Synthesis and Characterization of Hydroxypropyl Terminated Polydimethylsiloxane-Polyurethane Copolymers

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ABSTRACT: Polyurethane (PU) block copolymers were synthesized using prepared hydroxypropyl terminated polydimethylsiloxane (HTPDMS MW 990) and polyether diols (N-210) as soft segment with 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol. This low molecular weight polydimethylsiloxanes (PDMS) containing hydroxypropyl end-groups displayed better compatibility with PU than common PDMS. In this article, we illustrate its synthesis routes and confirmed the proposed molecular structures using NMR and infrared radiation (IR). We varied the contents of HTPDMS and N-210 in soft segments (HTPDMS—N-210: 0 : 100, 20 : 80, 40 : 60, 60 : 40, 80 : 20, and 100 : 0) to synthesize a series of PDMS-PU copolymer. IR spectroscopy showed the assignment characteristic groups of each peak in copolymers and confirmed that the desired HTPDMS-PU copolymers have been prepared. The different thermal, dynamic mechanical and surface properties of the copolymers were compared by thermogravimetry, DMA, contact angle and solvent resistance. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2152–2160, 2013

INTRODUCTION

Polysiloxanes are the major representatives of a class of polymers having inorganic main chains. Linear low molar mass polydimethylsiloxanes (PDMS) with the simples repeating unit $(CH_3)_2SiO$ which incorporates siloxane bonds, impart superior flexibility, and heat resistance as well as resistance to oxidative damage by oxygen or ozone. The main advantages of PDMS are stability from UV, hydrophobicity, thermostability, low coefficient of friction, good gas permeability, and biocompatibility.[1–5] PDMS is nonpolar owing to the methyl groups set outside the siloxane chain and it has uniformly positive partial charge ($\delta+$) in all directions. The methyl groups in PDMS are able to form a highly hydrophobic cover at the polymer-air interface, yielding a low surface energy. The increased interest in multiphase copolymers based on PDMS is mainly due to their unique combination of properties being related to their chemical structure and macromolecular architecture.[6–10]

Polyurethane (PU) materials are known to offer high performance due to toughness, abrasion resistance, mechanical flexibility and chemical resistance.[11–13] Repeating unit in PUs is the urethane link produced from the reaction of an isocyanate (—N═C═O) with an alcohol (—OH). The modification of PU with low surface energy polymers has attracted much attention and many useful improvements in the bulk and surface properties of PU copolymers has been achieved.[14–16] Although PUs display resistance to solvents and excellent mechanical properties, their tensile strength decreases sharply if the external temperature exceeds 80°C. Thus an excessively high processing temperature results in thermal degradation.[5] In many cases, the flexibility available in the selection of raw material components has made it possible to custom tailor the properties of PUs.

Therefore, PDMS can be utilized in the synthesis of PU block copolymers as a soft segment. The resulting siloxane-containing copolymers displayed good thermal and mechanical properties owing to the strength of the hydrogen bonding between the hard segments in a "hard-soft" system. PDMS-based segmented PU copolymers have been prepared and a comprehensive study made of their interesting phase-separated microstructures. Excellent biostability and biocompatibility were achieved. The presence of PDMS would enrich the copolymer surface and

improves other desirable characteristics such as water and oil resistance.[4,17–20] So, the PU blocked PDMS copolymers possess the excellent properties of hydroxypropyl terminated polydimethylsiloxane (HTPDMS) and PU which presents better water resistance, flexibility at low temperature, and thermal property. Thus, PU block copolymers through HTPDMS modified can be widely applied in many areas including industry, construction industry, and so forth. In general, to decrease the degree of phase separation between PU and PDMS, the PDMS content was not very high. A few research works were reported on PU incorporated very high content of PDMS because of bad compatibility between the two kind polymers. So in our work, we prepared a series of copolymers and varied the HTPDMS contents from 0 to 100% (i.e., there was only HTPDMS in the soft segment) to compare their properties.

This study describes the way to synthetize HTPDMS-PU copolymers with prepared HTPDMS (MW 990) and polyether diols (N-210) as mixed soft segment and test the properties at different contents of HTPDMS. The copolymers were prepared via polymerization of mixed soft segment with isocyanate (MDI), and then incorporate 1,4-butanediol (BDO) as chain extender to the noted prepolymer. Infrared radiation (IR), Thermogravimetry (TG) were used to investigate the HTPDMS molecular weight and microstructure of the copolymers. Measurement of water contact angles, water and oil absorption on the copolymer films were done to confirm the physical properties. The effects of HTPDMS content in soft segment on thermal, dynamic mechanical properties and solvent resistance were discussed.

EXPERIMENTAL

Materials

Allyl alcohol, trimethyl chlorosilane, Chengdu Kelong Chemical Reagent Factory. Hexamethyldisilazane (HMDS), tetramethyldisiloxane, octamethyl cyclotetrasilazane (D4), China Bluestar Chengrand Chemical Co, Chloroplatinic acid, Shenyang Research Institute of Nonferrous Metals. Allyl. Alcohol was dried before using.

4,4′-diphenylmethane diisocyanate (MDI), Yantai Wanhua PU Polyether diols (N-210 MW 1000), China Bluestar Chengrand Chemical, BDO, Chengdu Kelong Chemical Reagent Factory. Hydroxypropyl terminated polysiloxane (MW 990), homemade. Polyether polyol and hydroxypropyl terminated polysiloxane dehydrated for 2 h under a vacuum of 0.096 Mpa. BDO was dried before using.

Synthesis of HTPDMS

Allyloxytrimethylsilane (ATMS) was prepared with HMDS and allyl alcohol. The ATMS reacted with tetramethyldihydrodisiloxane to generate 1,3-bis(3-hydroxypropyl)-1,1,3-tetramethyl disiloxane (BHTS) by alcoholysis reaction. Under catalyzing of trifluoromethanesulfonic acid, BHTS reacted with octamethyl cyclotetrasiloxane (D4) to prepare hydroxypropyl terminated polydimethylsiloxane (HTPDMS) after equilibrium reaction.[21–24] The proposed reaction pathway is presented in Scheme 1.

Excess HMDS (181 g) was added dropwise to allyl alcohol (87 g) in four-neck flask equipped with stirrer, thermometer, reflux
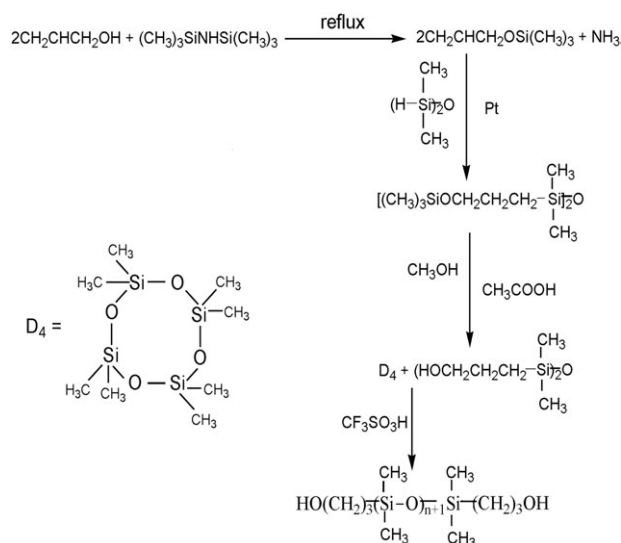
Scheme 1. Synthesis of hydroxypropyl terminated polydimethylsiloxane (HTPDMS).

condenser tube and constant pressure dropping funnel. Raised temperature to 102°C after reflux 120 h and collected fraction below 99°C using Vigreux column. Yield: 100%, purity: 85%, refractive index $(-n_D^{25})$: 1.3940.

Incorporated the prepared ATMS (76.5g) and appropriate chloroplatinic acid/isopropanol catalyst and then heated to 90°C. Reaction was carried out in a four-neck flask equipped with stirrer, thermometer, reflux condenser tube, and nitrogen inlet. Added tetramethyldihydrodisiloxane (55 g) slowly to the above reaction system, after reacting for 6 h, the reaction mixture was heated to 110°C for a period of 4 h. 1,3-bis(3-trimethyl silicon oxy-propyl)tetramethyl disiloxane (BTTS) was distilled in a vacuum of 0.096 MPa under 160°C, removing non-reacted low boiling point products by reduced pressure distillation. Yield: 75%, refractive index $(-n_D^{25})$: 1.4243.

The BTTS (39.6 g) was placed in a three-neck flask equipped with stirrer, thermometer, reflux condenser tube. Added 6 mL acetic acid and 10 mL methanol into the flask and then reflux for a period of 10 h under 66°C. To remove the excess methanol, acetic acid and other byproducts by vacuum distillation and obtain 22.5 g BHTS. Yield: 90%, refractive index $(-n_D^{25})$: 1.4461.

Hundred microliter trifluoromethanesulfonic acid was added to a three-neck flask containing 100 g D4 and 75 g BHTS. Reaction was carried out at 85°C for 25 h with stirring. The HTPDMS was prepared after removing low molecular weight byproducts and nonreacted D4 in a vacuum of 0.096 MPa under 150°C.

Synthesis of HTPDMS-PU Copolymer

A mixture of HTPDMS and N-210 reacted with MDI to form —NCO terminated prepolymer, and then incorporated BDO to expand macromolecule chains. The proposed mechanism reaction is presented in Scheme 2. Measured HTPDMS and N-210 were placed in a three-neck flask equipped with stirrer, nitrogen inlet and a dropping funnel after dehydration. Measured MDI was added to the flask over a period of 1 h under a slow stream
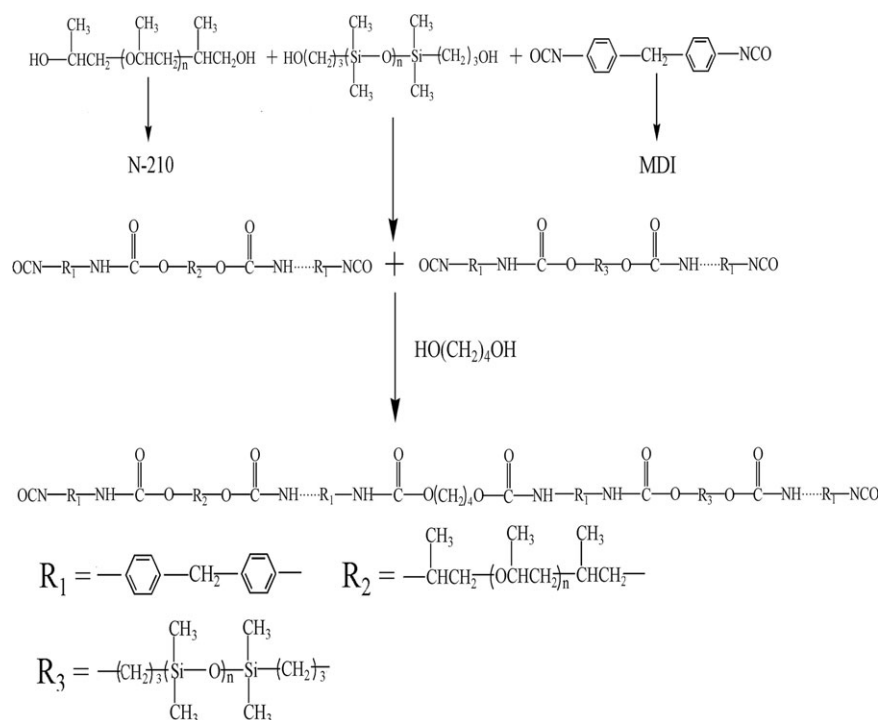
Scheme 2. Synthesis of HTPDMS-PU copolymer.

of dry nitrogen. After the addition was over, the reaction mixture was heated to 80°C for 1 h under a vacuum of 0.096 Mpa with stirring. After deaeration for 15 min, measured dried BDO was added to the prepolymer and deaerated for 7 min. Then poured it onto an aluminum foil mould quickly and cured for 24 h under 100°C.

Prepared copolymers are designated as Co-X, where X denotes the molar percentage of HTPDMS in the soft segment. For instance, Co-20 refers to the copolymer containing 20% HTPDMS in the soft segment. The molar ratios of each compositions are shown in Table I.

CHARACTERIZATION

^{1}H-NMR was performed on DPX300 NMR spectrometer of Switzerland Bruker Biospin Corporation (CDCl3 as solvent).

IR was measured on 170SX FT-IR Spectrometer of Thermonicolet Corporation, using attenuated total reflection.

Refractive index was performed on 2WA-J Abbe refractometer (test temperature 25°C).

Water contact angle samples were measured on an OCA series of contact angle measuring device (Dataphysics Corporation), and the average value of five points measurements were taken at room temperature.

Sliced samples were soaked in deionized water and standard oil respectively for 7 days at room temperature, samples removed and surfaces wiped with filter paper. Water absorption ratio, oil absorption ratio $= (W - W_0)/W_0 \times 100\%$, where W_0 and W represent the film weight before and after deionized water and

standard oil absorption, respectively. For each film with different HTPDMS contents, at least six measurements were taken.

Thermogravimetry analysis (TGA) was performed on a Q50 thermogravimetric analyzer (Perkin-Elmer Corporation): heating rate 20°C/min, nitrogen atmosphere, nitrogen flow rate 50 mL/min with testing temperature from room temperature to 800°C.

Dynamic thermomechanical analysis (DMA) was tested on a Q800 Dynamic Mechanical Analysis: heating rate 5°C/min, test frequency 40 HZ with range of testing temperature from −120 to 120°C in compressed mode.

RESULTS AND DISCUSSION

NMR Characterization of HTPDMS
^{1}H-NMR was measured to characterize the structure of HTPDMS and intermediate products in synthetic reaction. The ^{1}H-NMR spectras are showed in Figure 1. In the ATMS spectra,

Table I. Molar Ratios of MDI, HTPDMS, and N-210 in the Series Copolymers

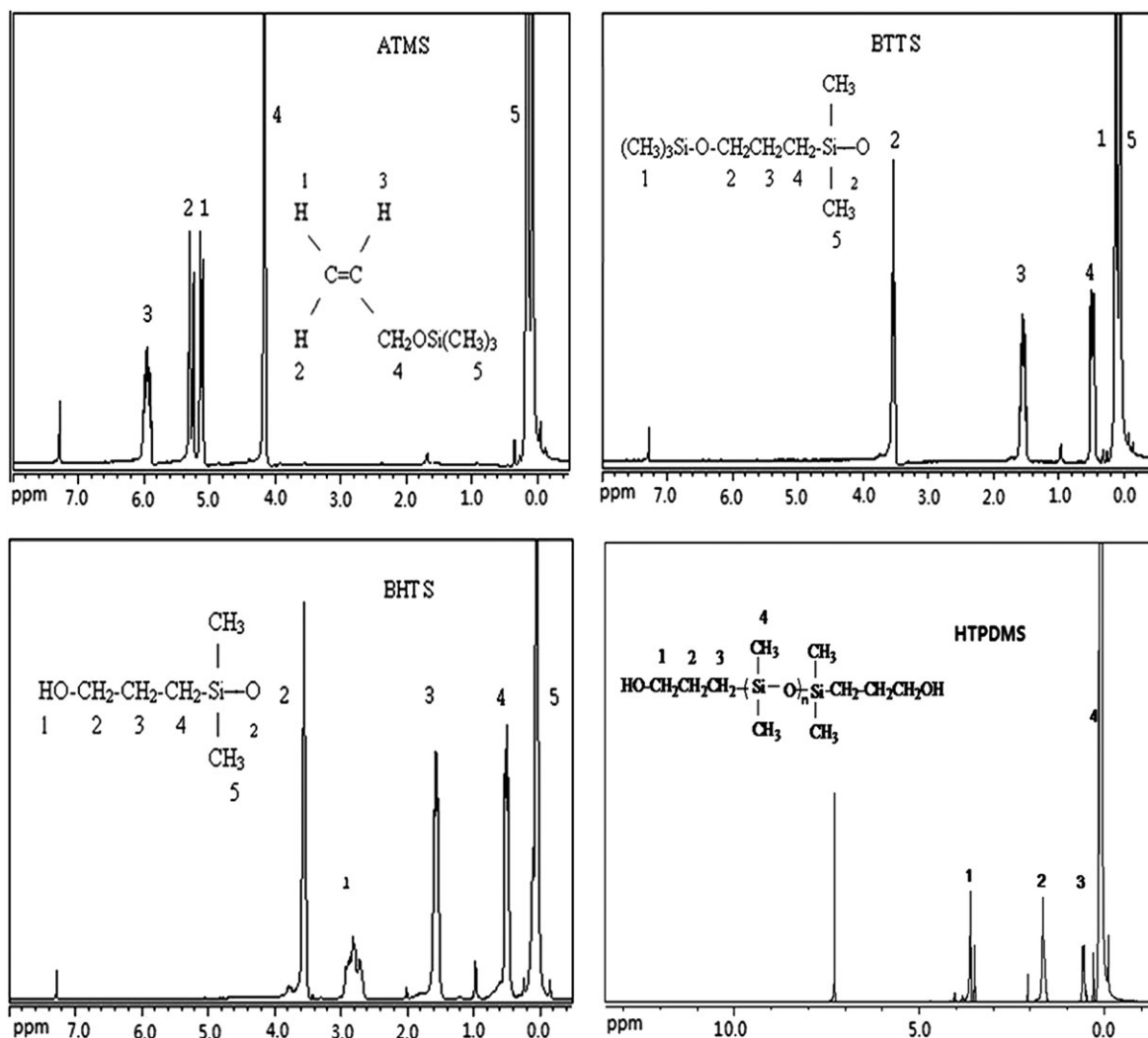| Sample code	MDI : HTPDMS : N-210 (molar ratio)	HTPDMS : N-210 (molar ratio %)
Co-0	2 : 0 : 1.02	0 : 100
Co-20	2 : 0.19 : 0.81	20 : 80
Co-40	2 : 0.4 : 0.62	40 : 60
Co-60	2 : 0.61 : 0.4	60 : 40
Co-80	2 : 0.82 : 0.21	80 : 20
Co-100	2 : 1 : 0	100 : 0

Figure 1. ^{1}H-NMR spectras of ATMS, BHTS, BTTS and HTPDMS.

the methyl containing proton 5 is connected to —Si, according to the peak value, it can be determined that the proton is located at 0.13 ppm. The methylene containing proton 4 is connected to oxygen and C—C bond and its chemical shift is near to 4.0 ppm, so it should be assignable to 4.14 ppm. Signals from 5.0 to 6.0 ppm are assignable to the hydrogen on C=C bond which were corresponding protons 1, 2, and 3. The assignment peaks were marked in spectra. As shown in H-NMR spectra of BTTS, the corresponding chemical shift of characteristic protons were marked. Signals of 0.5, 1.6, and 3.8 ppm in the spectrum are assignable to the three CH_2 groups respectively, this further confirming additional reaction and indicated that the desired product 1,3-bis(3-trimethyl silicon oxy-propyl) tetramethyl disiloxane (BTTS) has been synthetized. The analysis of the spectra about BHTS shows the assigned protons of each peak and the proportion is 1 : 2 : 2 : 2 : 6. It confirmed that BHTS has been prepared through alcoholsis and product structure was as expected. Hydrogen proton in hydroxyl is active so it can form hydrogen bonds and exchange reaction. Its chemical shift may change within limits and hard to determine.

As shown in HTPDMS spectra, protons 1, 2, 3, 4 were assigned to 3.7, 1.6, 0.55, and 0.1 ppm, respectively, and its structure after NMR characterization was as expected.

IR Characterization of HTPDMS-PU Copolymer
The IR spectrum of copolymer at different HTPDMS contents are shown in Figure 2. The corresponding group of —NCO disappeared at the location of 2270 cm^{-1} indicating that the monomers have been polymerized. The bands in 3301 and 1727cm^{-1} belong to N—H and C=O groups in urethane of IR spectra of Co-0. To compare the IR spectra of the copolymers, we first normalized all to the absorbance of the N—H stretching vibration at 3301 cm^{-1}. The copolymers have the same hard segment chemistry and content, and the N—H stretching peak should consequently have the same intensity for each.[20] According to Hermandez et al,[25–27] comparison of the relative absorbance of strong hydrogen-bonded, loose hydrogen-bonded and non-hydrogen-bonded carbonyl groups in the different materials, proved that the quantity of hydrogen-bonded carbonyls can be related to the extent of hard segment bonding in hard
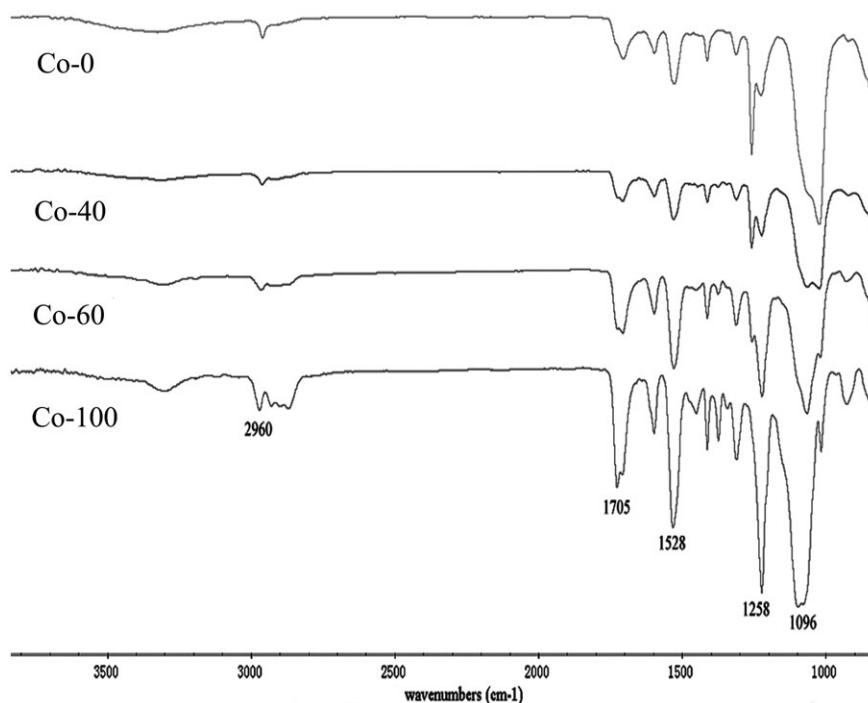
Figure 2. IR spectra for mixed soft segment in copolymers Co-0, Co-40, Co-60, and Co-100.

domains. The stretching vibration peak observed at 1727 cm^{-1}, can be attributed to C=O group in polyurea, however, N—H group in polyurea was not obvious because of low PU content. In Figure 2, the broad peak should be N—H synthetic peak of polyurea and urethane at the location of 3327cm^{-1}. The peak at 1705 cm^{-1} should belong to C=O group in urethane, however, the corresponding peak of C=O group was not detected clearly in the spectrum may be on account of the peak's movement to low band and merging near 1705cm^{-1}. From the IR spectrum, the molecular structures of copolymers have been confirmed and the desired copolymers have been synthesized. In spectra of Co-100, C=H group in Si—CH$_3$ at 1258 cm^{-1} was not detected in spectra of Co-0 because the sample without HTPDMS. In addition, the absorption peaks at 3301 and 3327 cm^{-1} [v (NH)], 2971 and 2960 cm^{-1} [v (CH$_3$)], 1727 and 1705 cm^{-1} [v (C=O)], 1096 cm^{-1} [v (C—O—C)], are the typical absorption peaks for the spectra of PU. Compared with the spectrum of PU without HTPDMS in Co-0 spectra, the peaks at 1023 cm^{-1} [v (Si—O—Si)] can be detected clearly as in Co-100 spectra.

TG Study of Copolymer

In several studies it has been concluded that the first and second stages of degradation of PU copolymers are related to the degradations of the hard and soft segments respectively. As shown in Figure 3, all the samples there are two notable decomposition peaks, namely, the peaks of hard segment (320–360°C) and soft segment (390–510°C). The temperature of maximum peak (T_{max}) in each stage of degradation corresponds to the degradation temperature of the maximum rate at this stage, therefore, each region of a degradation stage can be determined from the T_{max} peaks corresponding to the regions of weight loss and temperature.[28,29] Compared with the other PU-PDMS

copolymers,[30,31] the temperature distribution of the copolymers prepared in this paper tend to be much narrower. In Figure 3, the first stage (320–360°C) displays much less temperature change while the derivative weight increased with increasing of HTPDMS content in soft segment. The temperature changes of second stage (390–510°C) are relatively significant while the derivative weight decreased. The first degradation stage of these copolymers at 320–360°C is mainly because of depolymerization of the urethane groups. After heated in N$_2$, the groups in the hard segment degrade to form isocyanate and carbon dioxide. Conversely, HTPDMS could degrade at low temperature because of its end groups, therefore, the increased of derivative weight may be due to the degradation of hydroxypropyl in
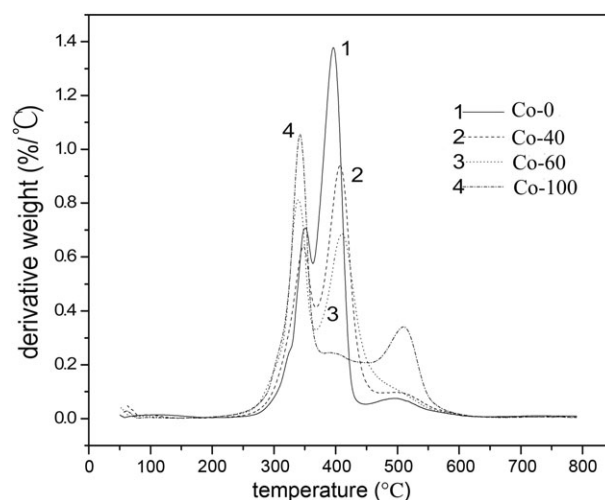

Figure 3. TG curve of copolymer at different HTPDMS contents.

Table II. Corresponding Temperature of Different Weight Loss Ratio at Different HTPDMS Contents

Sample T (°C)	Weight loss ratio (%)													
	0.5	1	1.5	2	3	5	10	15	20	30	40	50	60	75
Co-0	96	133	203	272	298	316	335	344	351	368	381	389	396	409
Co-20	84	123	220	262	286	303	321	331	340	359	379	396	403	430
Co-40	87	180	253	271	288	303	321	331	340	359	380	374	404	433
Co-60	94	191	241	261	280	295	316	326	333	346	371	393	409	439
Co-80	242	264	276	284	294	305	320	328	334	345	371	393	413	454
Co-100	132	226	250	264	279	295	313	323	330	339	352	389	434	496

HTPDMS.[31,32] The second degradation stage at 390–510°C has been ascribed to decomposition of soft segment including HTPDMS and N-210. In the second stage, as the HTPDMS content increased of soft segment (N-210 content decreased), the T_{max} increased while the derivative weight decreased. This should be attributed to the higher thermal stability of the HTPDMS component and increasing of HTPDMS will greatly enhance the decomposition temperature of the mixed soft segment because of its decomposition temperature is over 500°C. So, incorporation of HTPDMS to the copolymer could improve the thermal stability.

In Table II, the corresponding temperatures at different contents of HTPDMS showed a rising trend when the weight loss ratio is between 0.5 and 1.5%, this section is mainly caused by decomposition of water and low molecular weight substances in the copolymer. As HTPDMS content increased, its water resistance and surface stability of the copolymers would improve at some level. In the section of weight loss ratio between 2 and 50%, the corresponding temperatures under the same ratio presented a downward trend with the increase of HTPDMS content. This may be due to poor thermal stability of hydroxypropyl end groups in HTPDMS, and through analysis can be found that it mainly occurred in the hard segment decomposition section. So, the decomposition of the hard segment take the lead in this process. In the section of weight loss ratio over 50%, the soft segment in copolymer decomposed. Its thermal-decomposition temperature rose significantly indicating improvement of copolymer heat resistance. Thus, which is agreeing with the conclusion of TG curve. Table III shows residues change of the copolymers with different HTPDMS contents at 800°C. The residual mass of sample Co-0 was 7.4% and Co-100 was 10.3%. In inert

atmosphere such as nitrogen, polydimethylsiloxane degraded by depolymerization. The depolymerization process is a conjunction of three different reaction mechanisms, named "unzipping," "random scission," and "externally catalyzed," respectively.[33,34] When the polymer is heated, its viscosimetric molecular weight sharply increases first, further increasing the temperature leads to a decrease of the polymer molecular weight. Silanol functions can "back-bite" to promote intramolecular redistribution reactions which generate low molecular weight cyclic siloxanes. When polymers are exposed to high enough temperatures, the thermal degradation of PDMS results in the formation of small cyclic products. So, the HTPDMS in soft segment degraded in nitrogen atmosphere mainly result in low molecular weight cyclic siloxanes while the part of polyether diols tend to generate several volatile and gaseous.[35–38] That is the major reason why the results show that the residual masses of the Co-0 was lower compared to Co-100.

DMA

The storage modulus and mechanical loss factor (tan δ) for the copolymers are presented in Figures 4 and 5. The storage modulus undergoes a large drop and then levels off, corresponding to a transition of the polymers from glassy state to a rubbery state. The decrease in the storage modulus with increase in the

Table III. Residual Masses of Copolymers at 800°C

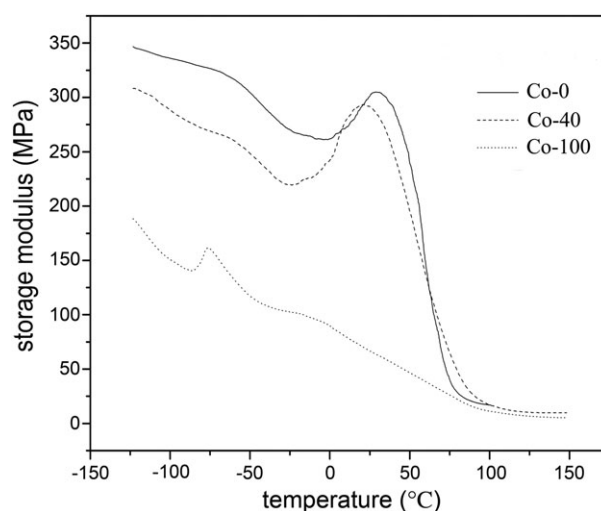| Sample	Residual mass(%)
Co-0	7.426
Co-20	11.39
Co-40	11.93
Co-60	9.649
Co-80	10.47
Co-100	10.31

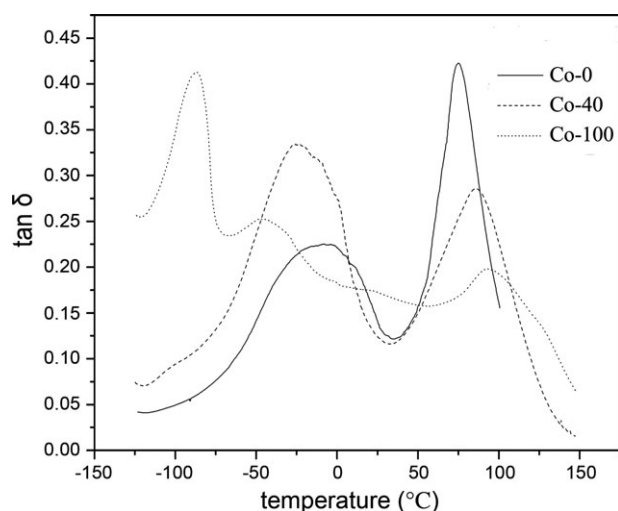**Figure 4.** Storage modulus of copolymer at different HTPDMS contents.

Figure 5. Loss factor (tan δ) of copolymer at different HTPDMS contents.

concentration of HTPDMS contents in soft segment was observed in Figure 4. It can be seen that the copolymer with less HTPDMS displays higher storage modulus. At -100 to $-75°C$, most of N-210 soft segment of copolymers at such temperatures are in glass state while most of the HTPDMS soft segments in copolymer are in a leather state so that Co-100 displays lower storage modulus. As storage modulus is a measure of material stiffness, the difference of storage modulus is related to the mechanical property of materials.[13] Beyond $80°C$, the storage modulus values for the copolymers close to 0, indicating that the mechanical properties are unsatisfactory for their application. The storage modulus values for Co-0 and Co-40 display a two-stage drop at -125 to $-25°C$ and 25 to $75°C$, but the values increased at $-25–25°C$. The decrease of storage modulus with increasing HTPDMS content may be attributed to the HTPDMS which reduces the interchain interactions and interrupts the PU hydrogen bonding formation.[39] The high steric hindrance of the HTPDMS soft segments inhibit the formation of intermolecular hydrogen bonds between the urethane hard segments. Notably, the modulus values of Co-0 and Co-40 increase at $-25–25°C$. The reason for this change may be related to urethane hard segment are easy to form hydrogen bond with N-210 soft segment compare to HTPDMS soft segment difficult to form hydrogen bond with it. High N-210 contents for copolymer imply that they have strong hydrogen bonding between them. Moreover, the storage modulus above $50°C$ quickly diminish due to the destruction of hydrogen bonding. The storage modulus curves of samples Co-0 and Co-40 showed broad peaks. This might due to the phase separation of N-210 in soft segment with HTPDMS and PU matrix phases. The discussion above propose that the incorporation of HTPDMS may not be enough to improve the mechanical properties alone, however, the interaction of polymers and their functional groups are all highly dependent.[40–43]

The loss factor tan δ is a measure of the energy dissipation and very sensitive to the structural transformation of the material. Therefore, tan δ data give an indication of the characteristic

behavior of macromolecular chain motion, such as the phase-transition region of the polymer and interactions of the macromolecular chain. The dynamic relaxation are more evident in the tan δ plots in Figure 5, there are two distinct transitions, the two curves of Co-0 and Co-40 indicating the addition of HTPDMS has no significant influence on the phase behavior of PU. These two peaks indicate that there were two different types of aggregations arising from the HTPDMS with N-210 and PU. The corresponding temperature of the peaks at $50–100°C$ show previously to be associated with the segmental relaxation of a mixed soft phase consisting of HTPDMS end group segments and some dissolved hard segments. The tan δ peak can be used to identify T_g of these composites, the T_g value of HTPDMS-PU copolymer depends on the nature of the interactions of the HTPDMS with the PU matrix, namely the organic groups especially the functionalities of HTPDMS. The high interaction between polymer matrices and the copolymer aggregates presents high T_g and the less interaction parts showing low T_g.[44–48] Through the DMA analysis, we would like to suggest that the copolymer occupies into separate domains in the polymer matrices because of the poor compatibility of HTPDMS with PU and the formation of a high order amorphous phase containing urethane group by phase mixing.

Water Contact Angle and Solvent Resistance

Table IV lists the water contact angle and solvent resistance of copolymer at different HTPDMS contents. The contact angle tend to become large with increasing HTPDMS content. It indicates that HTPDMS has changed the surface properties of samples so that surface tension decreases and contact angle increases. This could be attributed to the low surface energy of the HTPDMS end groups which are enriched on the surface of the copolymer film and form a hydrophobic surface. Copolymer surface has been able to basically cover and saturate when HTPDMS content reached to 20%, so HTPDMS has low impact to the copolymer contact angle above this point. According to Fatima et al.,[4] higher siloxane intensities of copolymers indicated that the surface enrichment is due to the greater freedom and mobility of the short siloxane chains. These short siloxane chains can migrate to the surface of a copolymer film and form a more uniform hydrophobic layer with higher contact angles than is the case with longer siloxane chains.

PU displays good oil resistance while HTPDMS presents poor oil resistance and good hydrophobic. From Table III, the water

Table IV. Contact Angle, Water Absorption Ratio, and Oil Absorption Ratio at Different HTPDMS Contents

Sample	Contact angle (°)	Water absorption (%)	Oil absorption (%)
Co-0	78	1.07	0.25
Co-20	101	0.78	0.35
Co-40	100	0.65	0.42
Co-60	103	0.58	0.47
Co-80	104	0.51	0.54
Co-100	104	0.28	0.59

absorption decreased while the oil absorption increased with increasing HTPDMS content in soft segment. This is due to the hydrophobicity of the HTPDMS molecules.[49,50] Overall, the water resistance of copolymer can be improved by increasing HTPDMS content in soft segment. On the other hand, oil resistance tend to decrease with increasing HTPDMS content. Actually, it is not easy to prepare waterborne PU with a relatively low concentration of the ionic moiety. So, it is important to adjust the water resistance and dispersion stability of waterborne PU by the subtle control of the content of HTPDMS and N-210. It can be concluded that by introducing hydrophobic HTPDMS into soft segment of PU chains, the water-resistance can be enhanced notable. Copolymer with excellent water and oil resistance can be prepared by regulating content of HTPDMS in soft segment.

CONCLUSIONS

This study shows the HTPDMS-PU copolymer which were obtained from the polymerization reaction of PU with HTPDMS totally different from the starting polymers in terms of structural, thermal, and surface properties. From the ^{1}H-NMR and IR spectroscopy, molecular structures of HTPDMS and the series of copolymers have been confirmed. The TG curves of all copolymers display two stages of degradation at 320–360°C (stage 1) and 390–510°C (stage 2) which are associated with the urethane hard segment and HTPDMS and N-210 mixed soft segment. The thermal stability between 320 and 360°C did not improve with increasing HTPDMS, whereas in the region 390–510°C it improved. The TGA thermograms revealed that the thermal stablility depended on both the urethane groups and the HTPDMS compound. The DMA results indicate HTPDMS has significant influence on PU chains and demonstrate the soft segment of the HTPDMS consists of N-210 and some other hard segments. Incorporation of HTPDMS may not be enough to improve the mechanical properties alone, but the interaction of polymers and their functional groups are all highly dependent. In addition, the storage modulus values of Co-0 and Co-40 increase at −25–25°C may be associated with that the copolymers display strong hydrogen bonding when the N-210 play a dominant role in the soft segment. Higher storage modulus at 0–25°C represents better mechanical property and better to be applied under normal temperature. The obtained copolymer proved to possess higher contact angle and better water resistance when HTPDMS content was higher than 20%. So the synthetic reaction of PU with HTPDMS represents a rapid and convenient method for the preparation of hydrophobic copolymer surface.

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