Research Article

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Synthesis and characterization of polyurethane–polysiloxane block copolymers modified by α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain

Abstract: In order to prepare polyurethane–polysiloxane block copolymers, α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain and α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate) siloxanes, were synthesized and characterized in this study. The syntheses process included hydroxyl protection, hydrosilylation, deprotection, and ring-opening equilibrium reactions. The intermediates and target products were characterized by Fourier transform infrared spectroscopy and ^{1}H nuclear magnetic resonance methods. The characterization results showed that each step was successfully carried out in all the cases. Then the waterborne polyurethane–polysiloxane block copolymers were prepared via step-growth polymerization. The properties of the block copolymer films were characterized by thermal gravimetric analysis, differential scanning calorimetry, and dynamic thermomechanical analysis methods in detail. The experimental results showed that the block introduction of hydroxyalkyl polysiloxane could reduce the water absorption of waterborne polyurethane from 62 to 11%, and significantly improve the water resistance of polyurethane. With the introduction of polysiloxane, the tensile strength decreased and the elongation at break increased. At the same time, with the increase of the polysiloxane content, the glass transition temperature of the soft segment decreased to −56.4°C and the thermal decomposition temperature increased to 300°C. The results revealed that the introduction of polysiloxane could effectively improve the comprehensive performance of polyurethane–polysiloxane block copolymer films.

Keywords: α,ω-hydroxyalkyl polysiloxanes, polyurethanes, synthesis, characterization

1 Introduction

It is well known that polysiloxanes exhibit the dual virtues of organic and inorganic materials and possess a variety of unique and superior properties, such as high- and low-temperature resistance, low surface energy, good water resistance, aging resistance, corrosion resistance, climate resistance, electric characteristics, good ultraviolet stability, physiological inertness, biocompatibility, and so on [1,2]. Copolymerization of polysiloxanes with reactive functional groups and other organic polymers can endow the organic polymers with the excellent properties of polysiloxanes so that new polymer materials with special properties can be obtained [3–5]. Hydroxyl polysiloxanes are often used to synthesize polyurethane–polysiloxane graft or block polymers, and it is an effective way to improve the performance of polyurethanes. Polyurethane is a polymer which is used widely in many fields [6–8]. Polyurethane materials possess outstanding properties, such as toughness, abrasion resistance, mechanical flexibility, and chemical resistance and are used in foams, coatings, and adhesives [9–13]. During the synthesis of waterborne polyurethane, due to the introduction of hydrophilic groups in the polyurethane chains, the water resistance of waterborne polyurethanes is usually inferior

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to solvent-based polyurethanes and their applications were greatly restricted. One of the most frequently used strategies to modify the performance of waterborne polyurethane is to prepare polyurethane–polysiloxane copolymers. Studies have mostly focused on polysiloxane copolymerization modification [14–18]. We know that hydroxyl silicone oil is the most commonly used organosilicon component in polyurethane modification. Hydroxyl silicone oil can introduce polysiloxanes into waterborne polyurethane through the reaction between the hydroxyl group and the isocyanate group, so as to achieve the purpose of block modification. Hydroxyl silicone oil reacts with the isocyanate group to produce the Si–O–C group, but the Si–O–C group is easy to hydrolyze under acidic and alkaline conditions, resulting in poor water resistance. α,ω-hydroxyalkyl polysiloxane can also react with the isocyanate group to form the Si–C–O group. Compared to the Si–O–C group, the Si–C–O group is more stable and difficult to hydrolyze. Therefore, α,ω-hydroxyalkyl polysiloxane can effectively improve the stability of polysiloxane–polyurethane copolymer materials. However, on the other hand, due to the polarity difference between non-polar polysiloxane and polar polyurethane segments, there will be obvious phase separation in the copolymerization process [19]. The introduction of polar groups in the polysiloxane chain might improve the compatibility between the polysiloxane chain segment and the polar polyurethane chain segment, thus improving the comprehensive properties of the polyurethane–polysiloxane copolymer.

Therefore, in order to solve the problem of easy hydrolysis and compatibility of waterborne polyurethane–polysiloxane copolymers, end-capping agent, 1,3-bis(2-methyl-3-hydroxypropyl)tetra methyldisiloxane and organosilicon ring, and tetra(2-methyl-methylpropanoate)tetramethylcyclotetra siloxane, were synthesized via hydroxyl protection, hydrosilylation, and deprotection. Then the α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain and α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxanes were prepared by ring-opening equilibrium reactions. The target product and intermediates were characterized by Fourier transform infrared spectroscopy (FT-IR) and ^{1}H nuclear magnetic resonance (NMR) methods. On the other hand, the polyurethane–polysiloxane block copolymers were prepared via step-growth polymerization, and the comprehensive properties were characterized by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMA), and mechanical property measurement in detail. The experimental results showed that the block introduction of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxanes could reduce

the water absorption of waterborne polyurethane and improve the water resistance of polyurethane. With the introduction of polysiloxane, the tensile strength decreased and the elongation at break increased. At the same time, with the increase of the α,ω-bis(2-methyl-3-hydroxypropyl) polymethyl(2-methyl-methylpropanoate)siloxanes content, the glass transition temperature (TG) of the soft segment decreased to –56.4ºC and the thermal decomposition temperature increased to 300ºC. The introduction of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxanes could effectively improve the comprehensive performance of waterborne polyurethane–polysiloxane block copolymers.

2 Experimental procedures

2.1 Materials

Methallyl alcohol (≥98%; purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd) and methyl methacrylate (MMA; ≥98%; purchased from Sinopharm Group Co. Ltd) were vacuum distilled before use. Hexamethyldisilazane (≥98%), tetramethyldisiloxane (≥98%), and tetramethyl-cyclotetra siloxane (≥98%), all industrial grade, were purchased from the Jiangxi Xinghuo Organic Silicone Plant. Dimethylformamide, methanol, and triethylamine (TEA) purchased from Sinopharm Group Co. Ltd were dried over 4 Å molecular sieves before use. Dicyclohexylmethylmethane-4,4′-diisocyanate (HMDI), hydroquinone, dibutyltin dilaurate, diethylenetriamine (DETA), trifluoromethanesulfonic acid, and chloroplatinic acid were used as received without further treatment. Poly(propylene glycol) (M_n = 2,000 g/mol), diethylene glycol (DEG), and dimethylolpropionic acid (DMPA) were dried by vacuum distillation at 100ºC for 3 h before use.

2.2 Synthesis of 1,3-bis(2-methyl-3-hydroxypropyl)tetramethyldisiloxane

The end-capping agent, 1,3-bis(2-methyl-3-hydroxypropyl) tetramethyldisiloxane, was synthesized by the hydroxyl protection, hydrosilylation, and deprotection reactions illustrated in Scheme 1. First, methallyl alcohol (72.0 g, 1.0 mol) and excessive hexamethyldisilazane (90.0 g, 0.57 mol) were charged into a four-neck flask equipped with a thermometer, magnetic stirrer, a nitrogen purge, and a reflux condenser. The flask was heated to 100ºC and kept at this
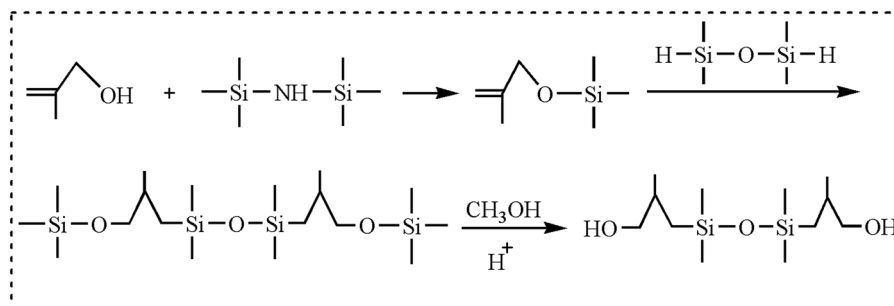
Scheme 1: Schematic illustration for synthesis of 1,3-bis(2-methyl-3-hydroxypropyl)tetramethyldisiloxane.

temperature for 8 h. Then 2-methylallyloxytrimethylsilane from 120–123°C was collected with a yield of 93%.

A round-bottomed flask equipped with a stirrer, a thermometer, a nitrogen purge, and a reflux condenser was charged with excessive 2-methylallyloxytrimethylsilane (50.0 g, 0.35 mol), 80 mL of toluene, and 20 μL of chloroplatinic acid solution. The flask was heated to 60°C, followed by dropwise addition of tetramethyldisiloxane (23.4 g, 0.17 mol). After that, the flask was kept for 1 h at this temperature. And then the flask was heated to 100°C for another 10 h. The toluene and excess 2-methylallyloxytrimethylsilane were removed by rotary evaporation and 1,3-bis(2-methyl-3-trimethylsilyloxypropyl) tetramethyldisiloxane was obtained at 140–145°C with a yield of 86.6% through distillation under reduced pressure.

Around 36.2 g of 1,3-bis(2-methyl-3-trimethylsilyloxy-propyl)tetramethyldisiloxane and 50 g of methanol were charged into the three-necked flask equipped with a thermometer, condenser, and magnetic stirrer, followed by addition of 0.1 mL of acetic acid as catalyst. The reaction mixture was stirred at reflux for 15 h. Acetic acid was then neutralized by adding 1 mL of potassium hydroxide methanol solution (1 mol/L). Methanol and substances with low boiling point were removed by vacuum and the deprotection product, 1,3-bis(2-methyl-3-hydroxypropyl) tetramethyldisiloxane, was collected by vacuum distillation with a yield of 82%.

2.3 Synthesis of tetra(2-methyl-methylpropanoate) tetramethylcyclotetrasiloxane

The organosilicon ring, tetra(2-methyl-methylpropanoate) tetramethylcyclotetra siloxane, was synthesized by hydrosilylation between MMA and tetramethylcyclotetrasiloxane which is illustrated in Scheme 2. The excess MMA, hydroquinone, and chloroplatinic acid catalyst were charged to a four-neck flask equipped with a thermometer, magnetic stirrer, a nitrogen purge, and a reflux condenser. The flask was heated to 90°C. After 30 min of flowing nitrogen, the reaction was carried out by adding tetramethylcyclotetrasiloxane for 10 h. The excess MMA was removed by vacuum distillation and tetra(2-methyl-methylpropanoate)tetramethyl cyclotetrasiloxane was collected at 250–260°C under reduced pressure.

2.4 Synthesis of α,ω-hydroxyalkyl polysiloxane with methacrylate side chain

The synthesis process of α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain was done as follows [20]: 1,3-bis(2-methyl-3-hydroxypropyl)tetramethyldisiloxane and tetra (2-methyl-methylpropanoate)tetramethylcyclotetrasiloxane in the presence of 20 μL of trifluoromethanesulfonic acid were
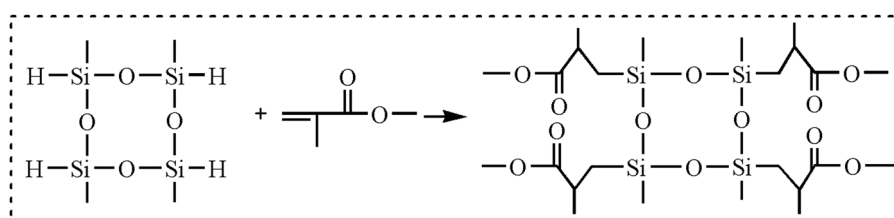

Scheme 2: Synthetic illustration for tetra(2-methyl-methylpropanoate)tetramethylcyclotetrasiloxane.

charged into a reaction vessel. The mixture was heated to 65°C for 12 h. Then the trifluoromethanesulfonic acid was neutralized by potassium hydroxide methanol solution. The α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain were obtained by removing substances with low boiling point under vacuum condition. The molecular weights were determined by the titration method.

2.5 Preparation of waterborne polyurethane–polysiloxane block copolymer emulsions

Poly(propylene glycol), dicyclohexylmethylmethane-4,4′-diisocyanate, and a drop of the catalyst (dibutyltin dilaurate) were mixed in the four-neck flask equipped with a mechanical stirrer, thermometer, and nitrogen inlet. The reaction system was kept for 1 h and stirred at 70°C. Then the α,ω-hydroxyalkyl polysiloxanes with methacylate side chain was added to the flask for 1 h. After that 2,2-dimethylolpropionic acid dissolved in N,N-dimethylformamide (20 mL) was added to the mixture for another 1 h. Then the chain extender, diethylene glycol, was added to the polyurethane prepolymer for 0.5 h, and then triethylamine was added into the system to neutralize the COOH group for 20 min to obtain the NCO-terminated polyurethane prepolymers. Finally, the prepolymer was added slowly to the water containing diethylenetriamine and emulsified through vigorous stirring to obtain stable waterborne polyurethane–polysiloxane block copolymer emulsions. The preparation processes are shown in Scheme 3 and the synthesis formula of waterborne polyurethane–polysiloxane block copolymer are listed in Table 1.
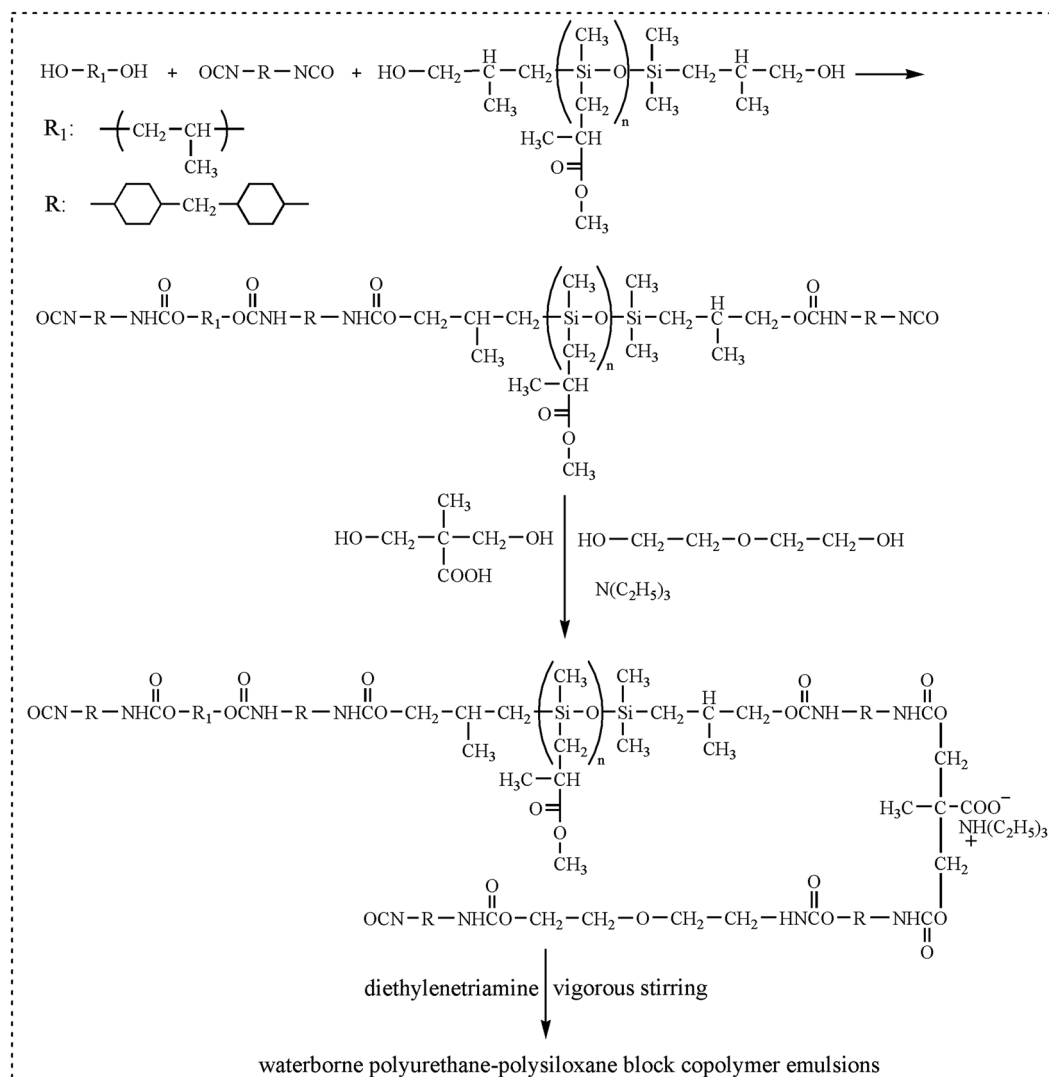
Scheme 3: Synthetic process of waterborne polyurethane–polysiloxane block copolymer emulsions.

Table 1: The formula for the preparation of waterborne polyurethane–polysiloxane block copolymer emulsion

Exp	PPG 2000 (g)	HMDI (g)	Polysiloxanes		DMPA (g)	DEG (g)	TEA (g)	DETA (g)
			(g)	(%)				
0	20.00	10.48	0	0	2.22	0.72	1.67	0.46
1	19.65	10.48	0.35	1	2.22	0.72	1.67	0.46
2	18.93	10.48	1.07	3	2.22	0.72	1.67	0.46
3	18.22	10.48	1.78	5	2.22	0.72	1.67	0.46
4	17.51	10.48	2.49	7	2.22	0.72	1.67	0.46
5	16.80	10.48	3.20	9	2.22	0.72	1.67	0.46

2.6 Characterizations

2.6.1 FT-IR

The FT-IR spectroscopy analysis was performed with a Nicolet Impact 400D Model spectrophotometer (Nicolet Impact, Madison, United States) using KBr pellets. The spectra were obtained over the wave-number range 4,000–400/cm at a resolution of 2/cm using an mercury cadmium telluride (MCT) detector with co-addition of 64 scans.

2.6.2 NMR

^{1}H NMR spectra were performed on a Bruker AVANCE 600 nuclear resonance instrument with chloroform-d as solvent and tetramethylsilane as internal standard at ambient temperature.

2.6.3 Determination of molecular weight

The molecular weight of α,ω-bis(2-methyl-3-hydroxy-propyl)polymethyl(2-methyl-methylpropanoate)siloxanes was determined by the titration method according to GB 12008-89. A sample was put in a dry and clean flask and the weight of the sample was expressed as *m*. Around 10 mL of pyridine–phthalate solution was added into the flask containing the sample and was shaken until the sample was dissolved. And then the flask was heated to 115°C and kept for 1 h. After that, the flask was taken out and cooled to room temperature, rinsing the condenser tube with 10 mL pyridine solution. The mixture was titrated with NaOH standard solution and its concentration was noted as *C*. The volumes of NaOH standard solution consumed in the blank sample and polysiloxane samples were expressed as V_0 and V_1, respectively. The hydroxyl value (OHV) is calculated by formula (1).

$$OHV = \frac{(V_0 - V_1) \times C \times 56.1}{m}. \tag{1}$$

The molecular weight of polysilxoane was determined by formula (2).

$$M = \frac{56.1 \times 2 \times 1{,}000}{OHV}. \tag{2}$$

2.6.4 Water absorption measurement

The water-resistance properties were determined as follows. The films by casting the emulsion on a leveled polytetrafluoro-ethylene (PTFE) plate were dried to constant weight in a vacuum oven at 100°C for 24 h. The weighed film (W_0) was immersed into distilled water at room temperature for 24 h, followed by wiping off of the water on the surface with a piece of filter paper to determine the weight (W_1). The absorbed water ratio (W_A) of the film was calculated by the formula (3).

$$W_A = \frac{W_0 - W_1}{W_0} \times 100\%. \tag{3}$$

2.6.5 Mechanical properties' measurements

The mechanical properties tests were carried out on a Zwick/Roell Z020 universal material tester (the test method was GB16421-1996) at room temperature with a speed of 50 mm/min. The testing samples were cut from the solution cast films and all the measurements have an average of four runs. The dumbbell type specimen was of 30 mm length at two ends, 0.2 mm thickness, and 4 mm wide at the neck. Each measurement was repeated at least four times.

2.6.6 DSC analysis

The physicochemical properties of pure waterborne polyurethane (WPU) and polyurethane–polysiloxane copolymer

were assessed by DSC. Samples (~5 mg) were sealed in the aluminum and subjected to a heating rate of 10°C/min for temperatures that ranged from –100 to 100°C.

2.6.7 Thermal gravimetric analysis

The thermal decomposition properties of all the samples were checked on a NETSCH STA 449 C thermogravimetric analyzer. The heating rate was 10°C/min and the test temperature range was from 25 to 600°C.

2.6.8 Dynamic thermomechanical analysis

The DMA tests were performed on a DMA-Q800 (TA instruments company). The scanning frequency was 1 Hz. The heating rate is 5 min and the temperature range was –75 to ~200°C.

3 Results and discussion

3.1 Synthesis and characterization of α,ω-bis(2-methyl-3-hydroxypropyl) polymethyl(2-methyl-methylpropanoate)siloxanes

Dehydrogenation reaction could occur between the OH of methally alcohol and the Si–H group of tetramethyldisiloxane, resulting in loss of yield and an increase in the content of by-products. In order to synthesize the end-capping agent, 1,3-bis(2-methyl-3-trimethylsilyloxypropyl)tetramethyldisiloxane, methallyl alcohol was first protected by hexamethyldisilazane via hydroxyl protection to avoid dehydrogenation. The hydroxyl protection product, 2-methylallyloxytrimethylsilane, was separated and then subjected to hydrosilylation with tetramethyldisiloxane to obtain the hydrosilylation product, 1,3-bis (2-methyl-3-trimethylsilyloxypropyl)tetramethyldisiloxane. Due to the instability of the Si–O–C group under acidic condition, the hydrosilylation product was alcoholyzed to synthesize hydroxyalkyl disiloxane, 1,3-bis(2-methyl-3-hydroxypropyl)tetramethyldisiloxane. During the synthesis process, all the intermediate products and the target product were separated by the distillation method. They were also subjected to FT-IR and ^{1}H NMR analyses.

2-Methylallyloxytrimethylsilane was first separated and subjected to FT-IR and ^{1}H NMR analyses which are

presented in Figure 1. The FT-IR spectra of raw materials and 2-methylallyloxytrimethylsilane showed that the OH vibration peak at 3,328/cm and the NH vibration peak at 3,380/cm had disappeared and that the C=C double bond vibration at 1,642/cm, Si–CH$_3$ vibration and Si–O–C vibration peaks at 1,251 and 1,099/cm were also observed in the spectrum of the hydroxyl protection product. The data of peaks in the ^{1}H NMR spectrum were easily recognized from the chemical shifts.

Then 2-methylallyloxytrimethylsilane was subjected to hydrosilylation reaction with tetramethyldisiloxane to obtain the hydrosilylation product, 1,3-bis(2-methyl-3-trimethylsilyloxypropyl)tetramethyldisiloxane, and the main characteristic of FT-IR (Figure 2) was the complete disappearance of C=C double bond vibration at 1,660/cm and Si–H vibration at 2,128/cm. This indicated that the hydrosilylation reaction had happened between the C=C double bond and Si–H. The data of peaks in the ^{1}H NMR spectrum were also easily recognized from the chemical shifts.

To create the OH in the molecules, the 1,3-bis(2-methyl-3-trimethylsilyloxypropyl)tetramethyldisiloxane was deprotected so that it became reactive toward the isocyanate group in a subsequent step to prepare polyurethane–polysiloxane copolymers. By deprotection reaction, the most obvious change between 1,3-bis(2-methyl-3-trimethylsilyloxypropyl)tetramethyldisiloxane and 1,3-bis (2-methyl-3-hydroxypropyl)tetramethyldisiloxane was that there was a vibration peak at 3,326/cm assigned to the OH group in the FT-IR spectra (Figure 3). Meanwhile all the products were subjected to ^{1}H NMR analyses and the data of peaks were easily recognized from the chemical shifts and the peak area integrations. It could be seen from the results of FT-IR and ^{1}H NMR that 1,3-bis(2-methyl-3-hydroxypropyl)tetramethyldisiloxane was successfully synthesized via hydroxyl protection, hydrosilylation, and deprotection reactions.

Due to the different polarities of the polysiloxane and polyurethane segments, the copolymerization of polysiloxane and polyurethane segments will lead to obvious phase separation. In order to improve their compatibility, we tried to synthesize the organosilicon ring with polar groups to prepare α,ω-hydroxyalkyl polysiloxanes with polar side chains. Therefore, the organosilicon ring, tetra (2-methyl-methylpropanoate)tetramethylcyclotetrasiloxane, was synthesized via the hydrosilylation reaction between tetramethylcyclotetrasiloxane and MMA. Figure 4 shows the changes of raw materials and the organosilicon ring in the FT-IR spectra. The complete disappearance of C=C double bond vibration at 1,638/cm and Si–H vibration at 2,128/cm could be seen from the spectra. This
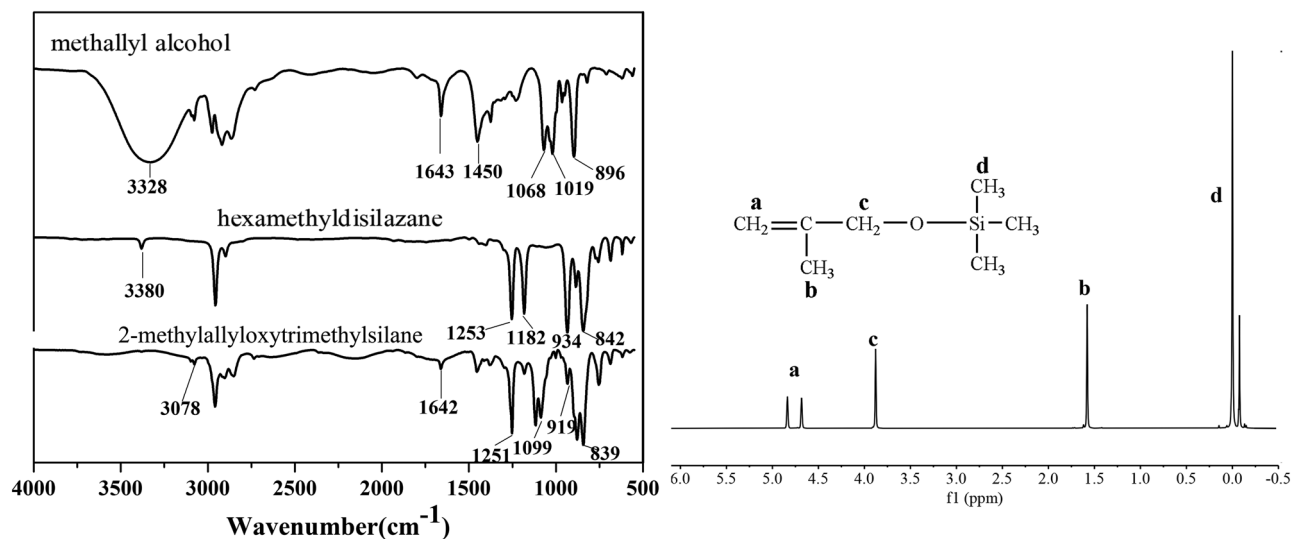
Figure 1: FT-IR spectra of methallyl alcohol, hexamethyldisilazane, and 2-methylallyloxytrimethylsilane and the ^{1}H NMR spectrum of 2-methylallyloxytrimethylsilane.

indicated that hydrosilylation reaction had happened between tetramethylcyclotetrasiloxane and MMA. The ^{1}H NMR spectrum of the organosilicon ring is illustrated in Figure 4 and the data of peaks were easily recognized from the chemical shifts and peak area integrations.

α,ω-Hydroxyalkyl polysiloxanes with methacrylate side chain were synthesized via 1,3-bis(2-methyl-3-hydroxy-propyl)tetramethyldisiloxane and tetra(2-methyl-methylpro-panoate)tetramethylcyclotetrasiloxane. The FT-IR and

^{1}H NMR spectra of α,ω-bis(2-methyl-3-hydroxypropyl) polymethyl(2-methyl-methylpropanoate)siloxanes are illustrated in Figure 5. The main characteristic was the appearance of the OH vibration peak at 3,461/cm and the ester vibration peak at 1,739/cm. The peak intensity of the ester vibration peak of tetra(2-methyl-methylpropanoate)tetra-methylcyclotetrasiloxane was stronger. The chemical shifts in the ^{1}H NMR also validated the occurrence of the ring-opening equilibrium reaction.
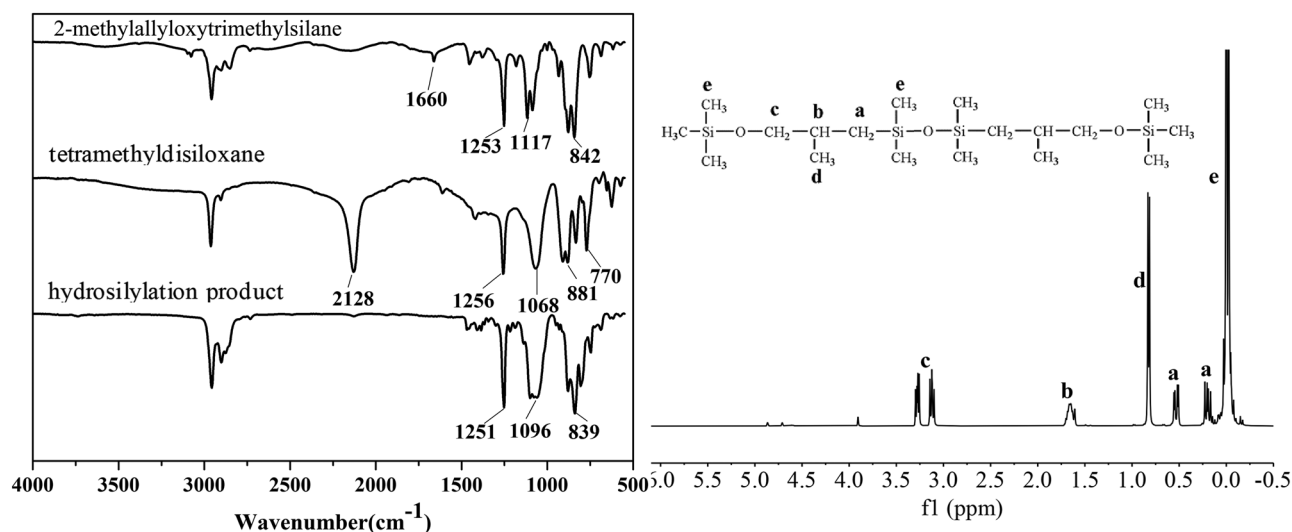

Figure 2: FT-IR spectra of 2-methylallyloxytrimethylsilane, tetramethyldisiloxane, and hydrosilylation product. ^{1}H NMR spectrum of hydrosilylation product.
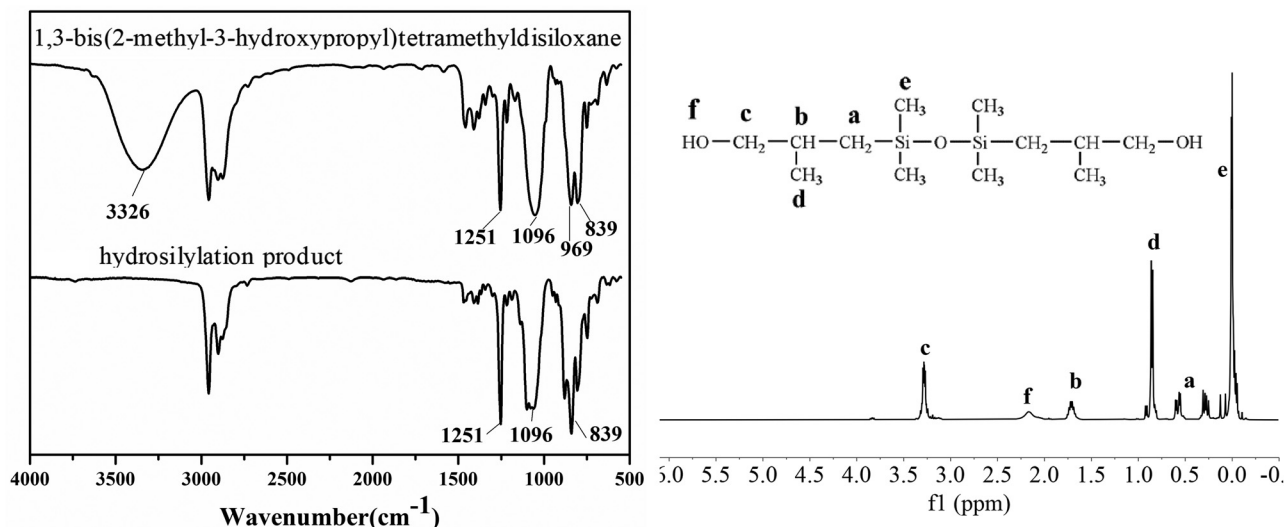
Figure 3: FT-IR spectra of 1,3-bis(2-methyl-hydroxypropyl)tetramethyldisiloxane and hydrosilylation product. ^{1}H NMR spectrum of 1,3-bis(2-methyl-hydroxypropyl)tetramethyldisiloxane.

3.2 Influences of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxane on the properties of waterborne polyurethane–polysiloxane block copolymer films

In order to study the influences of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate) siloxane on the properties of waterborne polyurethane–polysiloxane block copolymers, α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate) siloxanes (M_n = 2,000 g/mol) were synesized in this study. The molecular weight was determined by the titration method. As we know, polysiloxanes have excellent flexibility and water-resistance properties. By blocking polysiloxane to the polyurethanes, the superior properties were also introduced to copolymers. Figure 6 reveals the influence of the content of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxane on the water absorption of waterborne polysiloxane–polyurethane block copolymer films. From the experimental results, it could be seen that the introduction
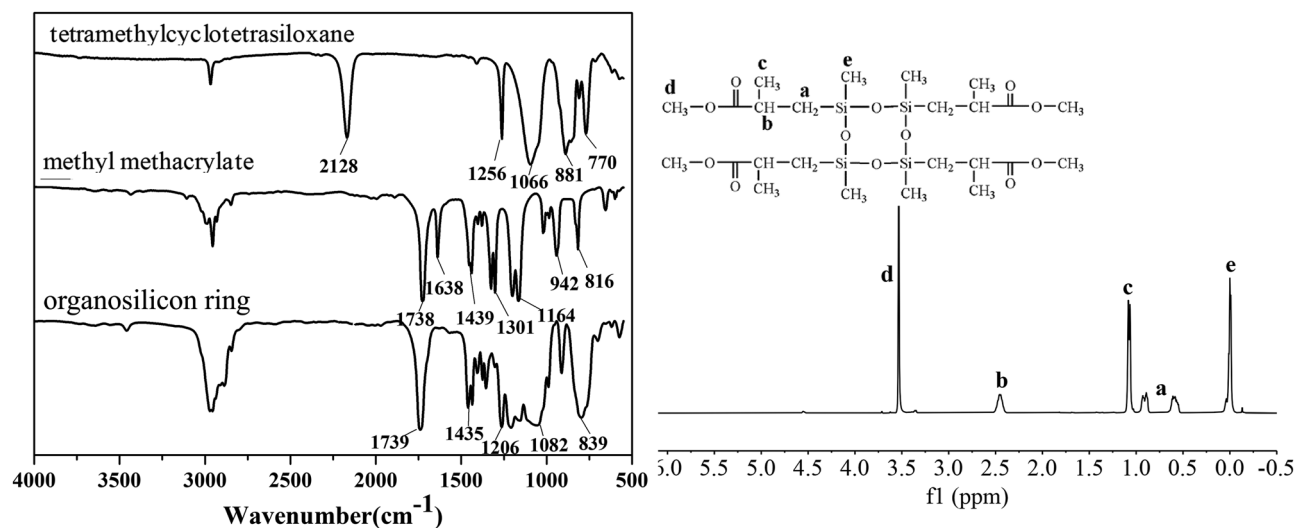

Figure 4: FT-IR spectra of tetramethylcyclotetrasiloxane, methyl meth acrylate, and tetra(2-methyl-methylpropanoate) tetramethylcyclotetrasiloxane.
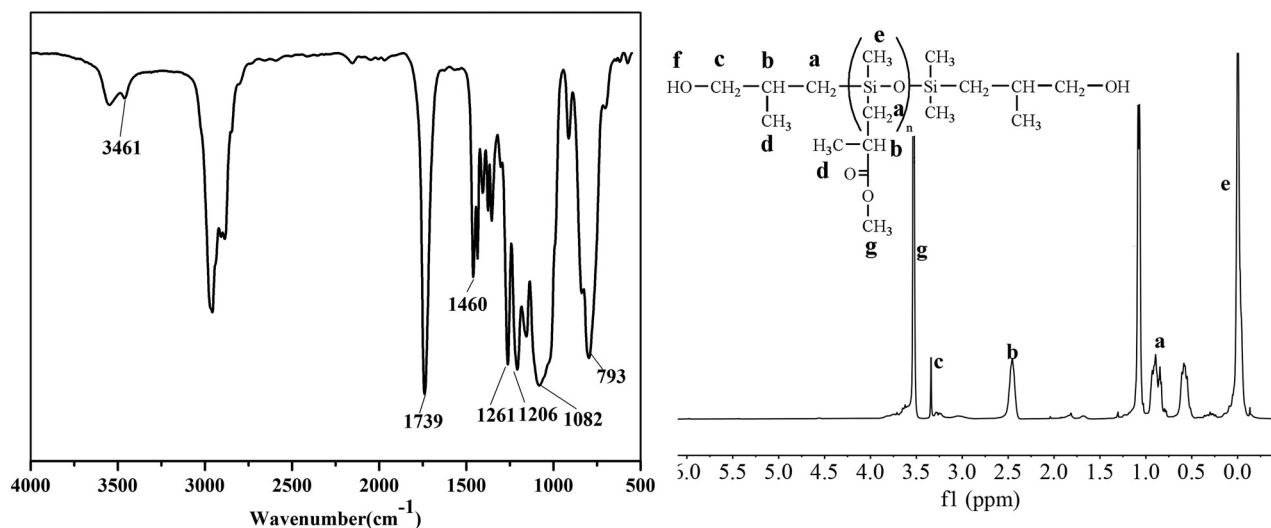
Figure 5: FT-IR and ¹H NMR spectra of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxanes.

of α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxane would reduce water absorption by the copolymer films effectively. The water absorption of the waterborne polyurethane–polysiloxane block copolymer films decreased with the increase in the polysiloxane content. The reason was that the polysiloxane segments possessed low surface energy and that the polysiloxane segments could migrate to the surface of the copolymer films to prevent the hydrophilic group from contacting water due to the low surface energy of polysiloxane segments.

To the best of our knowledge, polyurethanes possessed urethane bonds so that they had high mechanical property.

However, the polysiloxane segments were flexible and it would be possible to cause degradation of the mechanical property. It could be seen from the synthetic process of the waterborne polyurethane–polysiloxane block copolymer, that the flexible polysiloxane chains were blocked to the polyurethane chains, and that the regularity of the urethane bonds was broken, resulting in the loss of the mechanical property to some extent. The changes in the tensile strength and elongation at break of the waterborne polyurethane–polysiloxane copolymer films modified by different polysiloxane content are illustrated in Figure 7. It could be seen that the tensile strength of the polysiloxane–polyurethane copolymer films decreased with the increase in
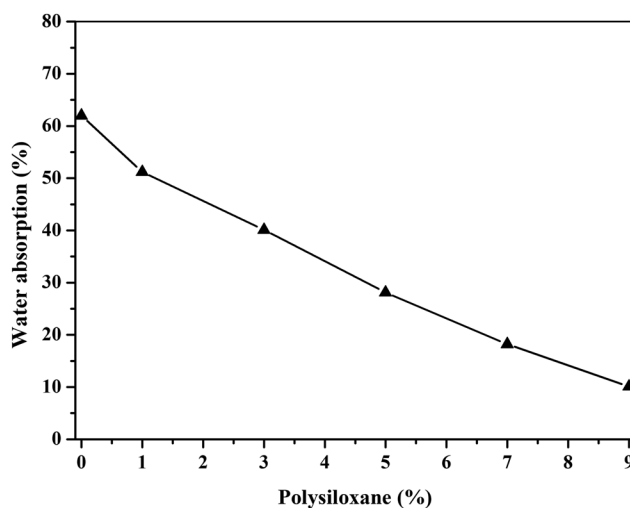

Figure 6: Influence of the polysiloxane content on water absorption of waterborne polysiloxane–polyurethane block copolymer films.
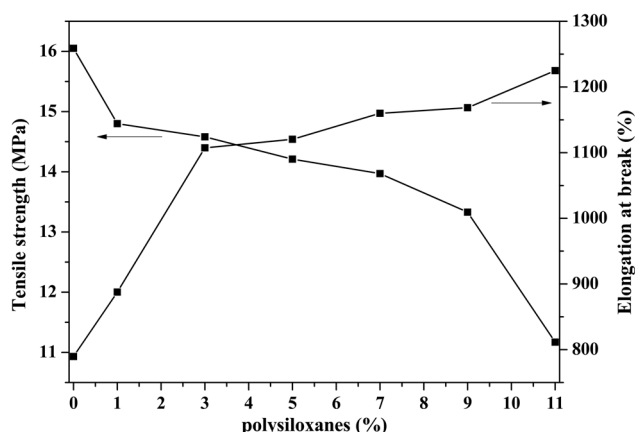
Figure 7: Influence of polysiloxane content on the mechanical properties of waterborne polysiloxane–polyurethane block copolymer films.

the polysiloxane content. However, the elongation at break improved due to the introduction of the flexible polysiloxane segments to the polyurethane chain.

DSC analyses of the waterborne polyurethane–polysiloxane block copolymers were also carried out and are shown in Figure 8. It could be found that the peak value of pure WPU appeared at −53.3°C, which was the TG of the soft segment of WPU. There was no TG belonging to the hard segment in the high temperature region. However, the TG of the hard segments of the polyurethanes modified by the polysiloxanes appeared at 74.1, 74.1, 76.1, and 72.1°C, respectively, at high temperature, and the TGs of the soft segments in the low temperature region shifted to the low temperature region. This phenomena indicated that polysiloxanes played a positive role in promoting the
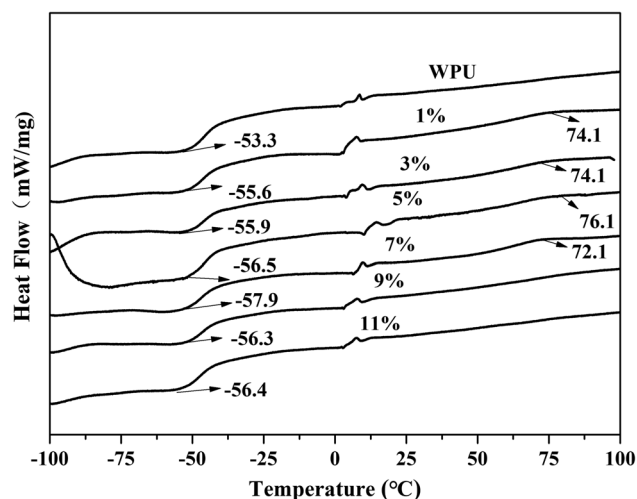
thermal stability of waterborne polyurethane. The thermal stability of the polyurethane–polysiloxane copolymer films was improved obviously. The reason was that the micro phase structures of the polyurethane were composed of a soft segment and a hard segment. When more polysiloxane was added into the soft segment, the soft segment in the chain segment would separate from the hard segment and thus the glass transition peak of them was changed slightly. The results also indicated that α,ω-bis(2-methyl-3-hydroxypropyl)polymethyl(2-methyl-methylpropanoate)siloxanes had been successfully introduced into the polyurethane as soft segments.

The thermal decomposition stability of all the samples were evaluated by TGA. The TGA curves of the waterborne polyurethane prepared with different polysiloxane contents are shown in Figure 9. It could be seen that the thermal decomposition rates of the WPU and the polyurethane–polysiloxane films are basically the same before 250°C and that the TGA curves were basically coincident, which was mainly due to the volatilization of the residual solvents and water in the samples. The TGA curve decreased sharply between 250 and 300°C mainly due to the decomposition of the hard segment in the polyurethane chain with the increase in temperature. When the temperature reached 300°C, the curve decreases sharply again. When the temperature increased, the soft segment also gradually decomposed. When the content of polysilxoane was less than 7%, the degradation temperature of the polyurethane–polysiloxane film was higher than that of the WPU film, showing a relatively slow thermal decomposition rate and a higher decomposition temperature. The reason was that the high temperature-resistance property of the sample was improved with the introduction of polysiloxane. However,
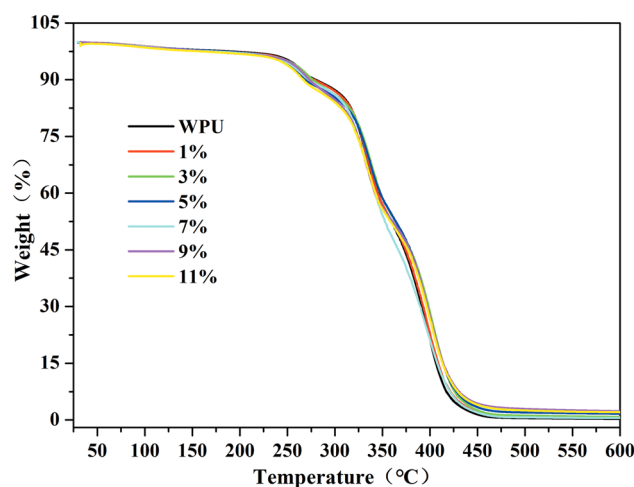

Figure 8: DSC curves of waterborne polyurethane–polysiloxane copolymer with different polysiloxane contents.

Figure 9: TGA curves of waterborne polyurethane–polysiloxane copolymer with different polysiloxane contents.

when the content of polysilxoane was higher than 7%, the decomposition temperature tended to be in the low temperature region because of microphase separation between the hard and the soft segments, resulting in the poor temperature resistance of the sample and the faster degradation rate.

All the polyurethane–polysiloxane copolymer films were subjected to DMA analyses and the storage modulus, loss modulus, and tan δ are illustrated in Figure 10. Storage modulus represents the ability of a material to store elastic deformation energy. Loss modulus, also known as viscosity modulus, usually refers to the energy dissipation caused by viscosity deformation in the process of material deformation. It could be found that the storage modulus of polyurethane–polysiloxane copolymer films gradually decreased with the increase in polysiloxane content. In Figure 10, the loss modulus gradually decreased with the increase of polysiloxane content, which was basically consistent with the storage modulus of polyurethane–polysiloxane copolymer films. The reason was that when the temperature was lower than the TG, the molecular segments were difficult to move and the energy loss was very small. When the temperature was higher than the TG, the molecular segments are easy to move and the loss of energy was less. The TGs decreased with the increase in polysiloxane. tan δ is the ratio of storage modulus to loss modulus, which could accurately show the TG of polymer materials. Figure 10 shows the temperature dependence curves of tan δ of WPU and polyurethane–polysiloxane copolymer films in the range from −80 to ~200°C. It could be seen that in the high temperature region, the hard segment had no obvious glass transition. When the content of polysiloxane was 7%, tan δ was the largest, which was consistent with the storage modulus and loss modulus of copolymer films. Therefore, when the content of polysiloxane was 7%, polyurethane–polysiloxane copolymer films had excellent viscoelastic properties.

4 Conclusion

With the main objective of preparing polyurethane–polysiloxane block copolymers and to improve the water-resistance property of waterborne polyurethane, α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain were synthesized and characterized via FT-IR and ^{1}H NMR methods. The waterborne polyurethane–polysiloxane block copolymers were prepared and subjected to TGA, DSC, DMA, and mechanical property tests. The comprehensive
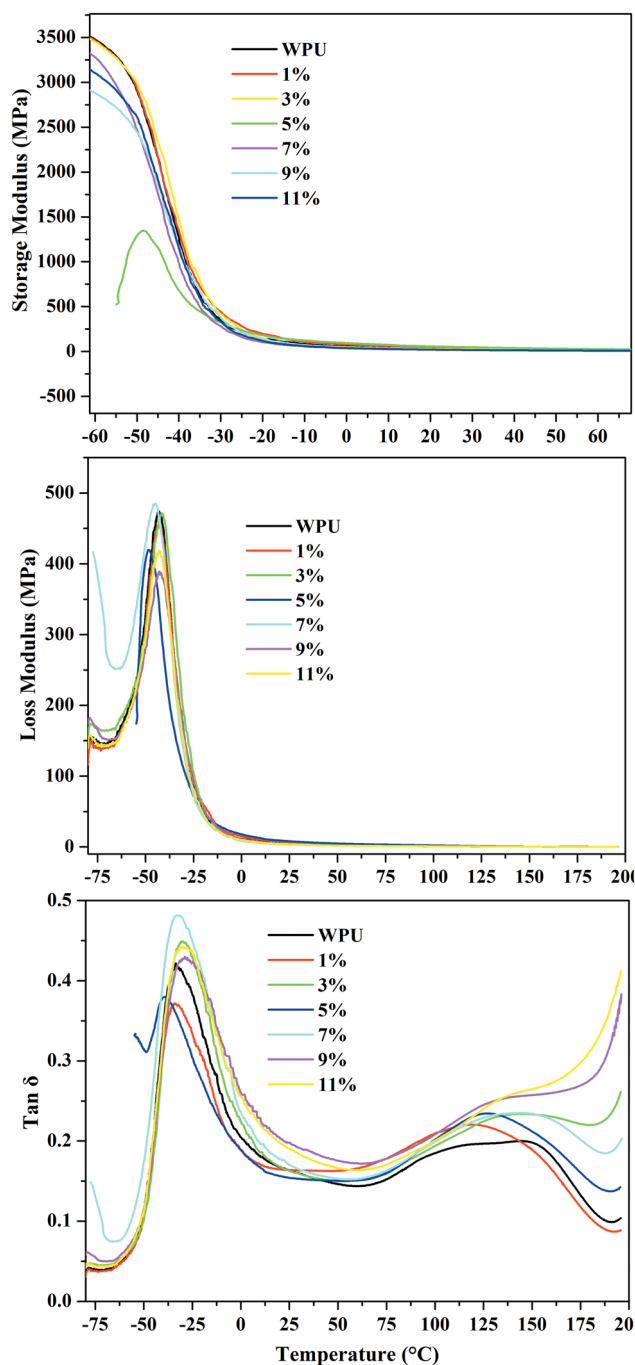

Figure 10: Influence of polysiloxane content on storage modulus, loss modulus, and tan δ of polyurethane–polysiloxane block copolymer films.

properties of polyurethane–polysiloxane block copolymers were improved effectively. The successful syntheses of α,ω-hydroxyalkyl polysiloxanes with methacrylate side chain and preparation of waterborne polyurethane–polysiloxane block copolymers will be a matter of primary importance for studies on block copolymerization.

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