

論文要約

Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) derivatives containing hydroxyl and amino groups by oxidative coupling copolymerization
酸化カップリング共重合によるヒドロキシ基やアミノ基を含む
ポリ(2,6-ジメチル-1,4 フェニレンオキシド)誘導体の合成
React. Funct. Polym., **89**, 49-53 (2014).

優れた熱、機械、電気特性を持つエンジニアリングプラスチックとして知られるポリフェニレンオキシド(PPO)への簡便な官能基導入を目的として、2,6-ジメチルフェノール(DMP)とヒドロキシ基やアミノ基を含む DMP 誘導体との酸化カップリング共重合を行った。
この重合系は溶媒の影響が大きく、特にメタノール混合溶媒などの極性溶媒を用いることで共重合ポリマーを非常に効率よく得ることが出来た。
得られた共重合ポリマーのヒドロキシ基やアミノ基をエステル基やウレタン基へと誘導し、ポリウレタンフィルムへ加えると、引張特性においてポリウレタンのみ、あるいは PPO を加えたものと比較して大幅に改善された。

Oxidative Coupling Copolymerization of
2,6-Dimethylphenol and Dihydroxynaphthalene Affording
Poly(phenylene oxide) Derivatives
ポリ(フェニレンオキシド)誘導体合成のための 2,6-ジメチルフェノールと
ジヒドロキシナフタレンとの酸化カップリング共重合
J of Polym., **2015**, Article ID 478729.

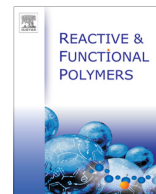
ポリフェニレンオキシド(PPO)への簡便な官能基導入を目的として、2,6-ジメチルフェノール(DMP)と 2,3-あるいは 2,6-ジヒドロキシナフタレン(DHN)との酸化カップリング共重合を行った。
この重合系は DHN の構造により大きく共重合性が変化し、DMP と 2,6-DHN との組み合わせは最も良い共重合性を示すことがわかった。
得られた共重合ポリマーは DHN 部位のヒドロキシ基をエステル基やウレタン基へと誘導することで、PPO と全く異なる溶解性を示すことが明らかになった。

Effective Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)
Derivatives by Oxidative Coupling Copolymerization of
Alkoxyphenols with Copper(II) Catalyst
銅(II)触媒下でのアルコキシフェノールとの酸化カップリング共重合による
ポリ(2,6-ジメチル-1,4 フェニレンオキシド)誘導体の効率的な合成
J Adv Cat Sci Technol., **4**, 1-7 (2017).

新規な PPO 誘導体の合成を目的に、2,6-ジメチルフェノールと種々のアルコキシ基を持つフェノール類との酸化カップリング共重合を行った。
この共重合においてアルコキシフェノール類は効果的に進行し、ポリマー中のユニット比は仕込み比に応じたものとなった。また、共重合におけるアルコキシフェノール類のカップリング位置選択性についても ¹H NMR にて解析を行った。
得られた共重合ポリマーは PPO と比較し、溶解性や熱特性などが大幅に変化した。

Formation of Polyurethane Film Containing Silicone Polymer with
Silanol Residue
シラノール残基を有するシリコンポリマーを含んだ
ポリウレタンフィルムの作成
Int J Biotec for Wellness Ind., **6**, 48-54 (2017)

シリカゲルからシラノール残基を有したシリコンポリマーを合成し、ジオール部位にカルボキシル基を含んだ 2,2-ビス(ヒドロキシメチル)プロピオン酸(BHMPA)を用いて合成したポリウレタン(PU)にシリコンポリマーを導入したフィルムを作成し、引張特性などについて調べた。
PU 鎖中のカルボキシル基の量およびシリコンポリマー中のシラノール残基の量はフィルムの機械的特性に大きく影響し、さらにシラノール残基を 3-アミノプロピルトリメトキシシラン (APTMS) で修飾することによって、より弾性率を向上させることが明らかになった。
これらの結果はシリコンポリマーと PU との分子間で働く様々な力によって引き起こされたものと考察される。



Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) derivatives containing hydroxyl and amino groups by oxidative coupling copolymerization



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ABSTRACT

Oxidative coupling copolymerization between 2,6-dimethylphenol (DMP) and functional monomers containing hydroxyl and amino groups, 2-hydroxymethyl-6-methylphenol and 2-(4-methylphenylamino)methyl-6-methylphenol, was carried out with a Cu catalyst under an O₂ atmosphere. The polymerization was significantly affected by the polymerization solvent used, and the copolymers were effectively obtained by polymerization in polar solvents, such as a mixed solvent system containing methanol. The obtained copolymer containing hydroxyl groups was further transformed into polymers containing ester and urethane groups, which were used as additives for the fabrication of polyurethane films. The tensile properties of the films containing the obtained copolymers were significantly improved compared to those of films prepared without an additive, as well as films containing the homo-polymer of DMP.

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1. Introduction

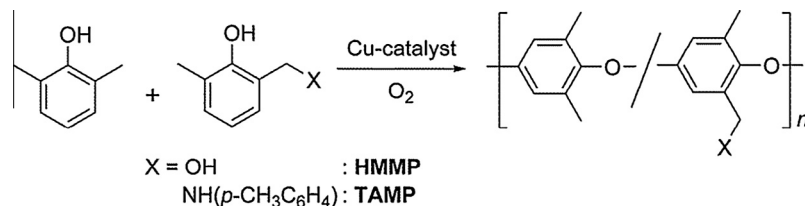
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is one of the most commonly used engineering plastics due its good thermal and electrical characteristics. In addition, the method used to synthesize PPO, oxidative coupling polymerization (OCP), is known to be environmentally friendly because the reaction proceeds under mild conditions in an oxygen atmosphere, producing only water as the by-product. Moreover, OCP mediates a radical coupling process involving highly active phenoxy radicals, which are very difficult to control. Therefore, few types of phenolic monomers, such as 2,6-dimethylphenol (DMP), have been used in practice, and the copolymerization leading to PPO derivatives is also restricted to some extent [1–3]. Although a typical strategy for the functionalization of PPO is the use of polymer reactions, such as the bromination of methyl side groups and further transformations of bromo-substituted polymers [3–8], there are few reports on the copolymerization of DMP derivatives, with the exception of 2-allyl-6-methylphenol, in which the limitation of the monomer source may also be a bottleneck [9–12].

In this study, the copolymerization of DMP with DMP derivatives containing hydroxyl and amino groups, 2-hydroxymethyl-6-methylphenol (HMMP) and 2-(4-methylphenylamino)methyl-6-methylphenol (TAMP) (Scheme 1), was examined, and the obtained polymers, functionalized PPOs, were used as an additive for the formation of polyurethane (PU) films. The DMP derivatives HMMP and TAMP can be easily synthesized from *o*-cresol via 2-hydroxy-3-methylbenzaldehyde [13–16], however, to the best of our knowledge, there is no report on the OCP of these compounds.

Polyurethanes are an important class of material extensively used in various applications, such as in coatings, fibers, foams, and elastomers requiring high performance [17–21]. For example, PUs can be found in basements, absorption materials, and biomedical devices, such as artificial heart valves and catheters, due to their good mechanical and biocompatible properties [22–27]. However, PUs exhibit poor thermal stability and susceptibility to the *in vivo* environment. Therefore, the physical stability of PUs must be improved. It is known that the inter-hydrogen bonding between the urethane groups of PUs, as well as the micro-phase structure of the hard and soft segments, significantly affects the macroscopic properties of the final materials. The incorporation of PPO containing functional groups that interact with the urethane groups of PU chains may control the properties of PU to

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Scheme 1. Oxidative coupling copolymerization between DMP and the DMP derivatives.

overcome the previously mentioned problems. Although silicone polymers are sometimes utilized for this purpose [27–31], little attention has been paid to PPO.

2. Experimental

2.1. General

^1H NMR spectra were obtained using a JEOL JNM-ECS400 (400 MHz for ^1H) spectrometer. Size exclusion chromatographic (SEC) analyses were performed on a Jasco PU-2080 Plus system equipped with a UV (Jasco UV-2075 Plus) detector using Shodex KF-803L and KF-806L columns for CHCl_3 or Tosoh TSK-G7000H and TSK-G3000H columns for THF connected in series (temp. = 25 °C, flow rate = 0.8 mL/min). Calibration was carried out with polystyrene standards. Tensile tests were performed using a Shimadzu EZ-L(500N) apparatus with dumbbell-shaped test pieces [film width = 5 mm, stress rate = 300 mm/min, 25 °C].

2.2. Material

The monomer DMP (Kanto) and the copper catalyst di- μ -hydroxo-bis[$(N,N,N',N'$ -tetramethylethylenediamine)copper(II)] chloride [$\text{CuCl}(\text{OH})\text{-TMEDA}$, TCI] [32–35] were used as received. The functional monomers HMMP and TAMP were synthesized from *o*-cresol as reported in the literature [13–16]. Poly(tetramethylene oxide) 650 (molecular weight = 600–710, PTMO, Wako), methylenediphenyl 4,4'-diisocyanate (MDI, Wako), 1,4-butanediol (Kanto), dibutyltin dilaurate (Wako), phenyl isocyanate (Wako), 4-methoxyphenyl isocyanate (TCI), and butyl isocyanate (TCI) were employed for PU synthesis [20] and the further transformation of the obtained PPO copolymer without further purification.

2.3. Typical procedure for oxidative coupling copolymerization of DMP

The catalyst was added to a mixture of DMP and a comonomer ([monomers]/[Cu] = 20/1, monomers: 1 mmol) in a solvent (2 mL), and the mixture was stirred at approximately 25 °C for 24 h under an O_2 atmosphere. The product was isolated as the MeOH-2 mol/L HCl (5/1 (v/v))-insoluble part by centrifugation, then repeatedly washed with methanol, and finally freeze-dried from the benzene solution.

2.4. Acetylation of the obtained copolymer

Pyridine (0.1 mL) was introduced into a mixture of copolymer (51 mg) and AcCl (0.1 mL) in CH_2Cl_2 (2 mL) at 25 °C; the mixture was stirred for 24 h. The product was isolated (55 mg) as the MeOH-2 mol/L HCl (4/1 (v/v))-insoluble fraction by centrifugation, washing with methanol, and freeze-dried from the benzene solution.

2.5. Transformation of the obtained copolymer with isocyanates

A mixture of copolymer (50 mg), RNCO (0.1 mL), and dibutyltin dilaurate (0.01 mL) in *N,N*-dimethylformamide (DMF, 2 mL) was stirred at 60 °C for 24 h. The methanol-insoluble products (R = Ph: 50 mg; 4-MeOC₆H₄: 56 mg; *n*-Bu: 60 mg) were obtained by washing with MeOH-2 mol/L HCl (4/1 (v/v)) and with methanol, and then freeze-dried from the benzene solution.

2.6. PU film formation

To a solution of PTMO (3.3 g) and MDI in tetrahydrofuran (THF: 10 mL) a Sn(IV) catalyst was added. After stirring at 50 °C for 2 h under a N_2 atmosphere, a THF solution of 1,4-butanediol was introduced ([PTMO]/[MDI]/[1,4-butanediol]/[Sn] = 1/2/1/0.02). The stirring was continued at 25 °C for 1 h to yield a THF solution of PU [13 wt%, MeOH-insoluble part: 89%, number-average molecular weight (M_n): 7.4×10^4 , weight-average molecular weight (M_w): 1.9×10^5].

Film formation was carried out using a mixture of the above-described THF solution of PU (4 g) and a solution of poly(DMP/HMMP) derivatives (2.5 mg, 0.5 wt% to PU) in THF (1 mL) using a Petri dish (45 mm \varnothing). Films were prepared by drying at 45 °C for 24 h, and the obtained films were further dried at 80 °C for 3 h under vacuum.

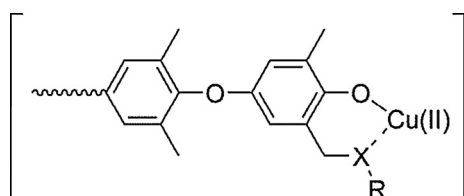
3. Results and discussion

DMP and the DMP derivatives (50:50 feed ratio) were copolymerized with the $\text{CuCl}(\text{OH})\text{-TMEDA}$ catalyst in various solvents under an oxygen atmosphere (Scheme 1). The results are summarized in Table 1. The homo-polymerization of HMMP with the CuCl -pyridine catalyst (5 mol%) in the presence of Na_2SO_4 in toluene at room temperature for 2 h did not afford a product, whereas a methanol-insoluble polymer was obtained in 50% yield by the polymerization of DMP under the same conditions [36]. Copolymerization with HMMP as the comonomer in toluene afforded a polymer in a low yield of 23%, whose unit ratio (DMP:HMMP) was determined to be 91:9 by ^1H NMR analysis (run 1). The solvents, CHCl_3 and THF, significantly improved both the yield and unit ratio, whose values were 76% and 67:33 in the latter case (run 3), respectively. Therefore, it is concluded that the polarity of the solvent affects the copolymerizability of HMMP.

The plausible active intermediate of the HMMP unit's ω -end is illustrated in Scheme 2, in which copper(II) is intra-molecularly coordinated by the hydroxyl group. A stable six-membered chelation ring may inhibit further coupling [2], whereas polar solvents, such as THF, should activate the copper(II) intermediate to induce polymerization, although the details of this process are not currently clear. To support this scheme, the copolymerization in methanol was examined (runs 4–6), although methanol has often been used for the oxidative coupling reaction and OCP, mainly because methanol easily dissolves the catalyst [37–41]. Actually, it was observed that the mixed solvent with methanol significantly

Table 1Copolymerization of DMP (1:1 feed ratio).^a

Run	Comonomer	Solvent	Yield (%) ^b	Unit ratio ^c DMP:comonomer	$M_w \times 10^{-3}$ (M_w/M_n) ^d
1	HMMP	Toluene	23	91:9	13.3 (2.5)
2	HMMP	CHCl ₃	51	81:19	9.1 (1.7)
3	HMMP	THF	76	67:33	3.1 (1.3)
4	HMMP	Toluene–MeOH ^e	31	82:18	7.0 (1.5)
5	HMMP	Toluene–MeOH ^f	24	54:46	6.0 (2.1)
6	HMMP	CHCl ₃ –MeOH ^e	39	76:24	4.4 (1.3)
7	TAMP	CHCl ₃	57	72:28	10.5 (2.0)
8	TAMP	CHCl ₃ –MeOH ^e	69	73:27	6.4 (1.7)

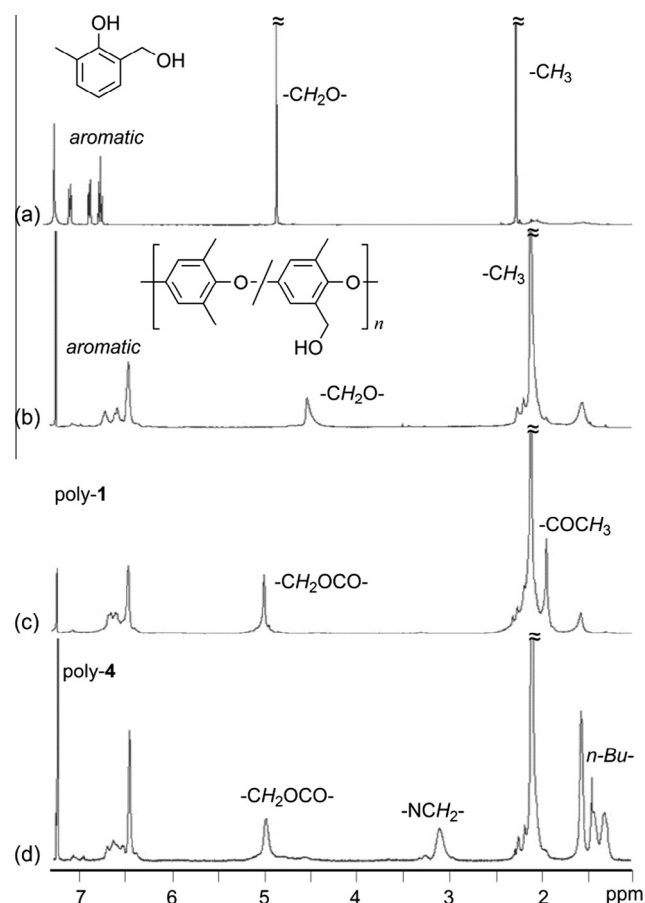
^a Conditions: catalyst = CuCl(OH)–TMEDA, temp. = r.t., time = 24 h, O₂ atmosphere.^b MeOH-insoluble part.^c Determined by ¹H NMR analysis.^d Determined by SEC (eluent: CHCl₃).^e 7/1 (v/v).^f 3/1 (v/v).**Scheme 2.** Plausible intermediate for the oxidative coupling copolymerization with the Cu(II) catalyst.

affected the unit ratio of the obtained polymers. For example, the polymerization in toluene–methanol (3/1, v/v) afforded a polymer with a unit composition of 54:46 in low yield.

The copolymerization of DMP with TAMP in CHCl₃ also afforded a copolymer in 57% yield with a unit ratio of DMP:TAMP = 72:28 (run 7). However, a similar value of the unit ratio was observed for the mixed solvent system containing methanol, whereas the polymer yield increased to 69% (run 8). Figs. 1(b) and 2(b) demonstrate the ¹H NMR spectra of the obtained copolymers, poly(DMP/HMMP) (run 3) and poly(DMP/TAMP) (run 7), together with those of the comonomers HMMP and TAMP (Figs. 1(a) and 2(a)), respectively. The peaks are assigned as shown in the figures.

Table 2 lists the results of the copolymerization between DMP and HMMP in various feed ratios. During the polymerization in toluene or CHCl₃, the copolymers, which mainly consisted of the DMP unit, were produced (runs 1–4). The copolymerization in the toluene–methanol mixed solvent clearly affected the polymerizability of HMMP, leading to a copolymer with an HMMP unit ratio higher than the unit ratios observed for the polymers obtained in toluene (runs 5–7).

Further transformations of the side-chain hydroxyl groups of poly(DMP/HMMP) were carried out to use the products as an additive for PU film formation (Scheme 3). The copolymer (Table 1, run 3) was treated with an excess amount of acetyl chloride and pyridine (poly-1) or an excess amount of isocyanate esters in the presence of the catalyst, dibutyltin dilaurate, (poly-2–poly-4) at room temperature for 24 h. After washing with methanol and freeze-drying from the benzene solution, the products were nearly obtained in quantitative yield. The ¹H NMR spectrum of the acetylated polymer, poly-1, is shown in Fig. 1(c). A shift in the methylene proton peak from 4.5 ppm for the original polymer to 5.0 ppm was clearly observed, and the unit ratio of DMP:YMMP was estimated to be 67:33, whose value is identical to the original one. The ¹H NMR spectrum of the polymer possessing the urethane group poly-4 is demonstrated in Fig. 1(d). The unit ratio was evaluated to be 68:32, which again is in good agreement with the original value. These results indicated that the transformation of the

**Fig. 1.** ¹H NMR spectra of (a) HMMP, (b) poly(DMP/HMMP) (Table 1, run 3), (c) poly-1, and (d) poly-4 (400 MHz, CDCl₃).

hydroxyl groups introduced by the copolymerization of HMMP was successfully attained. Moreover, the SEC analyses in CHCl₃ revealed an M_w value of 8.5×10^4 ($M_w/M_n = 1.7$) for poly-1 but were unsuccessful for poly-2–poly-4, most likely because significant aggregation should occur in the eluent.

A PU solution in THF was prepared using PTMO, MDI, and 1,4-butanediol as the extender (1:2:1) in the presence of the Sn(IV) catalyst [18]. In addition, poly(DMP) was synthesized by polymerization with CuCl(OH)–TMEDA in CHCl₃ at room temperature under an O₂ atmosphere (methanol-insoluble part: 76%, $M_w = 1.1 \times 10^4$, $M_w/M_n = 5.1$). The polymers poly(DMP), poly(DMP/HMMP) (Table 1, run 3), and poly-1–poly-4 were used as an additive (0.5 wt%) for PU film formation.

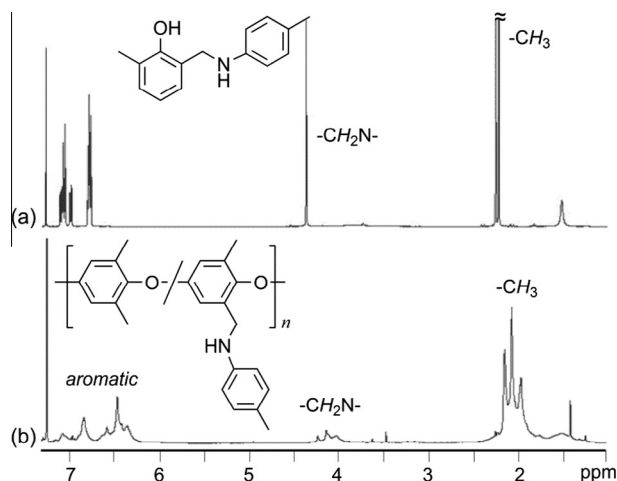


Fig. 2. ^1H NMR spectra of (a) TAMP and (b) poly(DMP/TAMP) (Table 1, run 7) (400 MHz, CDCl_3).

Colorless and clear films were obtained; their properties are summarized in Table 3. The average thickness was approximately 180 μm . When poly(DMP) was used as an additive, the elastic modulus of the resulting film was significantly reduced to 1.92 N/mm^2 (run 2) compared to that observed for the film prepared without an additive (run 1). In contrast, the PU films containing PPO with the functional groups showed values that were comparable or greater than the value measure for the original PU film. In particular, a value of approximately 3.2 N/mm^2 was observed for the films prepared with poly-1 and poly-3, which contained ester and urethane groups, respectively (runs 4 and 6). In

Table 3

Properties of PU films containing poly(DMP/HMMP) derivatives.

Run	Additive (0.5 wt%)	Thickness (μm)	Elastic modulus (N/mm^2)
1	None	185.1	2.88
2	Poly(DMP) ^a	184.3	1.92
3	Poly(DMP/HMMP) ^b	193.0	2.83
4	Poly-1	181.9	3.17
5	Poly-2	187.2	3.04
6	Poly-3	180.5	3.22
7	Poly-4	182.6	3.05

^a $M_w = 1.1 \times 10^4$, $M_w/M_n = 5.1$.

^b Table 1, run 3.

the latter, the structure of the urethane group also affected the PU film properties (runs 5–7). These results suggest that the hydrogen-bond interaction between PU and PPO should play an important part in controlling the properties of the PU films.

A PU containing isocyanate end groups was then prepared using PTMO, MDI, and 1,4-butanediol in a ratio of 1:2:0.8, and the obtained THF solution was used for film formation by adding poly(DMP/HMMP) (Table 1, run 3) (0.5 wt%). During the film formation process, the isocyanate of PU should react with the hydroxyl group of PPO to form a covalent bond [42]. The PU films obtained with and without poly(DMP/HMMP) were again colorless and clear; the thicknesses of the films were 174 and 157 μm , respectively. The former, which contained the additive, showed an elastic modulus of 3.80 N/mm^2 , whereas a value of 3.30 N/mm^2 was observed for the latter. Thus, poly(DMP/HMMP) is significantly effective in controlling PU film properties as an additive; in addition, the values obtained are quite different from those observed for the films prepared using the normal PU (Table 3, runs 1 and 3).

Table 2

Copolymerization of DMP and HMMP^a.

Run	Solvent	Feed ratio DMP:HMMP	Yield (%) ^b	Unit ratio ^c DMP:HMMP	$M_w \times 10^{-4}$ (M_w/M_n) ^d
1	Toluene	3:1	72	96:4	3.9 (3.8)
2	Toluene	2:1	49	94:6	5.6 (1.8)
3	Toluene ^e	3:1	78	89:11	2.6 (23)
4	CHCl_3	3:1	79	92:8	17.8 (14)
5	Toluene–MeOH ^f	3:1	66	93:7	6.5 (5.8)
6	Toluene–MeOH ^f	2:1	48	81:19	5.6 (1.8)
7	Toluene–MeOH ^f	1:3	49	30:70	7.1 (2.1) ^g

^a Conditions: catalyst = $\text{CuCl}(\text{OH})$ –TMEDA, temp. = r.t., time = 24 h, O_2 atmosphere.

^b MeOH-insoluble part.

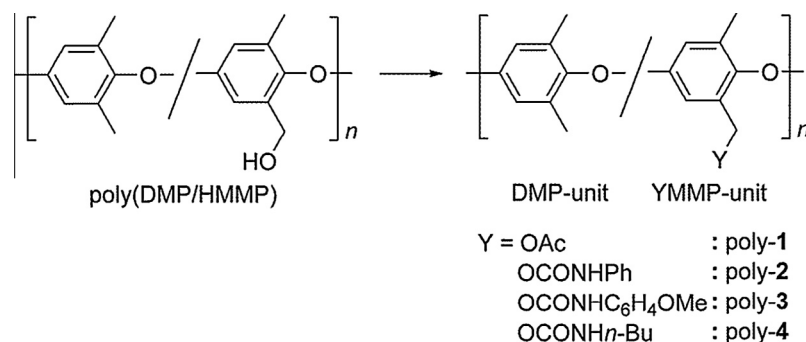
^c Determined by ^1H NMR analysis.

^d Determined by SEC (eluent: CHCl_3).

^e Catalyst = $\text{CuCl} + 2$ pyridine.

^f 7/1 (v/v).

^g Determined after acetylation of the original polymer with an excess amount of AcCl and pyridine in CHCl_3 .



Scheme 3. Transformations of poly(DMP/HMMP) into polymers possessing ester (poly-1) and urethane groups (poly-2–poly-4).

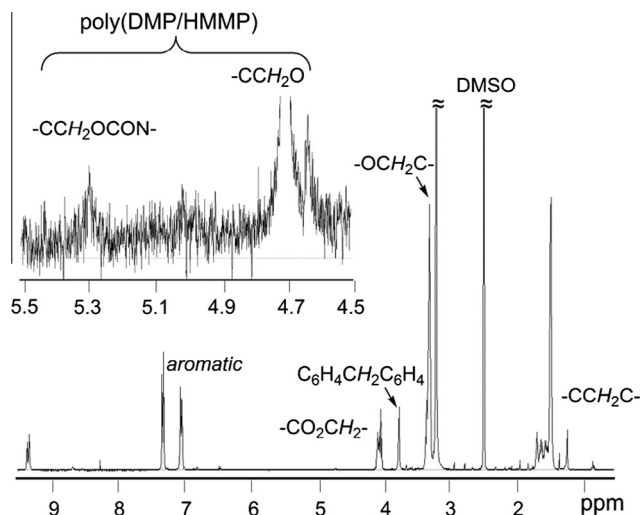


Fig. 3. ^1H NMR spectra of the PU containing poly(DMP/HMMP) (0.5 wt%) (400 MHz, $\text{DMSO}-d_6$).

The film obtained using the poly(DMP/HMMP) additive was dissolved in $\text{DMSO}-d_6$ and a submitted to ^1H NMR analysis (Fig. 3). The peaks based on the PU are assigned as shown in the figures. The expanded spectrum shows a region of methylene protons of poly(DMP/HMMP). The peaks at approximately 4.7 ppm correspond to those of the original polymer, whereas the small absorption peak at 5.3 ppm must be attributed to the methylene protons of the neighboring urethane group. Therefore, some of the hydroxyl groups reacted with the isocyanate terminal of PU, and the integral ratio of these two peaks was estimated to be 9:1. These results suggest that urethane bond formation between PU and PPO significantly affects the properties of the resulting films.

4. Conclusion

The copolymerization of DMP and DMP derivatives containing hydroxyl and amino groups was carried out, and the preparation of PPO with functional groups was successfully achieved. The copolymerization was affected by the polymerization solvent used, and the polar solvent, a mixed system containing methanol, yielded the copolymer in an effective manner. The obtained PPO derivatives were used as an additive for PU film formation, and the formation of intermolecular hydrogen and covalent bonds was observed significantly improve the tensile properties of the resulting films.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.reactfunctpolym.2014.07.009>.

References

- [1] A.S. Hey, Prog. Polym. Sci. 24 (1999) 45–80.
- [2] S. Kobayashi, H. Higashimura, Prog. Polym. Sci. 28 (2003) 1015–1048.
- [3] A.S. Hey, J. Polym. Sci., Part A: Polym. Chem. 36 (1998) 505–517.
- [4] Y.-C. Lin, H.C. Feng, M.-S. Yang, H.-A. Yu, C.-C. Huang, M. Liang, Polym. Int. 61 (2012) 719–726.
- [5] N. Li, Y. Leng, M.A. Hickner, C.-Y. Wang, J. Am. Chem. Soc. 135 (2013) 10124–10133.
- [6] N. Li, T. Yan, Z. Li, T. Thurn-albrecht, W.H. Binder, Energy Environ. Sci. 5 (2012) 7888–7892.
- [7] C.-C. Huang, M.-S. Yang, M. Liang, J. Polym. Sci., Part A: Polym. Chem. 44 (2006) 5875–5886.
- [8] H. Chang, M.-S. Yang, M. Liang, React. Funct. Polym. 70 (2010) 944–950.
- [9] C.-W. Chen, I.-H. Lin, C.-C. Lin, M. Horie, Polymer 54 (2013) 5684–5690.
- [10] T. Fukuhara, Y. Shibasaki, S. Ando, M. Ueda, Polymer 45 (2004) 843–847.
- [11] J. Nonoshige, H. Akahoshi, Y. Shibasaki, M. Ueda, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 5278–52826.
- [12] K. Matsumoto, Y. Shibasaki, S. Ando, M. Ueda, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 149–156.
- [13] P. Payne, J.H.P. Tyman, S.K. Mehet, A. Ninagawa, J. Chem. Res. (2006) 402–405.
- [14] W. Nagata, K. Okada, T. Aoki, Synthesis (1979) 365–368.
- [15] H.F. Anwar, L. Skattebøl, T.V. Hansen, Tetrahedron 63 (2007) 9997–10002.
- [16] Z. Tang, Z. Zhu, Z. Xia, H. Liu, J. Chen, W. Xiao, X. Ou, Molecules 17 (2012) 8174–8185.
- [17] M. Furukawa, Y. Mitsui, T. Fukumaru, K. Kojio, Polymer 46 (2005) 10817–10822.
- [18] N.J. Clayden, U.A. Jayasooriya, J.A. Stridea, P. King, Polymer 41 (2000) 3455–3461.
- [19] M. Rogulska, W. Podkomcielny, A. Kultys, S. Pikus, E. Posdzik, Eur. Polym. J. 42 (2006) 1786–1797.
- [20] S. Oprea, Polym. Bull. 65 (2010) 753–766.
- [21] E.M. Maafi, L. Tighzert, F. Malek, Polym. Bull. 66 (2011) 391–406.
- [22] J. Chen, Q. Nan, L. Guo, Y. Zhou, J. Appl. Polym. Sci. 115 (2010) 2190–2196.
- [23] I. Alferiev, S.J. Stachelek, Z.B. Lu, A.L. Fu, T.L. Sellaro, J.M. Connolly, R.W. Bianco, M.S. Sacks, R.J. Levy, J. Biomed. Mater. Res. 66A (2003) 385–395.
- [24] D.K. Han, K. Park, K.D. Park, K.D. Ahn, Y.H. Kim, Artif. Organs 30 (2006) 955–959.
- [25] Q.B. Bao, G.M. McCullen, P.A. Higham, J.H. Dumbleton, H. Yuan, Biomaterials 17 (1996) 1157–1167.
- [26] D. Sarkar, J.-C. Yang, S.T. Lopina, J. Appl. Polym. Sci. 108 (2008) 2345–2355.
- [27] J. Wang, W. Xia, K. Liu, X. Tuo, J. Appl. Polym. Sci. 121 (2011) 1245–1253.
- [28] Q. Fan, J. Fang, Q. Chen, X. Yu, J. Appl. Polym. Sci. 74 (1999) 2552–2558.
- [29] A. Simmons, J. Hyvarinen, R.A. Odell, D.J. Martin, P.A. Gunatillake, K.R. Noble, L.A. Poole-Warren, Biomaterials 25 (2004) 4887–4900.
- [30] K. Tsuchiya, T. Ohashi, S. Miyamachi, N. Osaka, H. Saito, K. Ogino, React. Funct. Polym. 71 (2011) 958–963.
- [31] D. Prządka, J. Jęczalik, E. Andrzejewska, B. Marciniak, M. Dutkiewicz, React. Funct. Polym. 73 (2013) 114–121.
- [32] M. Noji, M. Nakajima, K. Koga, Tetrahedron Lett. 43 (1994) 7983–7984.
- [33] M. Nakajima, S. Hashimoto, M. Noji, K. Koga, Chem. Pharm. Bull. 46 (1998) 1814–1815.
- [34] Y. Sasada, Y. Shibasaki, M. Suzuki, M. Ueda, Polymer 44 (2003) 355–360.
- [35] S. Habaue, M. Ohnuma, M. Mizoe, T. Temma, Polym. J. 37 (2005) 625–628.
- [36] K. Takeshi, K. Okuyama, Y. Ohba, M. Ueda, J. Photopolym. Sci. Technol. 12 (1999) 353–358.
- [37] M. Smrčina, J. Poláková, S. Vyskočil, P. Kočovský, J. Org. Chem. 58 (1993) 4534–4538.
- [38] M. Nakajima, I. Miyoshi, K. Kanayama, S. Hashimoto, J. Org. Chem. 64 (1999) 2264–2271.
- [39] S. Habaue, T. Seko, Y. Okamoto, Macromolecules 36 (2003) 2604–2608.
- [40] S. Habaue, R. Muraoka, A. Aikawa, S. Murakami, H. Higashimura, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 1635–1640.
- [41] S. Habaue, H. Aoyagi, S. Murakami, H. Higashimura, Polym. Bull. 59 (2007) 303–310.
- [42] N. Hori, A. Takemura, K. Shigyo, H. Ono, J. Packaging Sci. Tech. Jpn. 15 (2006) 261–270.

Formation of Polyurethane Film Containing Silicone Polymer with Silanol Residue

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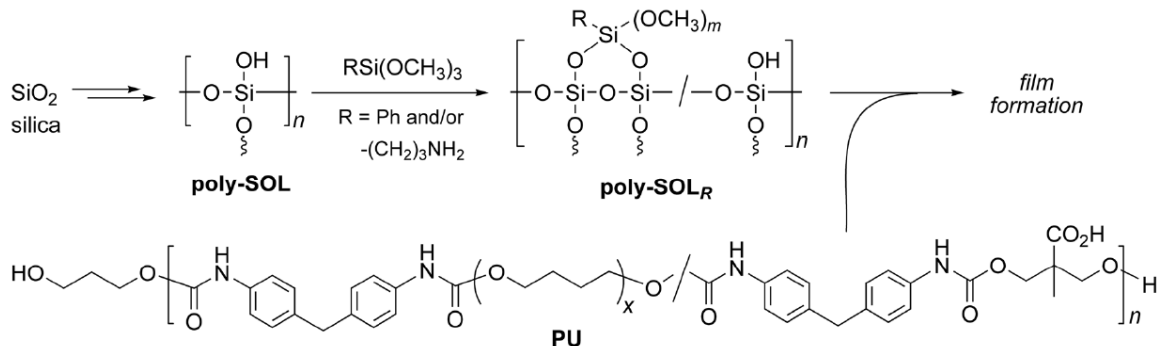
Abstract: The silicone polymers containing a silanol residue were synthesized from silica gel, while the polyurethanes (PUs) bearing a carboxyl moiety were prepared using 2,2-bis(hydroxymethyl)propionic acid (BHMPA) as one of the diol components. The fabrication of the PU films was carried out using 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 ($E = 5.36 \text{ N/mm}^2$), 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

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 [$\text{RSi}(\text{OR}')_3$]. Therefore, the structure of the produced



Scheme 1: Film formation from PU and silicone polymer.

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].

polymers are quite different from the silsesquioxanes with the empirical formulas of $\text{RSiO}_{3/2}$ [6,7], as well as the typical silicone polymer, poly(dialkylsiloxane).

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

Measurements

The ^1H NMR spectra were recorded by a Jeol JNM-ECS400 (400 MHz for ^1H) 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 °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 °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 °C.

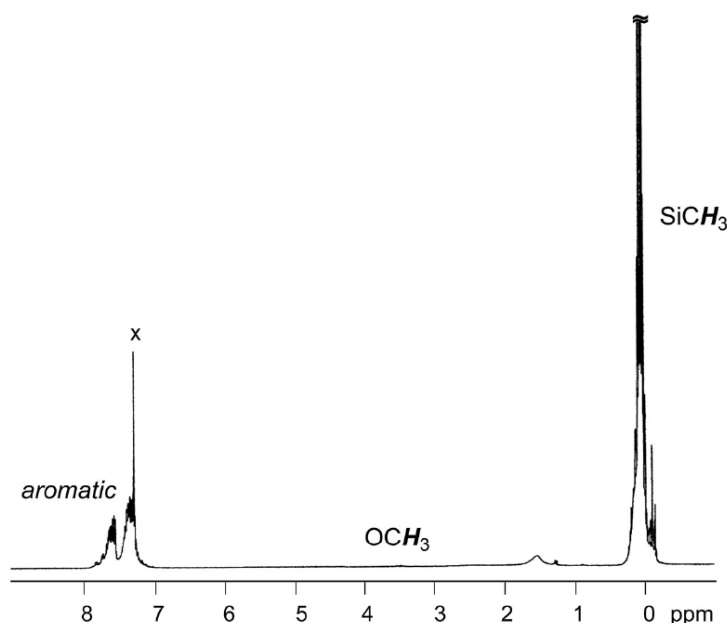


Figure 1: ^1H NMR spectrum of poly-SOL_{Ph(0.2)}-TMS (Table 1, run 1) (CDCl_3 , 55 °C).

Table 2: Preparation of PU

PU (abbreviation)	Feed ratio of diols			M_w^a ($\times 10^4$)	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.

^aMeOH-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/mm², which is much higher than that of the film of PU_(10/0) of 2.10 N/mm². 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/mm² (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

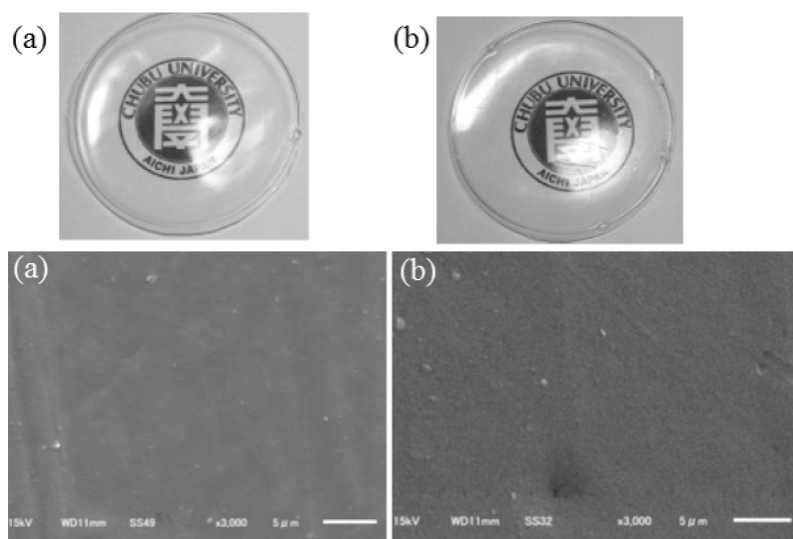


Figure 2: Photo and SEM images of the films prepared from PU_(7/3) (a) without and (b) with the incorporation of poly-SOL_{Ph(0.6)} and APTMS (white bar indicates 5 μ m).

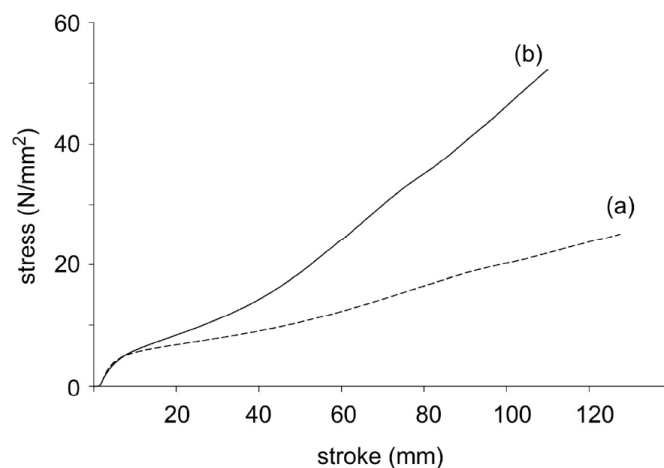


Figure 3: Stress versus stroke curves of the films prepared from PU_(7/3) (a) without and (b) with the incorporation of poly-SOL_{Ph(0.6)} and APTMS.

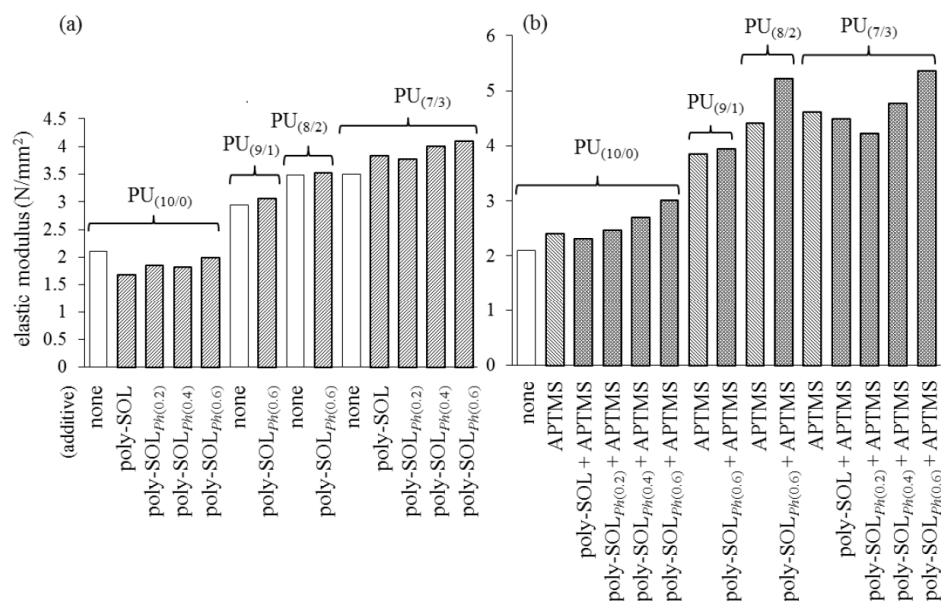


Figure 4: Observed elastic modulus values for the films prepared (a) without and (b) with the incorporation of APTMS.

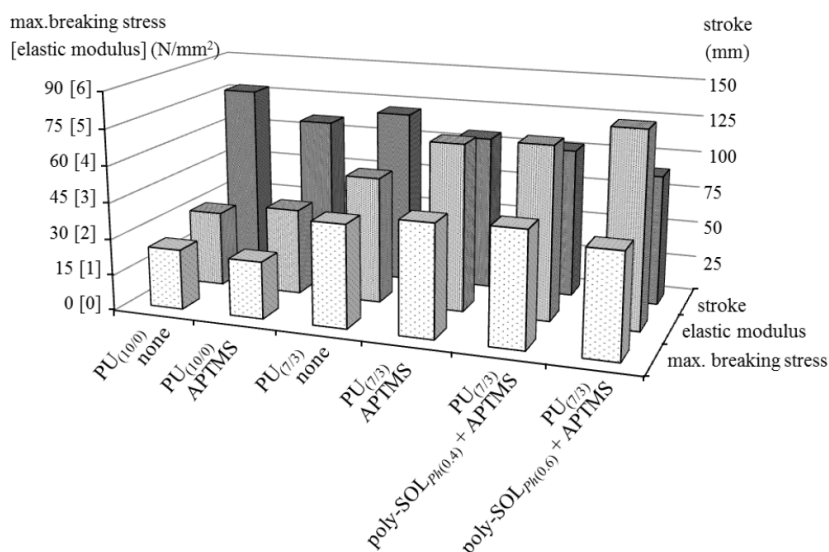
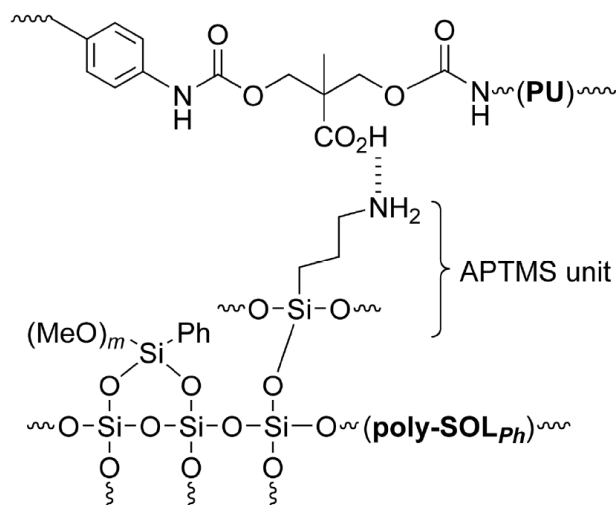


Figure 5: Observed mechanical properties (maximum breaking stress, elastic modulus, and breaking point) for the selected films.

increase with an increase in the BHPMA 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/mm², 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.

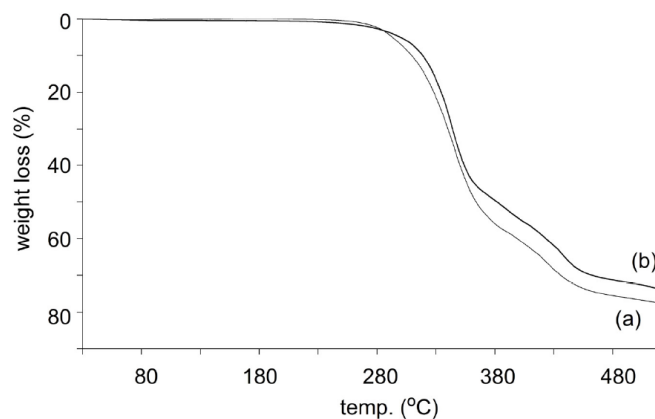


Figure 6: TG traces of the films prepared from PU_(7/3) (a) without and (b) with the incorporation of poly-SOL_{PH(0.6)} and APTMS.

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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REFERENCES

- [1] Kohama S, Inoue H, Yasuda T. Silylation of Water Glass. I. Solvent Extraction and Trimethylsilylation of Silicic Acid. *J Polym Sci: Polym Chem Ed* 1980; 18(7): 2357-69. <https://doi.org/10.1002/pol.1980.170180728>
- [2] Abe Y, Misono T. Preparation of Polysiloxanes from Silicic Acid. II. Esterification of Silicic Acid with Various Alcohols and Isolation of Esterification Products by Silylation. *J Polym Sci: Polym Lett Ed* 1982; 20(4): 205-10. <https://doi.org/10.1002/pol.1982.130200401>
- [3] Gunji T, Nagao Y, Misono T, Abe Y. Condensation and structure of silicic acid in tetrahydrofuran. *J Polym Sci Part A: Polym Chem* 1992; 30(9): 1779-87. <https://doi.org/10.1002/pola.1992.080300901>
- [4] Habaue S, Hirasa T, Akagi Y, Yamashita K, Kajiwaru M. Synthesis and Property of Silicone Polymer from Chrysotile Asbestos by Acid-Leaching and Silylation. *J Inorg Organomet Polym Mater* 2006; 16(2): 155-60. <https://doi.org/10.1007/s10904-006-9038-7>
- [5] Habaue S, Sato K, Yamashita K, et al. Polysiloxanes Derived from Chrysotile Asbestos via Acid-Leaching and Silylation Processes. *J Appl Polym Sci* 2008; 110(5): 2891-7. <https://doi.org/10.1002/app.28899>
- [6] Baney RH, Itoh M, Sakakibara A, Suzuki T. Silsesquioxanes. *Chem Rev* 1995; 95(5): 1409-30. <https://doi.org/10.1021/cr00037a012>
- [7] Abe Y, Gunji T. Oligo- and polysiloxanes. *Prog Polym Sci* 2004; 29(3): 149-82. <https://doi.org/10.1016/j.progpolymsci.2003.08.003>
- [8] Bao QB, McCullen GM, Higham PA, Dumbleton JH, Yuan H. The artificial disc: theory, design and materials. *Biomaterials* 1996; 17(12): 1157-67. [https://doi.org/10.1016/0142-9612\(96\)84936-2](https://doi.org/10.1016/0142-9612(96)84936-2)
- [9] Alferiev I, Stachelek SJ, Lu ZB, et al. Prevention of polyurethane valve cusp calcification with covalently attached bisphosphonate diethylamino moieties. *J Biomed Mater Res* 2003; 66A(2): 385-95. <https://doi.org/10.1002/jbm.a.10896>
- [10] Han DK, Park K, Park KD, Ahn KD, Kim YH. *In vivo* Biocompatibility of Sulfonated PEO-grafted Polyurethanes for Polymer Heart Valve and Vascular Graft. *Artif Organs* 2006; 30(12): 955-9. <https://doi.org/10.1111/j.1525-1594.2006.00327.x>
- [11] Wang J, Xia W, Liu K, Tuo X. Improved adhesion of silicone rubber to polyurethane by surface grafting. *J Appl Polym Sci* 2011; 121(3): 1245-53. <https://doi.org/10.1002/app.33008>
- [12] Fan Q, Fang J, Chen Q, Yu X. Synthesis and properties of polyurethane modified with aminoethylaminopropyl poly(dimethyl siloxane). *J Appl Polym Sci* 1999; 74(10): 2552-8. [https://doi.org/10.1002/\(SICI\)1097-4628\(19991205\)74:10<2552::AID-APP25>3.0.CO;2-X](https://doi.org/10.1002/(SICI)1097-4628(19991205)74:10<2552::AID-APP25>3.0.CO;2-X)
- [13] Simmons A, Hyvarinen J, Odell RA, et al. Long-term *in vivo* biostability of poly(dimethylsiloxane)/poly(hexamethylene oxide) mixed macrodiol-based polyurethane elastomers. *Biomaterials* 2004; 25(20): 4887-900. <https://doi.org/10.1016/j.biomaterials.2004.01.004>
- [14] Habaue S, Iwai S, Kubo H, et al. Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) derivatives containing hydroxyl and amino groups by oxidative coupling copolymerization. *React Funct Polym* 2014; 83: 49-53. <https://doi.org/10.1016/j.reactfunctpolym.2014.07.009>
- [15] Chujo Y, Ihara E, Kure S, Saegusa T. Synthesis of triethoxysilyl-terminated polyoxazolines and their cohydrolysis polymerization with tetraethoxysilane. *Macromolecules* 1993; 26(21): 5681-6. <https://doi.org/10.1021/ma00073a023>
- [16] Chujo Y, Matsuki H, Kure S, Saegusa T, Yazawa T. Control of pore size of porous silica by means of pyrolysis of an organic-inorganic polymer hybrid. *J Chem Soc Chem Commun* 1994; (5): 635-6.
- [17] Tamaki R, Chujo Y. Synthesis of chitosan/silica gel polymer hybrids. *Compos Interfaces* 1998; 6(3): 259-72.
- [18] Schhipunov YA, Karpenko TY. Hybrid Polysaccharide-Silica Nanocomposites Prepared by the Sol-Gel Technique. *Langmuir* 2004; 20(10): 3882-7. <https://doi.org/10.1021/la0356912>

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