Formation of Polyurethane Film Containing Silicone Polymer with Silanol Residue

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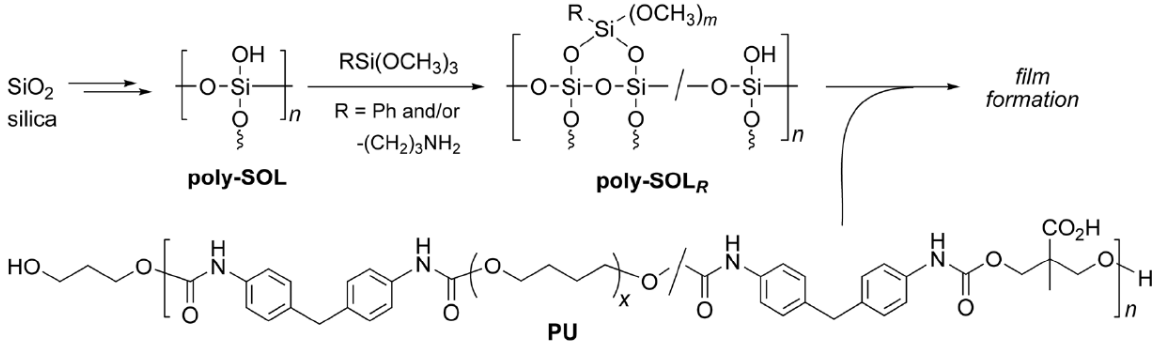
Abstract: The silicone polymers containing a silanol residue were synthesized from silica gel, while the polyurethanes (PUs) bearing a carboxyl moiety were prepared using 2,2-bis(hydroxymethyl)propionic acid (BHMPA) as one of the diol components. The fabrication of the PU films was carried out using these two polymers, then the tensile and thermal properties were investigated. Both the amounts of the carboxyl side groups of the PU chain and the residual silanol of the silicone polymer significantly affected the mechanical property of the film, in addition, the incorporation of 3-aminopropyltrimethoxysilane (APTMS) was quite effective for enhancing the elastic modulus (*E*). As a result, the film prepared from the polyurethane containing the BHMPA unit with a combination of APTMS and the silicone polymer, having a proper amount of silanol groups, showed the highest effect (E = 5.36 N/mm^2), while that observed for the film prepared without using BHMPA and a silicone polymer was 2.10 N/mm^2. An acid-base interaction between the carboxyl moiety of the PU and amino group of APTMS occurred, while the formation of the siloxane linkage through the silylation reaction between the trimethoxysilyl group of APTMS and silanol also took place.

Keywords: Silicone polymer, silanol, polyurethane, film, elastic modulus.

INTRODUCTION

The silicone polymer, whose main chain consists of a siloxane Si–O–Si linkage, is considered to be one of the high-performance polymers with a wide range of applications, for instance, as organic-inorganic hybrid materials. Among the present synthetic methods, it can be prepared from water glass and silica gel (SiO_2), etc., by way of silicic acid [1-5]. For example, we reported that the silica gel with a fibrous morphology, derived from chrysotile asbestos by acid-leaching, was effectively transformed into polysiloxanes by processes involving the reaction with various silylation reagents during the course of our study about the disposal and utilization of hazardous chrysotile asbestos as a nontoxic and valuable material [4,5].

Some characteristics of this method are as follows: an intermediate, silicic acid (poly-SOL, Scheme **1**), has reactive silanols (-SiOH) as a side group, and various functional groups can be introduced by the reaction of silanols with silylation reagents, such as the trialkylchlorosilanes (R_3SiCl) and trialkoxysilanes [$RSi(OR')_3$]. Therefore, the structure of the produced polymers are quite different from the silsesquioxanes with the empirical formulas of $RSiO_{3/2}$ [6,7], as well as the typical silicone polymer, poly(dialkylsiloxane).



Scheme 1: Film formation from PU and silicone polymer.

On the other hand, polyurethanes (PUs) are another important class of materials extensively utilized in a variety of applications, such as in high-performance coatings, fibers, foams, and elastomers. Especially, we can find them in biomedical devices, such as artificial heart valves, blood pumps, catheters, and pacemaker insulation due to their good physical and biocompatible properties [8-10]. However, the PU is sometimes susceptible to the *in vivo* environment causing degradation and cracking, mainly based on hydrolysis,

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therefore, improvement of the bio- and physical stabilities of the PU is required. The silicone polymers were often employed for this purpose [11-13].

It is known that the inter-hydrogen bonding between the urethane groups (-OCONH-) of the PUs, as well as the micro-phase structure of the hard and soft segments, significantly affects the macroscopic properties. For example, we recently reported the incorporation of one of the engineering plastics, poly(2,6-dimethyl-1,4-phenylene oxide), with functional groups, which interact with the urethane groups of the PU chains to control the properties of the PU film and overcome the previously mentioned problems to some extent [14]. The formation of hydrogen bonds between the silanol residue and amide groups (-CONRR') of the organic polymers, such as poly(2-methyl-2-oxazoline), poly(vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide), plays an important role during the preparation of silica hybrid nanocomposites by the sol-gel method to produce monolithic materials [15-18]. Therefore, the silicone polymer with a silanol residue may be a good candidate as an additive for the fabrication of PU films, however, there is no report on it to the best of our knowledge. In addition, the obtained materials should be suitable for biomedical use, because both the PUs and silicone polymers have biocompatible properties.

In this study, the silicone polymers containing silanol groups were synthesized from silica gel and incorporated into the PU to form films, whose mechanical properties were investigated (Scheme **1**). As the silylation reagents for the silicone polymer synthesis, trimethoxyphenylsilane (TMPhS) and 3-aminopropyltrimethoxysilane (APTMS) introducing phenylsilyl- and 3-aminopropylsilyl groups as side chains of the silicone polymer, respectively, were used, whereas methylenediphenyl 4,4'-diisocyanate (MDI), poly(tetramethylene oxide) (PTMO), 1,4-butanediol (BDOL), and 2,2-bis(hydroxymethyl)propionic acid (BHMPA) were employed as the starting materials to give a PU bearing a carboxyl function as a side group. In addition to the hydrogen bond formation between the silanol residue and urethane moiety, the acid-base interaction between the amino and carboxyl groups should cooperatively contribute to enhance the properties of the PU film.

EXPERIMENTAL

Measurments

The ^{1}H NMR spectra were recorded by a Jeol JNM-ECS400 (400 MHz for ^{1}H) spectrometer (Jeol, Jpn). The size exclusion chromatographic (SEC) analyses were performed using a Jasco PU-2080 Plus system equipped with a UV (Jasco UV-2075 Plus) detector (Jasco, Jpn) and TSKgel G7000H and G3000H columns for tetrahydrofuran (THF) connected in series (Tosoh, Jpn). Calibration was carried out using polystyrene standards. The scanning electron micrographs (SEM) were taken by a Jeol JSM-6510LA instrument. The thermogravimetric (TG) analyses were conducted using a Rigaku Thermo-plus EVO2 instrument (heating rate: 10 ^{o}C/min, under air) (Rigaku, Jpn). Tensile tests were performed using a Shimadzu EZ-L(500N) instrument with dumbbell-shaped test pieces (film width = 5 mm, stress rate = 300 mm/min, 25 °C, number of samples $N \geq 3$) (Shimadzu, Jpn).

Materials

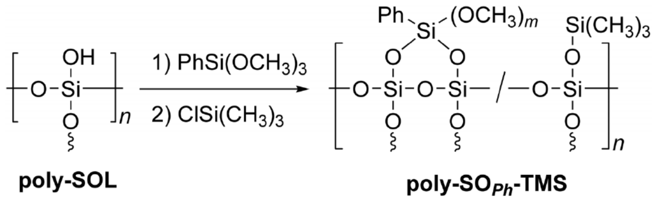
The silica gel [spherical (particle size: 63-210 μm), neutral] (Kanto, Jpn) and silylation reagents, such as TMPhS (TCI, Jpn), APTMS (Wako, Jpn), chlorotrimethylsilane (TMSCl, TCI) were used as received. PTMO 650 (molecular weight = 600-710) (Wako), MDI (Wako), BDOL (Kanto), BHMPA (TCI), and a solvent, dehydrated THF (Kanto), were used for the PU synthesis [14].

Preparation of Silicone Polymer Solution in THF [4,5]

A mixture of the silica (3.0 g) and aqueous NaOH (0.4 mol/L, 60 mL) was stirred at 0 ^{o}C for 3 h. HCl (2 mol/L, 60 mL) was then added with stirring, followed by the addition of THF (180 mL) and NaCl (36 g). The organic layer was separated and dried over $MgSO_4$, then the pale yellowish THF solution was concentrated by evaporation to a total volume of 30 mL (poly-SOL/THF).

The appropriate amount of TMPhS was added to the prepared poly-SOL/THF (5.0 mL, 1.6 mol/L converted into the used SiO_2) at room temperature. After stirring for 2 h, the obtained THF solution of the silicone polymer was directly used for the PU film formation (poly-SOL$_{Ph}$/THF, Scheme **1**).

Isolation of the prepared silicone polymers was carried out after the reaction of the residual silanol with TMSCl (0.5 mL), which was added to the THF solution of poly-SOL$_{Ph}$ and the stirring was further continued for 4 h (Scheme **2**). The products (poly-SO$_{Ph}$-TMS) were isolated as the methanol-water [4/1 (v/v)]-insoluble fraction by centrifugation and drying under reduced pressure at 60 ^{o}C.



Scheme 2: Synthesis of poly-SO$_{Ph}$-TMS.

PU Film Formation [14]

A mixture of PTMO (22 g), MDI (17 g), and dehydrated THF (60 mL) was stirred at 70 °C for 2 h under a N_2 atmosphere with cooling by a reflux condenser. A THF solution of BDOL and BHMPA was introduced ([PTMO]/[MDI]/[BDOL + BHMPA] = 10/20/10) and the stirring was continued at 70 °C for 6 h. During the reaction, THF was occasionally added until the total amount of THF was 270 mL (Scheme **2**). The obtained THF solution of PU (13.5 wt%) was directly used for the PU film formation.

A part of the obtained PU solution was poured into MeOH, and the insoluble fraction was recovered by centrifugation and drying under reduced pressure at 60 ^{o}C to determine the molecular weight.

Film formation was carried out using a mixture of the above-described THF solution of PU (3.5 g), a solution of silicone polymer (0.1 mL, ca 2wt% converted to the used silica) in THF, and APTMS (0.01 mL) using a PFA Petri dish (50 mmϕ). The films were initially prepared by drying at 45 °C for 12 h, then the obtained films were further dried at 60 °C for 3 h and 80 °C for 3 h under vacuum.

RESULTS AND DISCUSSION

Due to the gel formation by a condensation reaction of silanols, the silicone polymers with the silanol residue, poly-SOL$_{Ph}$, as well as poly-SOL, cannot be isolated. To evaluate the details of the polymer structure used for the PU film synthesis, a further silylation reaction of poly-SOL$_{Ph}$ with TMSCl was carried out to obtain a polymer, poly-SO$_{Ph}$-TMS, in which the content of the trimethylsilyl (-SiMe$_3$, TMS) group should correspond to that of the silanol groups in the original one (poly-SOL$_{Ph}$) (Scheme **2**). These results are summarized in Table **1**.

For example, 0.34 g of the polymer was isolated from the reaction of poly-SOL$_{Ph(0.2)}$ prepared with 0.2 equiv. of TMPhS to the used SiO_2 (run 1). Here, in the parentheses denoting the abbreviation for the silicone polymer, an equivalent value of the used TMPhS is specified. The unit ratio was estimated to be Ph/ MeO/ TMS = 44/ <1/ 56 by ^{1}H NMR analysis, as shown in Figure **1** with the peak assignments. Accordingly, the original poly-SOL$_{Ph(0.2)}$ was expected to contain 56% of the silanol residue. The yield and unit ratio of the phenyl group increased with the increasing amount of the TMPhS used, while the amount of the introduced TMS groups decreased. The methoxy group was hardly observed in the obtained polymers, indicating that the condensation between the silanol and methoxysilyl groups of TMPhS effectively occurred. When 0.8 equiv. of TMPhS was used, the condensation to form a cross-linking should take place and the produced polymer showed higher molecular weight and distribution values (run 4).

Table **2** shows the feed ratio of the diols for the PU preparation and the molecular weight values of the MeOH-insoluble fraction of the obtained polymers. The ratio of the diisocyanate, MDI, and the diol, PTMO, was fixed at 20/ 10 in every case, while the ratio of the other diols, BDOL and BHMPA, changed from 10/0 to 7/3. They are shown in the parentheses of the abbreviations, such as PU$_{(10/0)}$ and PU$_{(7/3)}$. The THF solutions of PU with and without carboxyl side groups were thus prepared.

Table 1: Synthesis of Poly-SO$_{Ph}$-TMS from THF Solution of Poly-SOL$_{Ph}$

run	poly-SOL$_{Ph}$		poly-SO$_{Ph}$-TMS			
	TMPhS (equiv.)	abbreviation	yield^{a} (g)	unit ratio^{b} (Ph / MeO / TMS)	M_w^{c} (x 10^3)	M_w/M_n^{c}
1	0.2	poly-SOL$_{Ph(0.2)}$	0.34	44 / <1 / 56	4.6	3.8
2	0.4	poly-SOL$_{Ph(0.4)}$	0.49	52 / <1 / 48	4.5	2.3
3	0.6	poly-SOL$_{Ph(0.6)}$	0.82	58 / 1 / 41	3.8	1.7
4	0.8	poly-SOL$_{Ph(0.8)}$	1.12	64 / 1 / 35	18.1	5.0

Conditions: SiO_2 = 0.50 g, THF = 5 mL, TMSCl = 0.5 mL.
[a] MeOH/H_2O (4/1)-insoluble part.
[b] Determined by ^{1}H NMR analysis ($CDCl_3$).
[c] Determined by SEC (THF, polystyrene standard).

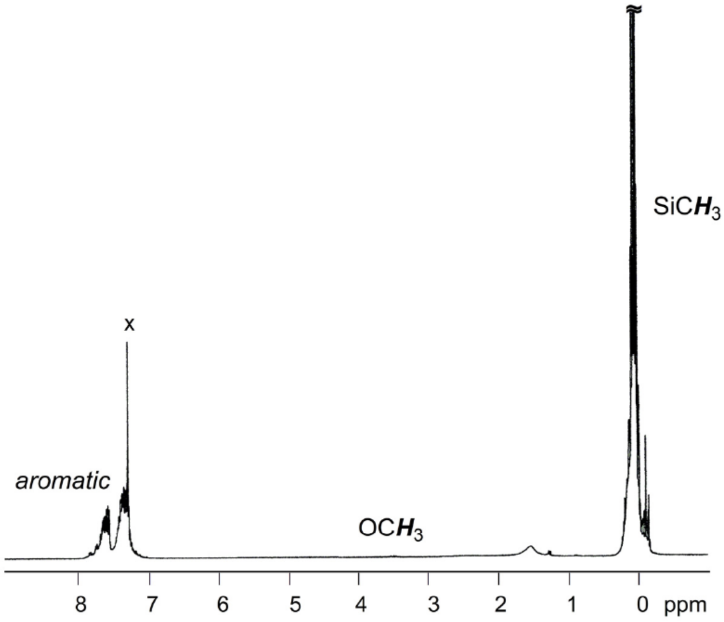


Figure 1: ^{1}H NMR spectrum of poly-SOL$_{Ph(0.2)}$-TMS (Table **1**, run 1) ($CDCl_3$, 55 °C).

Table 2: Preparation of PU

PU (abbreviation)	Feed ratio of diols			M_w[a] (x 10^4)	M_w/M_n[a]
	PTMO	BDOL	BHMPA		
PU$_{(10/0)}$	10	10	0	4.6	1.7
PU$_{(9/1)}$	10	9	1	3.2	1.8
PU$_{(8/2)}$	10	8	2	3.8	2.4
PU$_{(7/3)}$	10	7	3	2.6	1.9

Conditions: MDI/diols = 20/20, solvent = THF, temp. = 70 °C, time = 8 h.
[a] MeOH-insoluble part, determined by SEC (THF, polystyrene standard).

During the synthesis of the silicone polymer with APTMS as the silylation reagent, a THF-insoluble polymer was immediately generated, then APTMS was added to a mixture of PU and the silicone polymer in THF just before film formation. The average thickness of the prepared films was approximately 170 μm. They were clear, while films containing the silicone polymers appeared slightly pale yellow (Figure **2**). Figure **2** also shows the SEM images of the films obtained using PU$_{(7/3)}$ without and with the incorporation of poly-SOL$_{Ph(0.6)}$ and APTMS. Both films demonstrate a flat and homogeneous surface morphology, indicating that fabrication of the film successfully occurred.

Figure **3** shows typical stress curves, and the mechanical properties observed for the films prepared with various combinations of the PU and silicone polymer in the absence or presence of APTMS are summarized in Figures **4** and **5**.

The observed elastic modulus for the films, which were prepared without using a silicone polymer, showed an obvious tendency to increase with the increasing BHMPA unit in the PU (white bars in the graphs). For example, the PU$_{(7/3)}$ film showed an elastic modulus of 3.50 N/mm^2, which is much higher than that of the film of PU$_{(10/0)}$ of 2.10 N/mm^2. When the poly-SOL and poly-SOL$_{Ph}$ containing silanol groups were used as an additive for PU$_{(10/0)}$, the elastic modulus of the resulting films was reduced in comparison to that observed for the film prepared without an additive. In contrast, the incorporation of silicone polymer into the films prepared with PUs containing BHMPA unit is effective for increasing the value of elastic modulus. For instance, the film formed by PU$_{(7/3)}$ and poly-SOL$_{Ph(0.6)}$ showed a value of 4.09 N/mm^2 (Figure **4a**). Therefore, both the carboxyl group in the introduced BHMPA unit into the PU chain and the residual silanol in the silicone polymer significantly affected the mechanical property of the PU film.

The incorporation of APTMS into the PU film is always effective for enhancing the elastic modulus, whose values again showed a clear tendency to

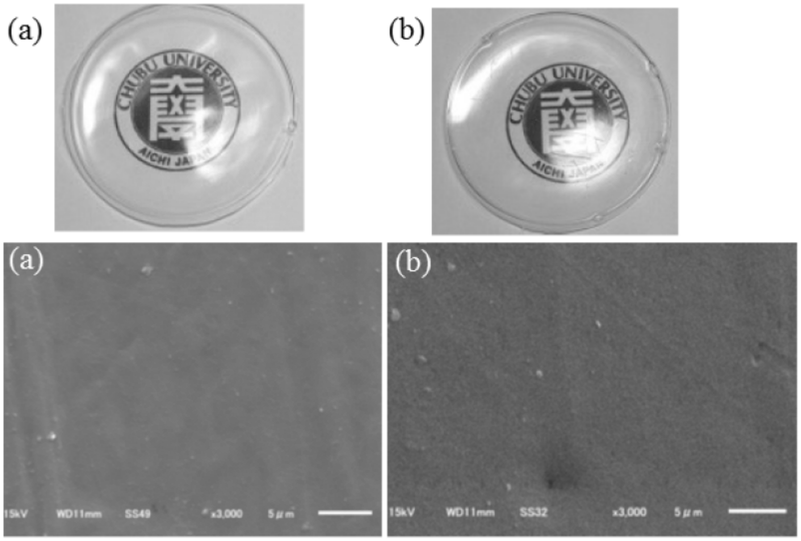


Figure 2: Photo and SEM images of the films prepared from $PU_{(7/3)}$ (**a**) without and (**b**) with the incorporation of poly-$SOL_{Ph(0.6)}$ and APTMS (white bar indicates 5 μm).

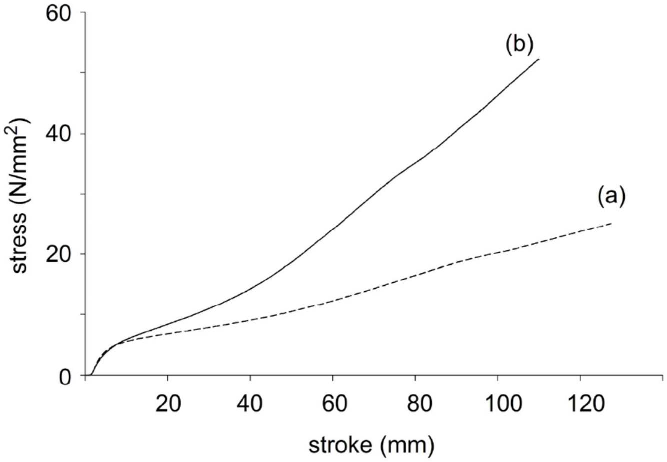


Figure 3: Stress versus stroke curves of the films prepared from $PU_{(7/3)}$ (a) without and (b) with the incorporation of poly-$SOL_{Ph(0.6)}$ and APTMS.

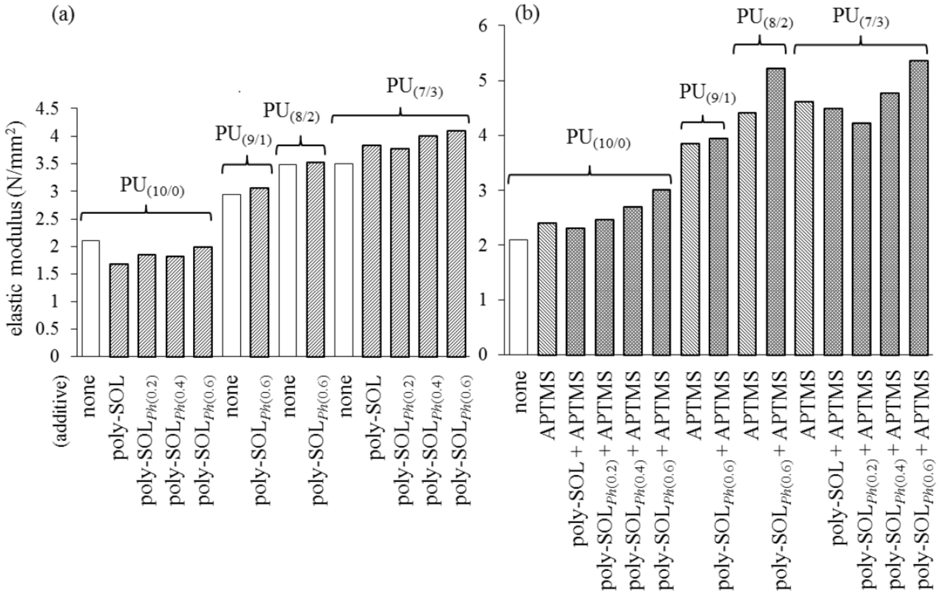


Figure 4: Observed elastic modulus values for the films prepared (**a**) without and (**b**) with the incorporation of APTMS.

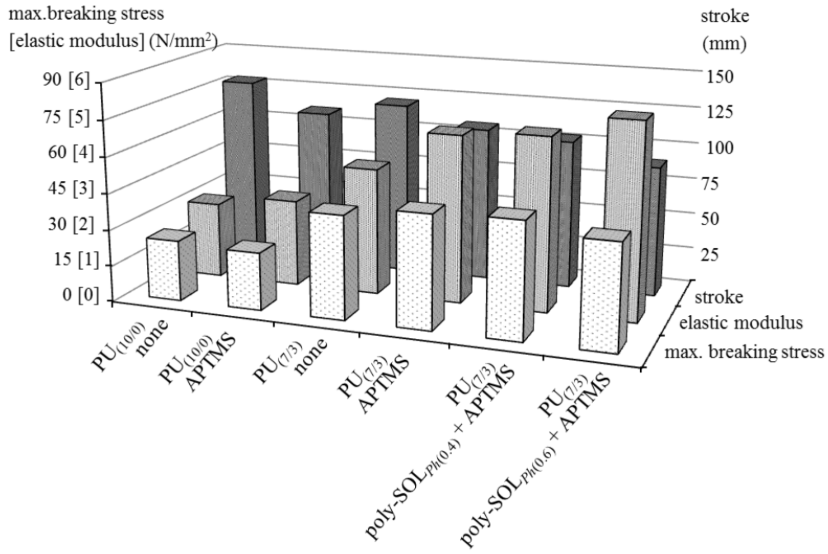
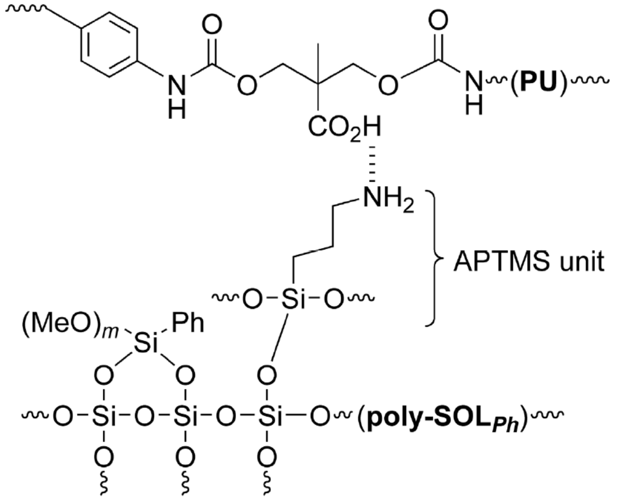


Figure 5: Observed mechanical properties (maximum breaking stress, elastic modulus, and breaking point) for the selected films.

increase with an increase in the BHMPA unit (Figure **4b**). Especially, the combination with poly-SOL$_{Ph(0.6)}$ showed a significant effect to provide films with the elastic modulus of 5.22 and 5.36 N/mm^2, when PU$_{(8/2)}$ and PU$_{(7/3)}$ were used respectively. In these films, in addition to the above mentioned interactions based on the carboxyl group and the residual silanol, an acid-base interaction between the carboxyl moiety of the PU and amino group of APTMS could occur and contribute to the film property, while the formation of the siloxane linkage through the silylation reaction between the trimethoxysilyl group of APTMS and silanol could also take place (Scheme **3**).



Scheme 3: Plausible structure of the film prepared from the PU containing BHMPA unit, poly-SOL$_{Ph}$, and APTMS.

The thermal stability of the films prepared from PU$_{(7/3)}$ without and with poly-SOL$_{Ph(0.6)}$ + APTMS as additives was measured by TG and the traces are depicted in Figure **6**. The 5 and 10% weight-loss temperatures were estimated to be 274 and 290 °C for the former and 281 and 300 °C for the latter, respectively. The increase in the thermal stability was also observed for the film containing the silicone polymer.

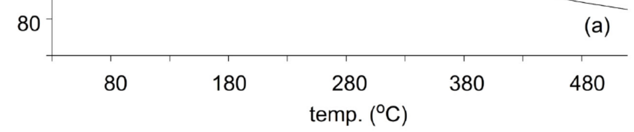


Figure 6: TG traces of the films prepared from PU$_{(7/3)}$ (a) without and (b) with the incorporation of poly-SOL$_{Ph(0.6)}$ and APTMS.

CONCLUSIONS

The polyurethane films containing a silicone polymer with a silanol residue were fabricated and their tensile and thermal properties were investigated. Both the carboxyl side groups of the PU chain and the residual silanol of the silicone polymer significantly affected the mechanical property of the film, and the incorporation of APTMS was also quite effective for enhancing the elastic modulus. As a result, the film prepared from the polyurethane containing the BHMPA unit with a combination of APTMS and poly-SOL$_{Ph}$, having a proper amount of silanol groups, showed the highest effect. The properties of the polyurethane film could be controlled by the design of the structures of the matrix polyurethane and the silicone polymer additive.

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