispherical electron analyzer and a position sensitive detector. The spectrometer was equipped with a Mg $K\alpha$ X-ray source operated at 15 kV and 20 mA. The pressure in the sample chamber was maintained at $\sim 10^{-8}$ Torr during spectra collection. Angle-dependent studies were done by rotating the circular probe rod. The depth of analysis decreased with the angle between the analyzer slit and the sample plate. Take-off angles (TOA) of 10 and 90° used were approximately corresponding to sampling depths of 10 and 50 Å, respectively. The elemental compositions were calculated from integrated peak areas, which resulted from the Si_{2p} , C_{1s} , and O_{1s} . The ratio of $\text{Si}_{2p}/\text{C}_{1s}$ was used to monitor the concentration change of Si in the surface region.

AFM. AFM analysis was performed on a Digital Instruments Dimension 3000 operating in tapping mode, using the micro-fabricated cantilevers with a force constant of approximately 40 N/m. The ratios of amplitudes used in feedback control were adjusted to 0.6 of the free air amplitudes for all the reported images. Under these moderate force tapping conditions, phase data are sensitive to local stiffness differences of domains in the top several nanometers from the uppermost surface. For cross-sectional morphology, the prepared thin films were embedded in epoxy resin and cured at room temperature. Before the embedding procedure, the films were gold sputtered to protect the surface from the embedding material. The embedded films were then microtomed normal to the film surface at liquid nitrogen temperature.

Friction coefficient. The setup for evaluating the friction coefficient was based on ASTM D1894. A rectangular

aluminum sled (200 g, $63.5 \times 63.5 \times 15 \text{ mm}^3$) was machined for the test. After a nylon string was attached to the sled, it was pulled 20 mm at a speed of 100 mm/min with a tensile tester (Instron model 4204) at ambient conditions. The friction force was recorded as a function of displacement of the sled and the kinetic friction coefficients were then calculated. Before each test, the counter aluminum surface of the sled was cleaned with acetone to remove any organic contaminants. The result was an average of at least three individual measurements for each given sample.

Mechanical properties. Wear tests were performed on Taber abraser based on the ASTM 1044-94. Wool felt type of abrading wheel (CS-5, Taber Industry) was used under a 500 g load. The weight loss (mg) was recorded after every 1000 wear cycle and the wear cycle was increased up to 10,000 cycles. The initial wear, that occurred during less than 1000 wear cycle, of each sample was discarded because the surface evenness, and conditions of abrading wheels as well as surface siloxane enrichment resulted in irreproducible data. The wear rates after 1000 wear cycles were reproducible within the error bounds of $\pm 10\%$. Three tests for each given sample were averaged. Tensile properties were measured on an Instron tensile testing machine (model 4204) using a cross-head speed of 5 mm/min. Dumbbell shaped tensile specimens (Type V) were used according to ASTM 638-94.

4. Results and discussion

4.1. Synthesis of hydroxyl-terminated PCZ and PCZ–PDMS block copolymer

The bisphenol Z polycarbonate is not soluble in methylene chloride but was soluble in THF. However, initial polymerization of bisphenol Z and phosgene in THF was not successful. The addition of triethylamine solubilized the bisphenol in methylene chloride due to the formation of the phenolate. Experimental results showed that bisphenol Z polycarbonates could be prepared in this manner. The polycarbonate–PDMS multi-block copolymers were successfully prepared employing the reactive oligomers prepared by the above method [3,4]. Several molecular characteristics are described in Table 1.

4.2. Surface composition

Fig. 3 shows the surface Si/C ratio of the PCZ containing block copolymer as a function of the PDMS content in the bulk. When the block copolymer content in the bulk was increased, a noticeable increase of the Si/C ratios was observed which finally reached a plateau when the bulk concentration of PDMS block was greater than about 2 wt%. It was noted that the measured Si/C ratios on the surface was much higher than that of theoretical bulk Si/C

Table 3
Effect of casting solvent for PCZ/Copoly1-1 on surface Si/C ratio

Casting solvent	Hansen's parameters (MPa ^{1/2})				SPD ^a (MPa ^{1/2})	Evaporation rate	Surface Si/C ratio ^b	
	δ_d	δ_p	δ_h	δ_t			15° TOA	90° TOA
Benzene	18.4	0.0	2.0	18.6	5.74	5.10	0.200 ± 0.008	0.071 ± 0.005
Toluene	18.0	1.4	2.0	18.2	4.80	1.90	0.242 ± 0.005	0.081 ± 0.004
<i>o</i> -Xylene	17.6	1.0	1.0	17.7	5.89	0.73	0.245 ± 0.007	0.089 ± 0.004
THF	16.8	5.7	8.0	19.4	3.11	4.72	0.222 ± 0.010	0.077 ± 0.004
1,3-Dioxolane	18.2	6.1	9.5	20.9	3.41	4.01	0.275 ± 0.015	0.101 ± 0.002
<i>p</i> -Dioxane	19.0	1.8	7.4	20.5	3.01	2.42	0.326 ± 0.013	0.097 ± 0.006
Chloroform	17.8	3.1	5.7	19.0	1.39	10.45	0.206 ± 0.006	0.070 ± 0.003
Dichloroethane	18.8	5.3	4.1	20.0	1.99	4.46	0.249 ± 0.014	0.099 ± 0.002
Chlorobenzene	18.8	4.3	2.1	19.6	3.71	0.84	0.299 ± 0.007	0.101 ± 0.003
Pyridine	19.0	8.8	5.9	21.8	4.52	0.93	0.274 ± 0.005	0.118 ± 0.002
THF/cyclohexane (9:1)						4.72/3.80	0.148 ± 0.012	0.057 ± 0.003
THF/MEK (9:1)						4.72/4.50	0.220 ± 0.011	0.068 ± 0.004

^a SPD between Copolymer1 and casting solvent: $\sqrt{((\delta_d - 18.5)^2 + (\delta_p - 4.3)^2 + (\delta_h - 5.8)^2)}$.

^b Theoretical Si/C ratio is 0.002.

ratios and even higher than the Si/C ratios of the copolymer itself (around 0.045). This suggests that the surfaces of all of the films were completely covered with the copolymer additives and the siloxane segments of the block copolymers were enriched on the uppermost surface. This is attributable to the migration of the copolymer and the orientation of siloxane segments due to their low surface energy as described in Section 1. Angular dependent results showed that the surface concentration of the siloxane was significantly increased with decreasing TOA from 90 to 15°. This result indicated that there was a concentration gradient of the siloxane in the surface region and this is quite consistent with previous results [35,36].

Fig. 3 also shows that the samples containing shorter siloxane block copolymer, i.e. Copolymer1, had lower Si/C values at both TOA than those samples with longer siloxane block copolymer, i.e. Copolymer2. This higher Si/C ratio of the sample containing longer siloxane segments is presumably due to the higher Si/C ratio of the block copolymer additive.

Table 3 shows the effect of the casting solvent on the surface Si/C ratio of the PCZ/Copoly1-1 sample. Comparing the Si/C ratio variations with Fig. 3, the effect of casting solvent is more significant than that of the copolymer additive composition. Films cast from pure *p*-dioxane and pyridine had the highest Si/C ratio at 15 and 90° TOA, respectively, while casting from benzene had the lowest Si/C ratio. Previous investigations [12,13] on solvent effects on siloxane migration found that the polymer–solvent interaction and evaporation rate were two key parameters. Solubility parameters for Copolymer1 were experimentally calculated by several methods [37–40] to further develop those relationships using 28 different solvents having solubility parameter range from 15.5 to 24.8 MPa^{1/2}. The solubility parameters of Copolymer1 are not significantly different, based on all different calculation methods [41]. To calculate the polymer–solvent interaction, the solubility

parameter for the Copolymer1 was taken as (i.e. $\delta_d = 18.5$, $\delta_d = 4.3$, $\delta_h = 5.8$) according to Hansen's method [37]. The polymer–solution interaction was then quantified by solubility parameter difference (SPD) as listed in Table 3. Another key factor affecting the siloxane migration would be the solvent evaporation rate, since the solvent with higher evaporation rates imparts less time for the polymer chains to rearrange into a favorable lower energy state during film formation. To the authors' knowledge, no quantitative relationship among evaporation rate and boiling point, vapor pressure and other parameters of a liquid has been reported. A relative evaporation rate of pure solvent compared with butyl acetate [42] was used and listed in Table 3. Based on the data in Table 3, the Si/C ratios of the sample were plotted with the SPD values and solvent evaporation rates shown in Fig. 4. It is clearly demonstrated that the Si/C ratio on the surface region increased with decreasing SPD when the evaporation rate of the solvents was similar Fig. 4(a). This may be explained by the fact that the copolymer chain dimensions tend to expand instead of contracting with low SPD value. On the other hand, when SPD value is similar, the Si/C ratio increased with decreasing solvent evaporation rate, since longer evaporation time helps in approaching the thermodynamic equilibrium state of the blend film (Fig. 4(b)).

THF containing solvent mixtures with non-solvents such as cyclohexane or methylethyl ketone (MEK), produced lower surface enrichment of the siloxane phase. The low Si/C values probably are due to the selective precipitation by the non-solvent moiety, of which composition increased during the evaporation process because of the lower vapor pressure of cyclohexane and MEK casting solvents.

4.3. Coefficient of friction

Table 4 shows the effects of additive composition on the kinetic coefficient of friction (COF). The COF values were

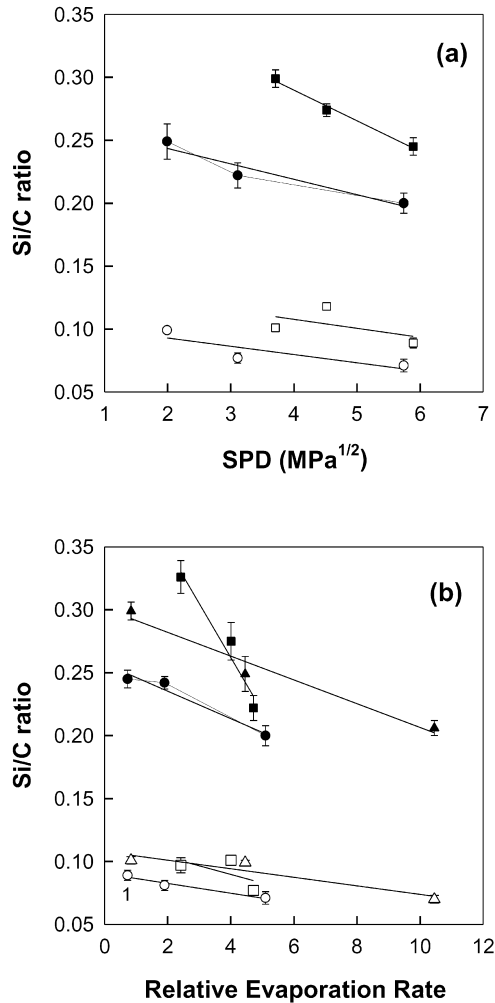


Fig. 4. Effect of polymer-solvent interaction and evaporation rate on surface Si/C atomic ratio. Filled symbol: measured at 15° TOA, Unfilled symbol: measured at 90° TOA; (a) polymer-solvent interaction: evaporation rate range: circle = 4.5–5.1, square = 0.7–0.9 (b) evaporation rate: SPD range: circle = 4.8–5.9, square = 3.0–3.5, triangle = 1.4–2.0.

significantly lowered as the composition of the copolymer additive increased, as expected. The pure PCZ homopolymer control showed the highest values of 0.60, while the COF of the PCZ/Copoly2-5 was as low as 0.14, which is comparable to that of pure PDMS [17]. The lubrication effect was more striking, when the surface Si/C ratio at 90° TOA was between 0.05 and 0.10. It was also found that the copolymer additives with longer siloxane block length were

Table 4
Effect of copolymer composition on COF (casting solvent: THF)

Sample	COF	Sample	COF
PCZ control	0.60 ± 0.02		
PCZ/Copoly1-025	0.57 ± 0.02	PCZ/Copoly2-025	0.53 ± 0.01
PCZ/Copoly1-05	0.52 ± 0.03	PCZ/Copoly2-05	0.30 ± 0.01
PCZ/Copoly1-1	0.39 ± 0.00	PCZ/Copoly2-1	0.23 ± 0.01
PCZ/Copoly1-2.5	0.30 ± 0.03	PCZ/Copoly2-2.5	0.17 ± 0.00
PCZ/Copoly1-5	0.20 ± 0.01	PCZ/Copoly2-5	0.14 ± 0.00

Table 5
Effect of casting solvent on COF (PCZ/Copoly1-1)

Casting solvent	COF
THF/cyclohexane (9:1)	0.52 ± 0.02
THF/methyl ethyl ketone (9:1)	0.45 ± 0.01
Toluene	0.36 ± 0.02
<i>p</i> -Dioxane	0.20 ± 0.01
Pyridine	0.13 ± 0.01

advantageous for effective lubrication, at the same siloxane content. This phenomenon may be explained by the brush effect [43,44], i.e. higher molecular weight of siloxane segment provides for larger brush thickness, which has a larger repulsive force between the polymer surface and sliding object.

Table 5 shows the effect of casting solvent on the friction reduction. It was found that the films cast from *p*-dioxane and pyridine showed relatively lower COF values for PCZ/Copoly1-1 sample, while the COFs of the films cast from mixed solvent had relatively high COF values. Considering Si/C values obtained from XPS experiments, this result indicated that the COF might be inversely proportional to the surface siloxane enrichment. Fig. 5 shows the relationship between the COF value and surface Si/C ratio measured at 90° TOA. This figure shows that when different siloxane copolymer additive was used, the COF values are dependent upon not only surface siloxane composition but also the molecular weight of siloxane segment. On the other hand, when the same copolymer was used as a surface modifier, the COF value exclusively depends on the surface siloxane concentration. That is supported by the fact that the COF values, which varies with different casting solvent, was located on the same line from those values with copolymer concentration.

4.4. Wear resistance and modeling

Table 6 shows the wear rate of PCZ films containing the copolymer additive. The effect of the additive compositions on the wear resistance of the samples shows that the wear rate had a minimum value at around 0.5 wt% of PDMS

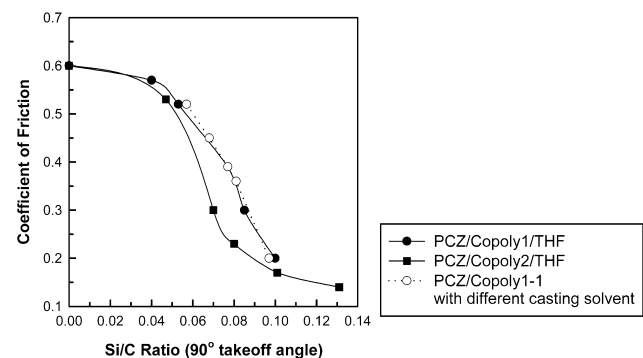


Fig. 5. Relationship between surface Si/C ratio and COF; Si/C ratio was taken by XPS at 90° TOA.

Table 6
Wear rate, Si/C ratio on the worn surface and calculated COF values

Sample code	Wear rate ^a (loss mg/1000 cycle)	Si/C ratio on the worn surface (90° TOA)	Calculated COF values ^b
PCZ control	0.76	0	0.60
PCZ/Copoly1-05/THF	0.57	–	–
PCZ/Copoly1-1/THF	0.54	0.006	0.60
PCZ/Copoly1-2.5/THF	0.65	–	–
PCZ/Copoly1-5/THF	1.5	0.016	0.58
PCZ/Copoly2-05/THF	0.45	–	–
PCZ/Copoly2-1/THF	0.47	0.007	0.59
PCZ/Copoly2-5/THF	0.85	0.017	0.58
PCZ/Copoly1-1/toluene	0.33	0.011	0.59
PCZ/Copoly1-1/ <i>p</i> -dioxane	0.40	0.006	0.60
PCZ/Copoly1-1/pyridine	6.80	–	–

^a Taken average during 1000–10,000 wear cycles.

^b Calculated from Si/C ratio on the worn surface and the curves from Fig. 5.

composition, e.g. the wear rates of the control, which had no copolymer additives, and of the blend film containing 5 wt% of Copolymer1, were relatively high (0.76 and 1.50, respectively), while the films containing 0.5 wt% of Copolymer2 showed the lowest wear rate of 0.45. Casting solvent also influenced the wear rate as well. The result indicates that the blend film cast from toluene solvent had the best wear resistance, but the films cast by pyridine solvent showed the worst wear resistance, probably due to the chemical degradation of the siloxane block by the basic pyridine solvent.

Up to this point, the friction behavior failed to correlate with wear, because wear behavior is not only related to the surface property but also bulk properties [45,46]. The Ratner model was applied for the prediction of wear resistance of the modified PCZ polymers [29]. This suggests that three consecutive stages are involved in the detachment of a particle: deformation by the penetration of an indenting asperity which is opposed by the hardness, H ; relative motion opposed by the frictional force, F , which is proportional to the coefficient of friction μ ; and final detachment involving the work to fracture approximated by the rupture energy, which is often expressed by the product of strength, σ and elongation at break, ε . The wear rate is thus expressed by

$$w \approx \frac{\mu}{H\sigma\varepsilon} \quad (1)$$

where w is wear rate, μ the friction coefficient, H the hardness, σ the tensile strength, ε the elongation at break. For the effect of the first stage, we replaced hardness, H , by $E^{3/4}$ according to the empirical equation [40], which seems to agree well with our qualitative experimental results. For the second stage, we measured Si/C ratio of the blend film after the wear test for prediction of COF, since the COF for the model referred not on the as-cast film surface but on the contacting worn surface. Table 6 depicted the Si/C ratio on the worn surface. The Si/C ratios of all worn surfaces at 90° TOA were less than 0.02, in spite of the minor difference among each sample. That means that the lubricating effect

discussed in previous section may disappear as the wear process proceeds. Based on the curves between the surface Si/C ratio and COF value shown in Fig. 5, the Si/C ratios of the worn surface can be converted to the COF values and they are listed in Table 6. This predicted COF values are all similar to the COF values of PCZ control because the significant COF reduction starts to decrease when the Si/C value reached approximately 0.05. This result indicated that the friction term might only have a negligible influence on the wear properties of this modified PCZ system.

The last term, rupture energy can be obtained from the tensile measurement. Fig. 5(a) shows composition dependence of PCZ containing block copolymer on the tensile properties. As for the films with less than 1 wt% copolymer, Young's modulus, and tensile strength increased with additive composition and decreased significantly with further increasing additive composition. We speculated that this unexpected phenomenon might be explained by an anti-plasticization effect, which is frequently observed in polycarbonates with small amounts of additives [47,48]. Elongation at break gradually increased with copolymer additives. Fig. 6(b) shows the stress–strain curves of four films of the PCZ/Copoly1-1 that were cast, respectively, from solutions of THF, toluene, pyridine and *p*-dioxane. It was markedly found that the greater elongation character of the film cast from the toluene casting solvent, while the film prepared with the pyridine solvent showed poor tensile properties. This solvent effect can be explained by the solvent preference to the siloxane block. That is, in toluene, the siloxane segments remain more extended in the solvent medium during the evaporation process since the toluene solvent has lower polarity (Table 3). This fact is also supported by the higher Si/C ratio of the toluene cast film on the worn surface as seen in Table 6. This solvent effect on mechanical properties has also been noted in other copolymer system [49,50]

Fig. 7 shows a comparison between the experimental wear rate and the predicted value by the modified Ratner model. One may note that a good correlation (correlation

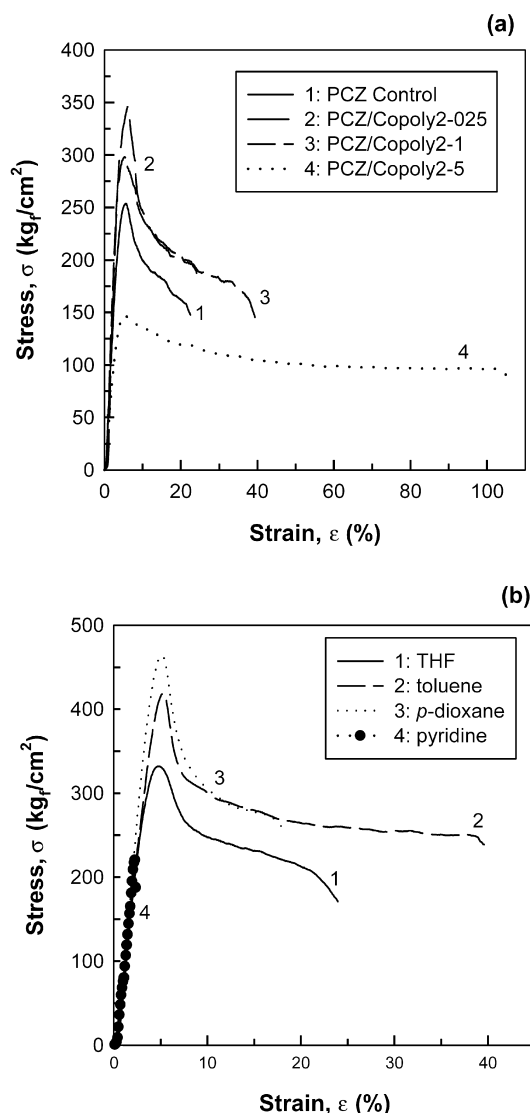


Fig. 6. Tensile stress–strain curves of PCZ containing block copolymer (a) effect of composition (b) effect of casting solvent.

coefficient is 0.994) is achieved with all samples, which has different copolymer composition, copolymer type and casting solvent. Conclusively, this result indicated that the wear resistance of the PDMS/PCZ modified PCZ was not affected by the surface segregation of siloxane, but by the rupture energy and modulus of the blend films. That is to say, the siloxane copolymer additives contributed to improving the wear resistance through increasing rupture energy of the PCZ.

4.5. Morphology

Fig. 8 shows the surface phase image of the PCZ containing block copolymer additive. It must be noted that when light tapping (feedback control amplitude ratio: ~ 0.8) was applied on the polymer surface, the phase-detection image generates uppermost surface morphology, while moderate tapping (feedback control amplitude ratio:

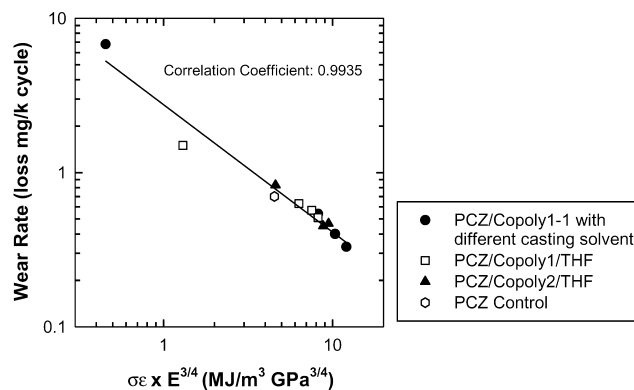


Fig. 7. Relationship between wear rate and modified Ratner model.

~ 0.6) produced near-surface morphology [51]. In our experiments, when light tapping was applied, surface appeared featureless due to the significant enrichment of PDMS segment. However, as the amplitude ratio increased, the phase image gained more contrast because of the larger magnitude of PCZ phase, in agreement with the result of the angle-dependent XPS results.

Under the moderate tapping conditions, all surfaces of the copolymer modified PCZ have a two-phase structure, represented by darker siloxane and brighter PCZ domains. At the same PDMS content, PCZ/Copoly2 sample had more phase contrast than that of PCZ/Copoly1 and the phase contrast increased with surface copolymer composition, while the domain size of darker siloxane-rich phase had no significant difference. Based on this fact and the XPS result, the higher phase contrast is caused by the more PDMS segment enrichment on the sample surface.

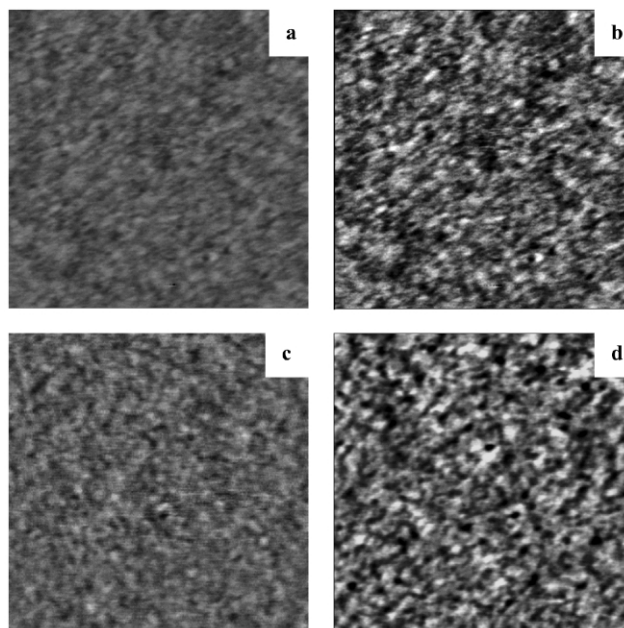


Fig. 8. TM-AFM surface morphology of PCZ containing block copolymers (a) PCZ/Copoly1-1/THF (b) PCZ/Copoly1-5/THF (c) PCZ/Copoly2-1/THF (d) PCZ/Copoly2-5/THF; All images are phase image with $500 \times 500 \text{ nm}^2$ scan area and phase angle of $0-10^\circ$.

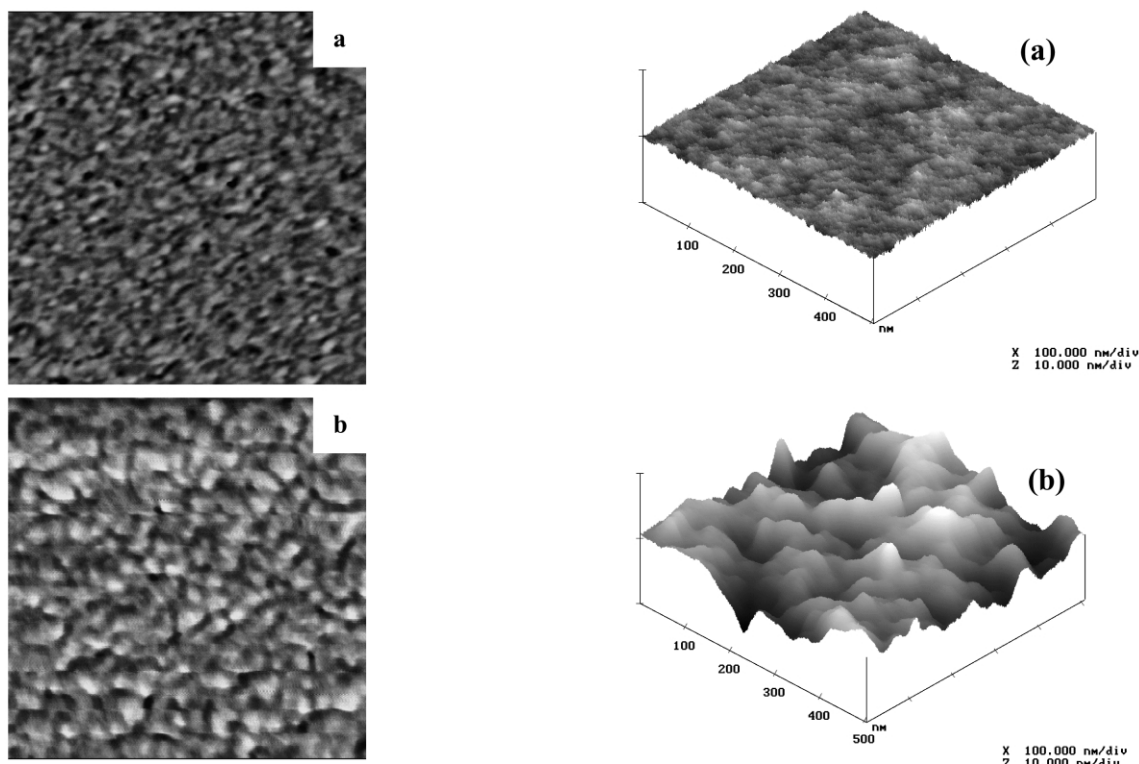


Fig. 9. TM-AFM cross-sectional morphology of the PCZ/Copoly1-1, casting solvent: (a) toluene (b) *p*-dioxane; All images are phase images with $500 \times 500 \text{ nm}^2$ scan area and phase angle of $0-10^\circ$.

Fig. 9 shows the cross-sectional morphology of the PCZ/Copoly1-1 obtained from *p*-dioxane and toluene casting solvents. Data illustrated by the images show that the cross-sectional morphology is also heterogeneous. Moreover, the domain size variations appeared among the samples by using different casting solvents. The film from toluene casting solvent had much smaller phase-separated domains on both the surface and cross-sectional morphologies than the sample cast from dioxane. Other systems such as THF, and pyridine showed similar domain size to the film from *p*-dioxane solvent, although some differences in phase contrast depending on surface Si/C ratio. This observation indicated that copolymer additive had greater phase mixing with PCZ when toluene was used. The higher mechanical strength and wear resistance of the film cast from toluene is probably due to this better compatibility between the PCZ and block copolymer, provided from the toluene casting solvent.

Fig. 10 shows the change in surface morphology of PCZ/Copoly2-1 sample as wear proceeded. Before the wear process, the height image showed a relatively smooth surface (root mean square roughness, RMS: 0.25 nm), while the surface after wear test exhibited a fairly rough (RMS: 1.7 nm). The phase image of the surface after wear clearly shows that the phase contrast and its size are much larger than those of the as-cast film (compare Figs. 8(c) and 10(c)). Furthermore, the dark phase structure has higher aspect ratio with wear track direction indicated by white arrow in the

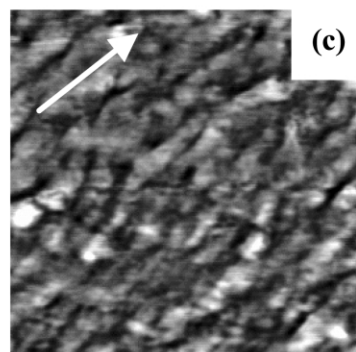


Fig. 10. TM-AFM surface topography of the PCZ/Copoly1-2/THF: (a) before wear; (b) after wear; (c) phase image after wear. All images are phase images with $500 \times 500 \text{ nm}^2$ scan area and phase angle of $0-10^\circ$.

frame. These results indicate that this domain structure is not caused by PDMS domain structure but by the abrasive microcutting procedure, supporting the assumption for the Ratner model described above.

5. Conclusions

PCZ–PDMS block copolymers were successfully synthesized in high molecular weight, tough, ductile, film forming compositions by reacting hydroxyl-terminated PCZ and dimethylamino-terminated PDMS oligomers and used as a modifier for the PCZ homopolymer. The modified PCZ systems showed surface enrichment of siloxane component. The surface Si/C ratio by the XPS experiment increased

with increasing copolymer composition, and siloxane block length. Accordingly, COF was significantly reduced with an increase in the surface Si/C ratio. Casting solvent changed the surface Si/C ratio and COF values, depending on the copolymer–solvent interaction and evaporation rate. Wear resistance of the modified PCZ was increased and then deteriorated as a function of the block copolymer composition. The optimum composition for wear resistance was found to be about 0.5 wt% PDMS. Toluene casting solvent was proved to be superior to other solvents in terms of producing film with excellent wear resistance. The wear rate was successfully predicted by a modified Ratner model, which shows that the rupture energy and modulus of the film play a key role in the wear rate. The morphology of the modified PCZ films showed a two-phase structure, of which contrast increased with siloxane composition. Samples cast from toluene solvent showed a relatively fine domain structure than those cast from other casting solvent, which confirmed the better phase mixing, which appears to result in the higher wear resistance.

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References

- [1] Noshay A, McGrath JE. Block copolymers: overview and critical survey. New York: Academic Press; 1977.
- [2] McGrath JE, Dunson DL, Meham SJ, Hedrick JL. *Adv Polym Sci* 1999;141:61.
- [3] Vaughn HA. *J Polym Sci, Part B* 1969;7:569.
- [4] Tang SH, Meinecke EA, Riffle JS, McGrath JE. *Rubber Chem Technol* 1980;53:1160.
- [5] Tang SH, Meinecke EA, Riffle JS, McGrath JE. *Rubber Chem Technol* 1984;57:184.
- [6] Buechner W, Noll W, Bressel B. *German Offen.* 2,162,418; 1973.
- [7] Thom KF, Maass G, Bech M. *German Offen.* 2,555,746; 1977.
- [8] Summers JD, Elsbernd CS, Sormani PM, Brandt PJA, Arnold CA, Yilgor I, Riffle JS, Kilic S, McGrath JE. Recent advances in organosiloxane copolymers. In: Zeldin M, Wynne K, editors. *Inorganic and organometallic polymers*. ACS Symposium Series No. 360. Washington, DC: ACS; 1988. Chapter 14.
- [9] Van Aert H, Nelissen L, Lemstra PJ, Brunell DJ. *Polymer* 2001;42:1781.
- [10] Dwight DW, McGrath JE, Lawson G, Patel N, York GA. Surface and bulk microphase separation in siloxane-containing block copolymers and their blends: the roles of composition and kinetics. In: Culbertson BM, editor. *Multiphase macromolecular systems*. New York: Plenum Publishing Corporation; 1989. p. 265.
- [11] Patel NM, Dwight DW, Hedrick JL, Webster DC, McGrath JE. *Macromolecules* 1988;21:2689.
- [12] Yilgor I, McGrath JE. *Adv Polym Sci* 1988;86:1.
- [13] Chen X, Gardella Jr. JA. *Macromolecules* 1994;27:3363.
- [14] Zhuang H, Gardella Jr. JA. *Macromolecules* 1997;30:3632.
- [15] Chen J, Gardella Jr. JA. *Macromolecules* 1998;31:9328.
- [16] Smith SD, DeSimone JM, Huang H, York G, Dwight DW, Wilkes GL, McGrath JE. *Macromolecules* 1992;25:2575.
- [17] Karal O, Hamurcu EE, Baysal BM. *Polymer* 1997;38:6071.
- [18] Viswanathan R, Tian J, Marr DWM. *Langmuir* 1997;13:1840.
- [19] Ward TC, Sheehy DP, Riffle JS, McGrath JE. *Macromolecules* 1981;14:1791.
- [20] Chen X, Gardella Jr. JA, Cohen RE. *Macromolecules* 1994;27:2206.
- [21] Wang L, Ji Q, Glass T, Muggli M, Ward TC, McGrath JE, Burns G, Sorathia U. *Polymer* 2000;41:5083.
- [22] Yorkgitis E, Tran C, Eiss Jr. NS, Wilkes GL, McGrath JE. *Adv Chem* 1984;208:137.
- [23] Yorkgitis E, Tran C, Eiss Jr. NS, Wilkes GL, McGrath JE. *Adv Polym Sci* 1985;72:79.
- [24] Eiss Jr. NS, Czichos H. *Wear* 1986;111:347.
- [25] Dieng AC, Lavielle L, Reiss G. *New Polym Mater* 1996;5:13.
- [26] Legrand DG, Bendler JT, editors. *Handbook of polycarbonate science and technology*. New York: Marcel Dekker; 2000.
- [27] Lancaster JK. *Wear* 1990;141:159.
- [28] Harron HR, Pritchard RG, Cope BC, Goddard DT. *J Polym Sci, Polym Phys* 1996;34:173.
- [29] Ratner RB. *Sov Plast* 1964;37.
- [30] Riffle JS, Shchori E, Banthia AK, Freelin RG, Ward TC, McGrath JE. *J Polym Sci, Polym Chem Ed* 1982;20:2289.
- [31] Odian G. *Principles of polymerization*, 2nd ed. New York: Wiley/Interscience; 1981. p. 113.
- [32] Matzner M, Noshay A, Robeson LM, Merriam CN, Barclay Jr. R, McGrath JE. *Appl Polym Symp* 1973;22:143.
- [33] Noshay A, Matzner M, Williams TC. *Ind Engng Chem Proc Res Dev* 1973;12(4):286.
- [34] Brandt PJA, Elsbernd CLS, Patel N, York G, McGrath JE. *Polymer* 1990;31:179.
- [35] Senshu K, Furuzono T, Koshizaki N, Yamashita S, Matsumoto T, Kishida A, Akashi M. *Macromolecules* 1997;30:4421.
- [36] Inoue H, Matsumoto A, Matsukawa K, Ueda A, Nagai S. *J Appl Polym Sci* 1990;41:1815.
- [37] Hansen CM. *J Paint Technol* 1967;39:505.
- [38] Pendyala VNS, Xavier SF. *Polymer* 1997;38:3565.
- [39] Bagley EB, Nelson TP, Scigliano JM. *J Paint Technol* 1971;43:35.
- [40] Van Krevelen DW. *Properties of polymers*, 3rd ed. Amsterdam: Elsevier; 1990.
- [41] Unpublished data. For example, the solubility parameter of Copolymer 1: By Barton's Method: 20.0 MPa^{1/2}; by Bagley's method 19.7 MPa^{1/2}.
- [42] Riddick JA, Bunger WB, Sakano TK. *Organic solvents, physical properties and methods of purification: techniques of chemistry*, vol. 2. New York: Wiley; 1986.
- [43] Klein J, Dumacheva Y, Yoshizawa H, Israelachvili JN, Fredrickson GH, Pincus P, Fetters LJ. *Macromolecules* 1993;26:5552.
- [44] Ndoni S, Jannasch P, Larsen NB, Almdal K. *Langmuir* 1999;3859:15.
- [45] Hill DJT, Killeen MI, O'Donnell JH, Pomery PJ, John DS, Whittaker AK. *J Appl Polym Sci* 1996;61:1757.
- [46] Yim CI, Lee KJ, Jho JY, Choi K. *Polym Bull* 1999;42:433.
- [47] Ngai KL, Rendell RW, Yee AF, Plazek DJ. *Macromolecules* 1991;24:61.
- [48] Pesetskii SS, Jurkowski B, Koyal VN. *J Appl Polym Sci* 2000;78:858.
- [49] Kambour RP. In: Aggarwal SL, editor. *Block polymers*. New York: Plenum Press; 1971. p. 263.
- [50] Okumura J, Yamaguchi K. *Kobunshi Ronbunshu* 1994;51:605.
- [51] Bar G, Thomann Y, Brandsch R, Cantow HJ, Whangbo MH. *Langmuir* 1997;13:3807.