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Organosilicon leather coating technology based on carbon peak strategy

Wenkai Wang¹, Haojun Fan^{1*}, Lijiang Song², Zhenya Wang¹, Heng Li¹, Jun Xiang¹, Qiang Huang³ and Xiangquan Chen³

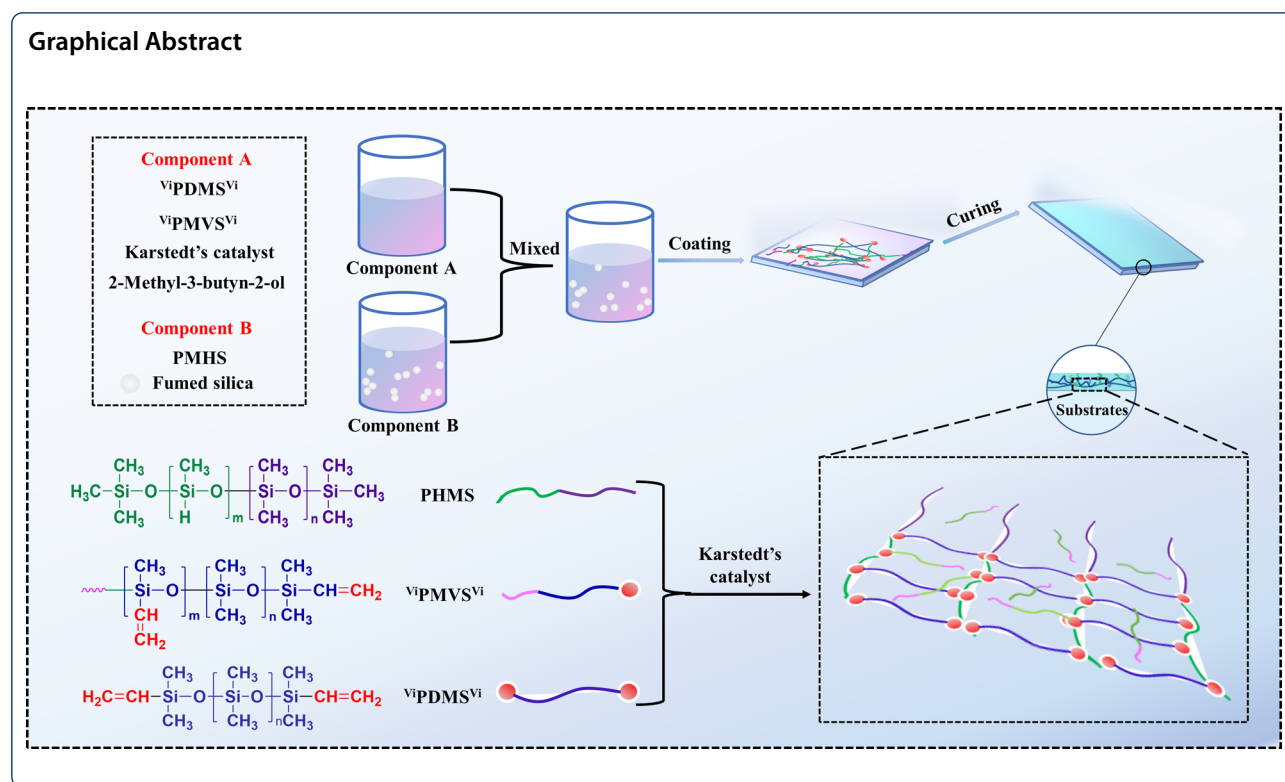
Abstract

Based on the demand of carbon peak and carbon emission reduction strategy, divinyl-terminated polydimethylsiloxane (^{vi}PDMS^{vi}), poly(methylhydrosiloxane) (PMHS), divinyl-terminated polymethylvinylsiloxane (^{vi}PMVS^{vi}), and fumed silica were used as primary raw materials, polydimethylsiloxane (PDMS) synthetic leather coating was in situ constructed by thermally induced hydrosilylation polymerization on the synthetic leather substrate. The effect of the viscosity of ^{vi}PDMS^{vi}, the active hydrogen content of PMHS, the molar ratio of vinyl groups to active hydrogen, the dosage of ^{vi}PMVS^{vi} and fumed silica on the performance of PDMS polymer coating, including mechanical properties, cold resistance, flexural resistance, abrasion resistance, hydrophobic and anti-fouling properties were investigated. The results show that ^{vi}PDMS^{vi} with high vinyl content and PMHS with low active hydrogen content is more conducive to obtaining organosilicon coating with better mechanical properties, the optimized dosage of ^{vi}PMVS^{vi} and fumed silica was 7 wt% and 40 wt%, respectively. In this case, the tensile strength and the broken elongation of the PDMS polymer coating reached 5.96 MPa and 481%, showing reasonable mechanical properties for leather coating. Compared with polyurethane based or polyvinyl chloride based synthetic leather, the silicon based synthetic leather prepared by this method exhibits excellent cold resistance, abrasion resistance, super hydrophobicity, and anti-fouling characteristics.

Keywords: PDMS polymer coating, Synthetic leather, In situ hydrosilylation, Coating performance, Carbon peak strategy

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1 Introduction

From the occurrence of the first generation of polyvinyl chloride (PVC) synthetic leather to the rapid development of the second generation of polyurethane (PU) synthetic leather, and then to the widespread use of the third generation of microfiber synthetic leather, whose appearance and performance are closer to natural leather [1–4], synthetic leather has completed its transformation from simple imitation to high simulation and occupied a significant position in people's daily life [5].

Up to now, solvent-based polyurethane has been used for coating in the traditional synthetic leather manufacturing process, and the annual consumption is about 2 million tons in China. The use and emission of a large number of organic solvents not only cause carbon emission but also bring serious environmental pollution [6]. At the same time, diisocyanate and polyol, the main raw materials used in polyurethane, are derivatives of the petroleum industry. With the increasing depletion of petroleum resources, the global petrochemical industry chain faces great challenges [7–9]. Therefore, how to develop novel coating materials to replace carbon based and petroleum based raw materials based on the demand of carbon peak and carbon emission reduction strategy has become an inevitable trend in the development of the synthetic leather industry.

In a narrow sense, organosilicon refers to polysiloxane, which is obtained from silicon ore in the earth's crust [10]. Organosilicon polymer has the characteristics of easy film formation, good aging resistance, high and low-temperature resistance, solvent resistance, flame resistance, hydrophobicity, insulation, and so on. According to the principle of polymer reaction injection molding (RIM) [11], organosilicon coating can be prepared by an in situ hydrosilylation reaction. First, the liquid raw materials of ${}^{\text{vi}}\text{PDMS}^{\text{vi}}$ (component A) and PMHS (component B) are directly coated on the surface of release paper after high-speed mixing, and then the in situ reaction of components A and B is induced under thermal induction to form polymer coating. Finally, this coating with an adhesive layer is transferred to the synthetic leather substrate and further dried to obtain organosilicon synthetic leather. There is no need to use any organic solvent, no water consumption and no by-products in the preparation process, the problems of long process flow and high volatile organic compounds (VOCs) emission of traditional synthetic leather will be alleviated. At present, silicones are primarily used in the field of leather manufacture in the form of additives such as water repellents [12], lubricating agents [13], and hand feeling agents [14], while few research has been conducted on silicones as leather coating materials themselves. Therefore, this paper intended to prepare polydimethylsiloxane (PDMS)

polymer coating by in situ hydrosilylation reaction in the thermally induced catalytic system, which is bonded with the substrate to prepare PDMS synthetic leather. At the same time, by exploring the effect of each component in the system on the tensile strength, elongation at break, and hardness of the coating film, the optimized regulation of physical properties of PDMS polymer coating was achieved. As the world's largest producer of organosilicon, China's organosilicon industry has an excellent overall development form [15], which provides a mature organosilicon supply chain for the development of related industries, and also makes silicon based synthetic leather have a good industrialization prospect.

2 Experimental

2.1 Materials

Divinyl-terminated polydimethylsiloxane (Vi PDMS Vi), with the viscosity and vinyl groups mass fraction: 10,000 mPa s/0.12%, 30,000 mPa s/0.07%, 50,000 mPa s/0.06%, 80,000 mPa s/0.04%, recorded as η -10,000, η -30,000, η -50,000 and η -80,000), divinyl-terminated polymethylvinyl-siloxane (Vi PMVS Vi), with the vinyl groups mass fraction of 2.30%), poly(methylhydrosiloxane) (PMHS, with the active hydrogen mass fraction 0.09%, 0.18%, 0.82%, 1.60%, recorded as PMHS-0.09, PMHS-0.18, PMHS-0.82 and PMHS-1.60) were obtained from Chen Guang Research Institute of Chemical Industry (Chengdu, China). Karstedt's catalyst [platinum (0)-1, 3-divinyl-1,1,3,3-tetramethyl disiloxane complex, Pt~2%], 2-Methyl-3-butyn-2-ol and diiodomethane were purchased from Tansoole Technology Co. Ltd. (Shanghai, China). Fumed silica was supplied by Evonik Industries AG (Germany). Adhesive was obtained from Dow Chemical (America). PU synthetic leather (CF-02501) was purchased from Changfeng New Material Co. Ltd. (Lishui, China). PVC synthetic leather (ZL-2007) was acquired from Zhen-glong Leather Co. Ltd. (Dongguan, China).

2.2 Preparation of PDMS polymer film

First, Vi PDMS Vi , Vi PMVS Vi , Karstedt's catalyst, and 2-Methyl-3-butyn-2-ol were added to a flask fitted with a mechanical stirrer. After stirring them evenly, PMHS and fumed silica were added with complete mixing, then the mixture was coated on a release paper by an automatic coating machine. The thickness of the mixture is about 0.7–1.0 mm. After completion, the release paper loaded with organosilicon slurry was heated and cured in an oven at 120–130 °C for 10–15 min to obtain PDMS polymer film. Then, the prepared PDMS polymer film was placed in an oven at 70–110 °C and continued to be cured

for 5–10 min to form a continuous and uniform film. The synthetic route and preparation process of PDMS polymer film were outlined in Fig. 1.

2.3 Preparation of PDMS synthetic leather

Similar to the traditional synthetic leather making process, the dry transfer coating method is employed to prepare PDMS synthetic leather, in which release paper was used as a carrier, and the process flow was outlined in Fig. 2. Evenly coated the mixed slurry prepared in 2.2 on the release paper, heated and cured the organosilicon slurry in an oven at 120–130 °C for 10–15 min, then coated with organosilicon adhesive, and heated at 120 °C for 3–5 min. When the adhesive was in a state of half dry, pressed the PDMS polymer coating with the substrate, and placed it in an oven at 120 °C for 10–15 min. Finally, the release paper was peeled off, and the PDMS synthetic leather was obtained.

2.4 Characterization

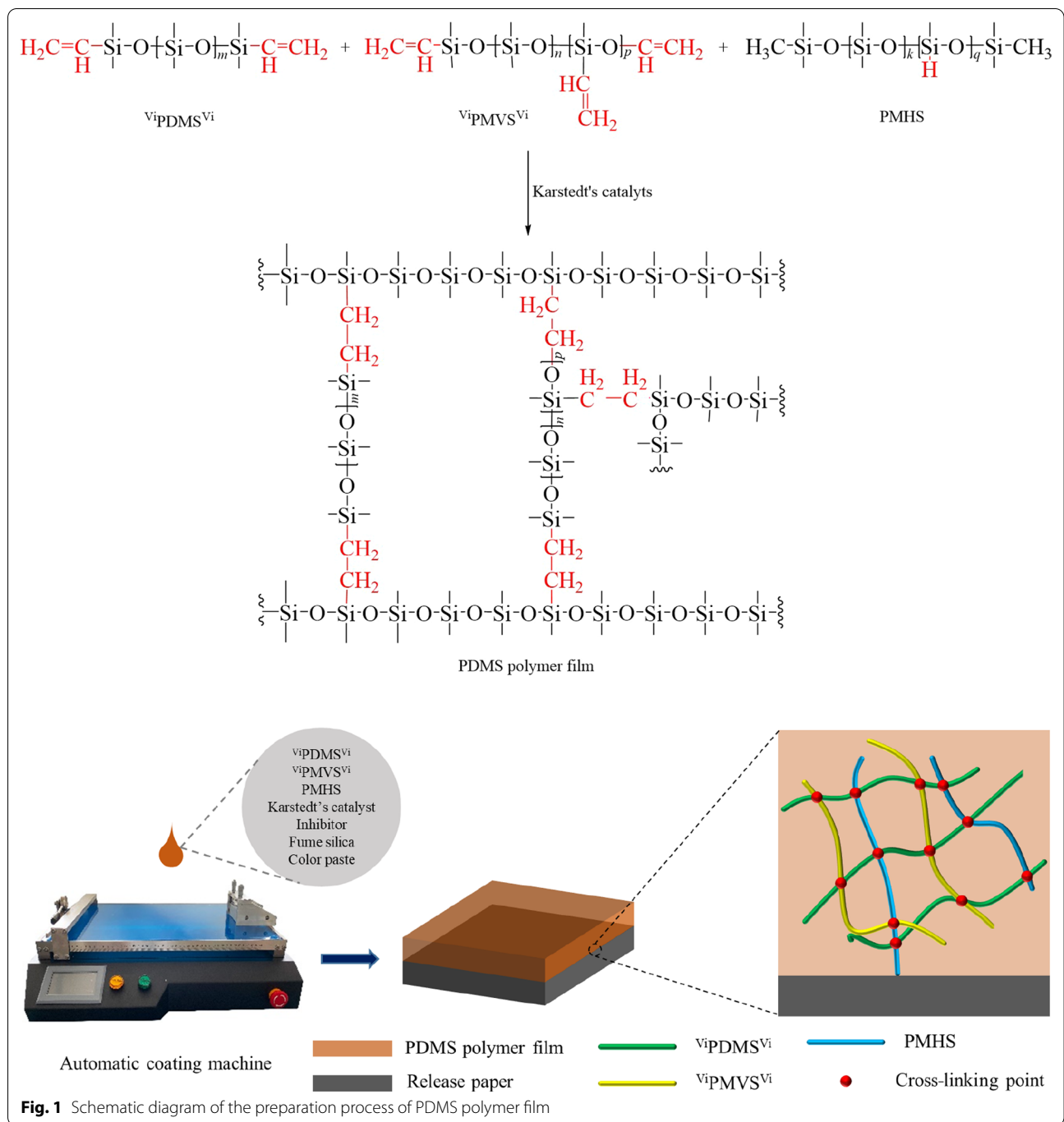
Fourier transform infrared (FT-IR) spectra were collected on an IS10 FT-IR spectrometer (Thermo Scientific, United States) using KBr pellets over the wavenumber range from 4000 to 400 cm^{-1} .

Mechanical properties tests were measured using an Electronic Universal Testing Machine UTM6203 (Jinan, China). Cast films were cut into micro-tensile specimens 50 mm in length and 10 mm in width. The specimens were elongated at a 50 mm/min rate at 25 °C.

The hardness of PDMS polymer coating was characterized by Shore A hardness tester LX-A (Shanghai, Chain). According to GB/T 531.1-2008, the PDMS polymer coating was made into a film with a thickness of 6 mm, and the hardness tester was used to test the indentation hardness.

Differential scanning calorimeter (DSC) was recorded on a DSC 200PC analyzer (NETZSCH, Germany). The glass transition temperature (T_g) of the coating material is the lower limit temperature for its use, so the T_g of the film can be used to characterize the cold resistance of the coating [16]. 5 mg of the PDMS polymer film was placed in the crucible, and tested at the cooling rate of 10 °C/min under N_2 atmosphere. The test temperature range was 0 °C to (–160) °C.

The low-temperature flexural test was carried out by a GT-7006-V30 vertical low-temperature tester (HITACHI, Japan). Prepared 70 mm in length and 25 mm in width samples according to the provisions of GB/T 39368-2020 and QB/T 2224-2012, conducted 60,000 bending tests at 25 °C and –20 °C, and then observed whether the bending part of the sample surface was damaged or cracked.



The abrasion resistance of PDMS leather coating was characterized by Martindale abrasion tester YG(B)401T (Wenzhou, Chain). According to GB/T 21196.3-2007, the sample with a diameter of 38 mm for a plane motion to rub with a standard abrasive. The test load was 96 g, the abrasive was 600 mesh sandpaper, and the wearing times were 5000 times. According to the visual change of sample surface wear, the abrasion resistance of the sample was preliminarily compared. Then the mass loss

was calculated according to the mass difference of the sample before and after the experiment. The abrasion index was calculated according to formula (1):

$$A = N / \Delta m \tag{1}$$

where A , N , and Δm were abrasion resistance index, the total number of wearing s and mass loss of the sample.

The contact angle was measured at 25 °C by the sessile drop method using a contact angle goniometer

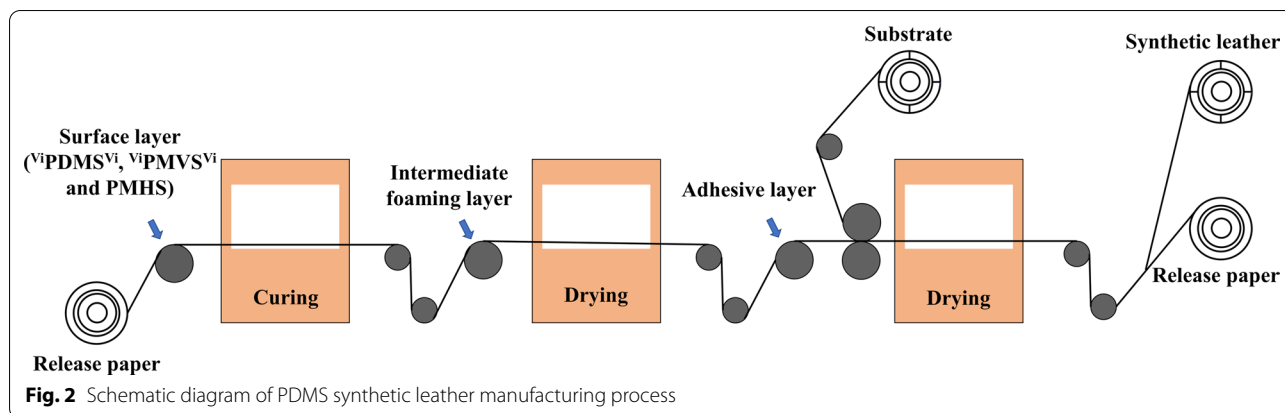


Table 1 Surface energy and their parameters of the test liquids [18]

Test fluid	γ_L (mN/m)	$\gamma^d L$ (mN/m)	$\gamma^p L$ (mN/m)
Water	72.8	21.8	51.0
Diiodomethane	50.8	48.5	2.3

OCAH200 (Dataphysics, Germany). Based on the contact angle data of water and diiodomethane on the surface of PDMS polymer coating, the surface energy of the coating was calculated by using Fowker’s equation [17]. The surface energy and itemized values of the above two test liquids were shown in Table 1.

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{2}$$

$$\gamma_{L1}(1 + \cos\theta_{L1}) = 2(\gamma_{L1}^d \gamma_s^d)^{1/2} + 2(\gamma_{L1}^p \gamma_s^p)^{1/2} \tag{3}$$

$$\gamma_{L2}(1 + \cos\theta_{L2}) = 2(\gamma_{L2}^d \gamma_s^d)^{1/2} + 2(\gamma_{L2}^p \gamma_s^p)^{1/2} \tag{4}$$

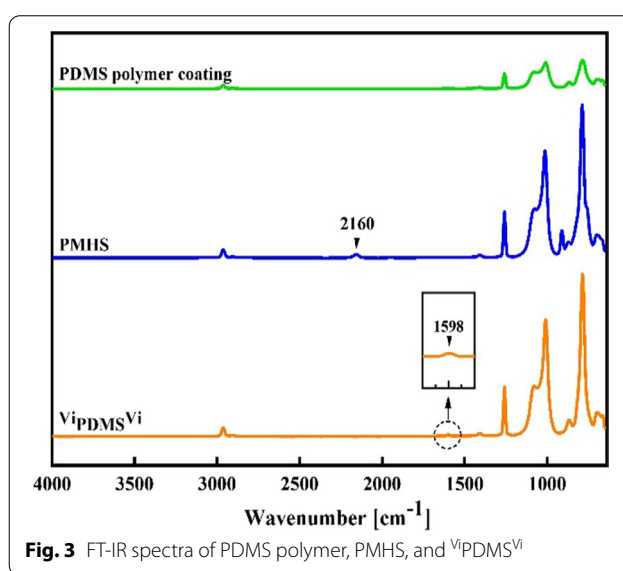
where $\gamma_s, \gamma_s^d, \gamma_s^p, \gamma_L, \gamma_L^d,$ and γ_L^p were solid surface energy, dispersion force part of solid surface energy, polar force part of solid surface energy, liquid surface energy, dispersion force part of liquid surface energy, and polar force part of liquid surface energy.

Drew a 5 cm straight line on the surface of PDMS polymer coating with an oily marker and observed if it could be completely erased with a paper towel without trace residue. If the ink shrinks on the surface of the coating and can be completely erased with a paper towel, it indicates that the coating has good anti-fouling (anti-graffiti) performance.

3 Results and discussion

3.1 FT-IR analysis of PDMS polymer film

The FT-IR spectra of $ViPDMS^{Vi}$, PMHS, and PDMS polymer film were shown in Fig. 3. It can be seen from the



spectrum of PDMS polymer film that the characteristic absorption peaks representing the C=C bond in $ViPDMS^{Vi}$ and Si-H bond in PMHS at 1598 cm^{-1} and 2160 cm^{-1} respectively disappeared, indicating that the hydrosilylation had occurred between the C=C bond in $ViPDMS^{Vi}$ and the Si-H bond in PMHS in the presence of the catalyst.

3.2 Mechanical properties of PDMS polymer coating

As a coating material, PDMS polymer should have suitable mechanical properties. Generally, >5 MPa tensile strength, >400% elongation at break, and 50–60 Shore A hardness were needed to meet the requirements of applications [5]. Therefore, the effect of each component on the mechanical properties of the coating was investigated.

Table 2 Effect of η PDMS η viscosity on mechanical properties of PDMS polymer film

η PDMS η viscosity (mPa s)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
η -10,000	0.32	417	8
η -30,000	0.25	452	5
η -50,000	0.19	487	3
η -80,000	0.09	593	2

Table 3 Effect of η PDMS η mixture with different viscosity on mechanical properties of PDMS polymer film

η PDMS η viscosity (mPa s)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
η -10,000 + η -30,000	0.29	449	7
η -10,000 + η -50,000	0.26	473	5
η -10,000 + η -80,000	0.25	511	4

3.2.1 Effect of η PDMS η viscosity on mechanical properties

Viscosity is closely related to molecular weight, and the greater the viscosity, the greater the molecular weight. Table 2 lists the effect of η PDMS η viscosity on the mechanical properties of PDMS polymer. Here, PMHS-0.18 was used as the cross-linking agent, the amount ratio of vinyl groups to active hydrogen was fixed to 1:1, and the amount of inhibitor was 24 μ L, respectively.

It can be seen that high viscosity η PDMS η can give higher elongation at break but low tensile strength and hardness, whilst low viscosity η PDMS η can provide higher tensile strength and hardness but low elongation at break. Therefore, it is necessary to mix η PDMS η with different viscosities to balance the mechanical properties of the PDMS polymer.

Keep other reaction conditions unchanged, the effect of η PDMS η blending with different viscosity on the mechanical properties of PDMS polymers are shown in Table 3. Compared with the single component, the mechanical properties of the mixed system showed an improvement trend. Especially, the mixture of η -10,000 and η -80,000 with a mass ratio of 1:1 as the base polymer can give moderate tensile strength, elongation at break and hardness of PDMS polymer film.

3.2.2 Effect of active hydrogen content on mechanical properties

As a cross-linking agent, the amount of active hydrogen in PMHS affects the mechanical properties of PDMS polymer. As shown in Table 4, when η -10,000 and η -80,000 were used as the base polymer, the mole ratio of vinyl

Table 4 Effect of active hydrogen content on mechanical properties of PDMS polymer film

Active hydrogen content (wt%)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
0.09	0.15	548	3
0.18	0.25	511	4
0.82	0.38	430	6
1.60	0.05	286	1

Table 5 Effect of molar ratio of vinyl groups to active hydrogen on mechanical properties of PDMS polymer film

Molar ratio of vinyl groups to active hydrogen	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
1:0.5	0.07	314	2
1:1	0.25	511	4
1:2	0.38	559	7
1:3	0.32	525	5

groups to active hydrogen was 1:1, with the increase of the active hydrogen content in PMHS, the tensile strength and hardness of PDMS polymer increased firstly and then decreased, and the elongation at break gradually decreased.

This is because with the increase of active hydrogen content in PMHS, the crosslinking degree of the polymer increases, which can disperse the stress on more molecular chains during the tensile process so as to improve the tensile strength and hardness. The increase of crosslinking degree also makes it difficult for relative slip between molecular chains, which is manifested by the decrease of elongation at break. When the hydrogen content in PMHS is too high, large an amount of active hydrogen will act as a diluent and reduce the crosslinking degree of the polymer. At the same time, the crosslinking points in the system are too dense, resulting in a smaller distance between the crosslinked links and the reduction of the crosslinked links bearing the external stress [19]. Therefore, the molecular chain of PDMS is easily damaged by the external force, resulting in a decrease in the tensile strength, hardness, and elongation at break of the polymer film.

3.2.3 Effect of mole ratio of vinyl groups to active hydrogen on mechanical properties

The mole ratio of vinyl groups to active hydrogen also influences the mechanical properties of PDMS polymer. When η -10,000 and η -80,000 were selected as the base polymer, PMHS-0.18 was used as the crosslinker, the effect of the amount ratio of vinyl groups to active

hydrogen on the mechanical properties of PDMS polymer film was shown in Table 5.

As shown in Table 5, the tensile strength, elongation at break, and hardness of PDMS polymer film showed an increase followed by a decrease as the percentage of active hydrogen in the system increased. This is because when the vinyl content in the system is higher than the active hydrogen content, the PDMS polymer film is not cured completely, the film is sticky, and the mechanical properties are low. The higher proportion of active hydrogen is conducive to hydrosilylation, which increases the crosslinking density and increases the tensile strength and hardness of PDMS polymer film but decreases the elongation at break. When the active hydrogen content continues to increase, the excess active hydrogen is unstable under the action of platinum catalyst, which is easy to dehydrogenate with a small number of water molecules in the air [20], resulting in bubbles. These uneven distributed bubbles encapsulated in the PDMS polymer film will inevitably decrease the tensile strength, hardness, and elongation at break of the PDMS polymer coating.

3.2.4 Effect of ^{Vi}PMVS^{Vi} mass fraction on mechanical properties

Another important factor affecting the mechanical properties of PDMS polymer is the mass fraction of ^{Vi}PMVS^{Vi}. ^{Vi}PMVS^{Vi} has reactive sites both at the chain ends and the lateral sites, which can form "concentrated crosslinking" during the curing process of the coating by simultaneous crosslinking and chain expansion reactions [21]. Here, ^{Vi}PMVS^{Vi} was used as a reinforcing agent to regulate the mechanical properties of PDMS polymer coating.

Under the same condition of η-10,000 and η-80,000 as base polymer, PMHS-0.18 as cross-linker, the amount of vinyl groups to active hydrogen mole ratio of 1:2, the effect of ^{Vi}PMVS^{Vi} on the mechanical properties of PDMS polymer film was shown in Table 6.

It was found that the tensile strength and hardness of PDMS polymer film increased rapidly with the increase

of the ^{Vi}PMVS^{Vi} mass fraction. When the mass fraction of ^{Vi}PMVS^{Vi} was 7 wt%, the resultant PDMS polymer film can remain >500% elongation at break and higher tensile strength and hardness.

3.2.5 Effect of fumed silica mass fraction on mechanical properties

Through the above discussion, we found that the tensile strength and hardness of polymer film is still lower after formula optimization, so their mechanical properties need to be further enhanced. Fumed silica with good compatibility with PDMS polymer, high a specific surface area of 110 m²/g and a primary particle size of 16 nm, has become a commonly used and best reinforcing filler for PDMS polymers. Table 7 lists the effect of the mass fraction of fumed silica on the mechanical properties of PDMS polymer film.

As shown in Table 7, as the mass fraction of fumed silica increased from 0 to 40 wt%, the largest tensile strength and >480% elongation at break as well as >50 Shore A hardness of PDMS polymer film was obtained, further increased the mass fraction of fumed silica, all mechanical properties show a decreased tendency except for hardness.

The reason may be that when the mass fraction of fumed silica is low, the rubber molecular chain is in a relaxed state [22], there is no filler network, and the force between fumed silica and silicone rubber matrix is small. When the filler reaches a certain amount, the tensile strength of the composite increases greatly. In this case, the filler has formed a continuous network in the rubber matrix [23]. When the mass fraction of fumed silica is too high, the uneven dispersion of fumed silica in rubber may be the main factor for decreasing tensile strength and elongation at break of the PDMS polymer. Moreover, the slurry is difficult to spread evenly, which is not conducive to processing.

In summary, the optimal formula with reasonable mechanical properties was as follows: η-10,000 and η-80,000 with a mass ratio of 1:1 as the base polymer, PMHS-0.18 as the cross-linker, the molar ratio of vinyl groups to active hydrogen was 1:2, the mass fraction of reinforcing agent ^{Vi}PMVS^{Vi} and fumed silica was 7 wt%

Table 6 Effect of ^{Vi}PMVS^{Vi} mass fraction on mechanical properties of PDMS polymer film

^{Vi} PMVS ^{Vi} mass fraction (wt%)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
0	0.38	559	7
3	1.07	539	14
5	1.85	524	18
7	2.73	503	21
9	3.52	439	25
12	4.07	388	28

Table 7 Effect of fumed silica mass fraction on mechanical properties of PDMS polymer film

Fumed silica mass fraction (wt%)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
0	2.73	503	21
20	4.87	499	45
40	5.96	481	58
60	5.31	301	70

and 40 wt%. As a result, the tensile strength of PDMS polymer coating reached 5.96 MPa, the elongation at break was above 480%, and the hardness was 58 Shore A, which satisfied the requirements of mechanical properties of the synthetic leather coating.

3.3 Characteristics of PDMS synthetic leather coating

Compared with PU, PVC, or other coating materials, PDMS polymer has unique characteristics, especially cold resistance, abrasion resistance, hydrophobicity, and antifouling.

3.3.1 Low-temperature flexibility of coating

The cold resistance of the synthetic leather coating was characterized by measuring the glass transition temperature (T_g) of the polymer film, and the results are shown in Fig. 4. It can be seen that the T_g of PDMS synthetic leather coating is $-131.8\text{ }^\circ\text{C}$, and crystallization temperature (T_c) is $-73.5\text{ }^\circ\text{C}$, while the T_g of the commonly used PU and plasticized PVC synthetic leather were $-50\text{ }^\circ\text{C}$ or so [24, 25]. This is because the molecular structure of organosilicon polymer is helical, the interaction force between chain segments is small, the main chain is soft and easy to rotate, and the rotation steric resistance of the Si–C bond side group is small. Especially when the side group is methyl, the bond length is about 0.188 nm, and the methyl can rotate freely around the Si–C axis without stopping at $-195\text{ }^\circ\text{C}$ [26], which gives the polysiloxane molecular chain excellent low-temperature flexibility.

Folding fastness was an important index to characterize the folding, bending, and cracking properties of synthetic leather coatings. In common, 60,000 times at normal temperature ($25\text{ }^\circ\text{C}$) and low temperature ($-20\text{ }^\circ\text{C}$) folding were used to determine whether the coating meet the

use requirements. As shown in Fig. 5, the PU, PVC and PDMS synthetic leather coating surfaces all showed slight creases after normal temperature testing. In the low-temperature test, some creases and damages appeared on the surface of PU and PVC coating, while there were only some slight creases on the PDMS coating, which reveals that the PDMS synthetic leather coating has excellent normal and low-temperature flexibility.

3.3.2 Abrasion resistance of coating

Sofa, seat, luggage, ball products put forward higher requirements for the abrasion resistance of the coating. Martindale abrasion resistance method is the common method to evaluate the abrasion resistance of synthetic leather coatings. The abrasion resistance index was calculated through the change in coating mass before and after wearing. As shown in Fig. 6, after the wearing test, the surfaces of the three samples were worn to a certain extent. The surface of PVC and PU synthetic leather coating was damaged and faded, while the surface texture of PDMS synthetic leather coating was still clear. Then, according to formula (1), the abrasion resistance index of PDMS synthetic leather coating was found to be 157.9 times/mg, which is higher than that of PU leather 75.2 times/mg and PVC leather 56.6 times/mg, indicating that PDMS synthetic leather coating shows highest abrasion resistance. Generally, the abrasion resistance of polymer coating is closely related to strength, toughness, and resilience [27]. The Si–O–Si bond in the main chain of polysiloxane has a larger bond angle and bond length, and the molecular chain is very soft, all give the polymer good toughness and resilience. Therefore, the PDMS synthetic leather coating shows excellent abrasion resistance.

3.3.3 Hydrophobicity and anti-fouling of coating

The hydrophobicity of the PDMS synthetic leather coating was characterized by measuring the contact angle and surface energy of the polymer coating. Generally, the coating with lower surface energy and higher water contact angle often exhibits superior hydrophobic performance [28]. For PDMS coating, the surface energy was 21.3 mN/m by Eqs. (2)–(4), the water contact angle was 112.4° , and the diiodomethane contact angle was 73.5° at 0 s (the droplet just drops to the coating surface). Meanwhile, the water contact angle only decreased by 7.3° from 0 to 180 s (as shown in Fig. 7). For commonly used PU/PVC synthetic leather coating, the water contact angles were $67.4^\circ/78.0^\circ$, and the surface energy was 44.0 mN/m [29]/ $33.0\text{--}38.0\text{ mN/m}$ [25], respectively, indicating that the PDMS synthetic leather coating shows more excellent hydrophobic properties.

How to improve the anti-graffiti property of coating is still a common technical problem for the leather industry.

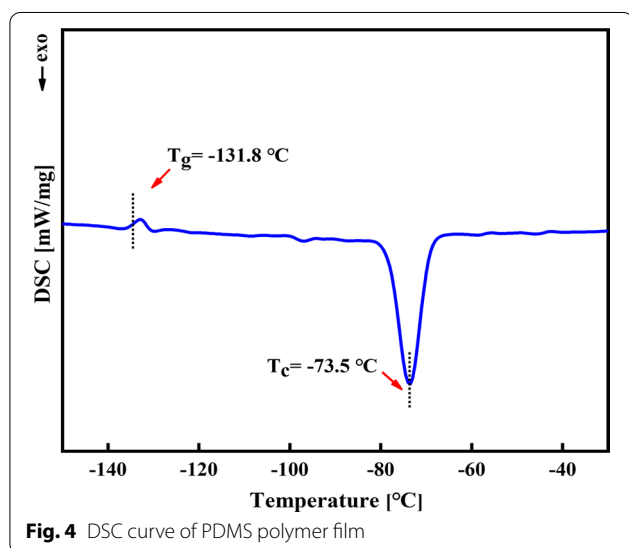


Fig. 4 DSC curve of PDMS polymer film

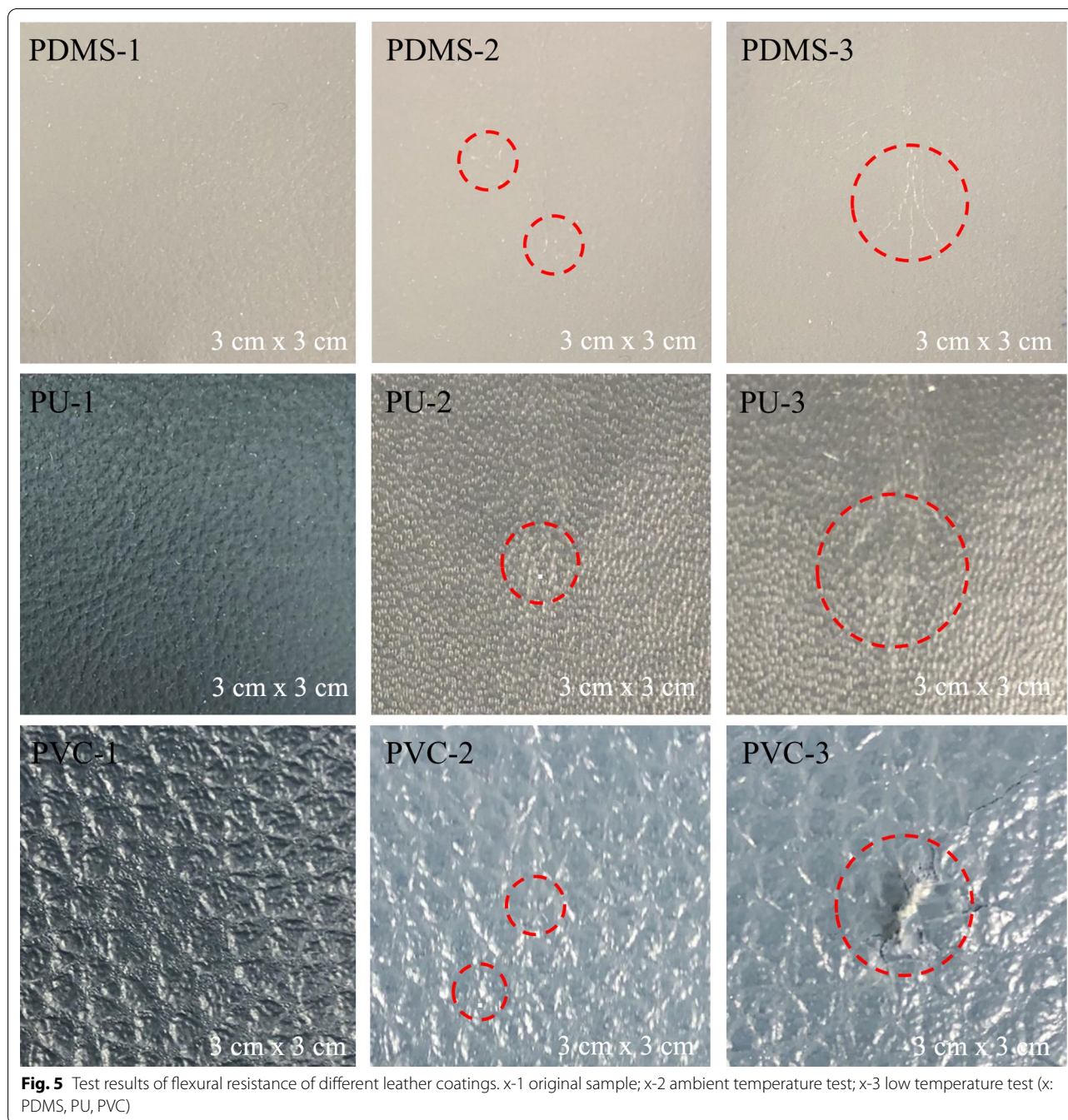
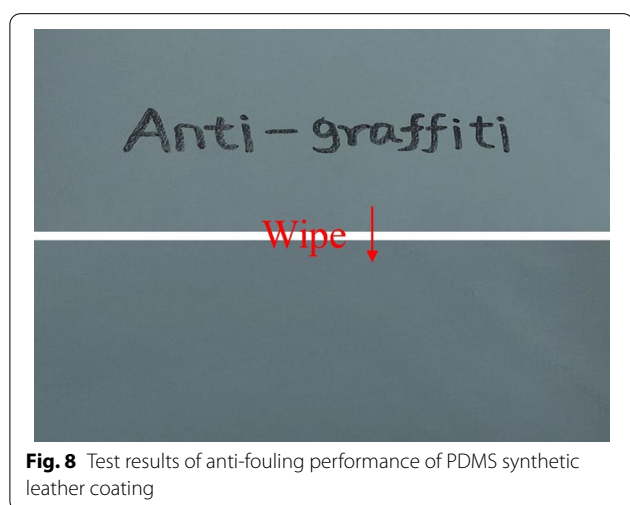
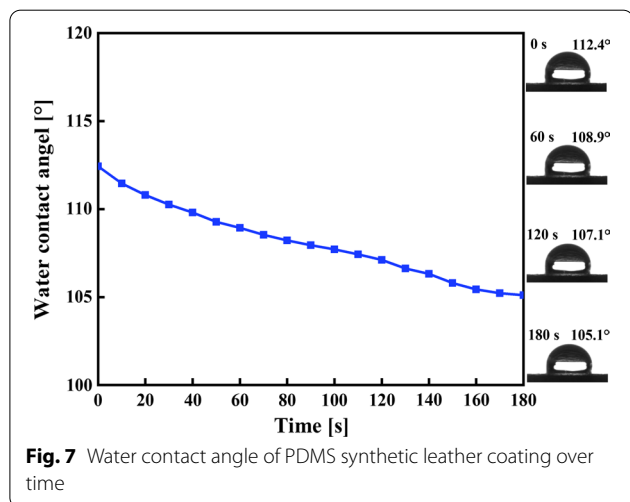
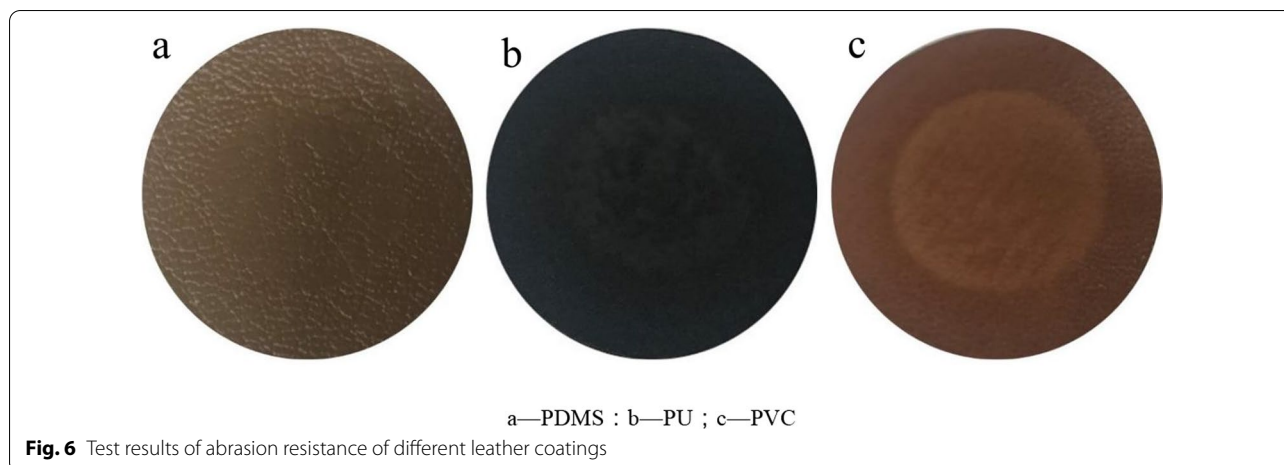


Fig. 5 Test results of flexural resistance of different leather coatings. x-1 original sample; x-2 ambient temperature test; x-3 low temperature test (x: PDMS, PU, PVC)

In our previous work, we proposed the construction method and key technology of anti-graffiti coating, that is, reduce the surface energy of the coating (reduce the wetting of ink) → improve the compactness of coating (prevent the penetration of ink) → block the polar groups of coating (weaken the interaction) [30].

As can be seen from the above discussion that the PDMS synthetic leather coating has low surface energy and a high oil–water contact angle, so the ink was hard to

wet and spread on the coating surface. During the preparation of PDMS synthetic leather coating, an amount of $\text{ViPMVS}^{\text{Vi}}$ (containing terminal vinyl and side vinyl) and side hydrogen organosilicon oil were added to increase the crosslinking density, so the small polluting molecules such as ink cannot penetrate into the inner of the coating. In addition, there are few polar groups in the PDMS polymer coating. Hence, the interaction between the ink and the coating is weak, making the adhesion of the



ink on the coating surface weak and easy to be removed. Therefore, the as-prepared PDMS synthetic leather coating should have excellent anti-graffiti performance.

As shown in Fig. 8, after the oily pen is used to doodle on the surface of PDMS synthetic leather coating, the handwriting can be easily removed with a paper towel. The experimental results are very consistent with the above molecular design.

4 Conclusions

In this paper, organosilicon synthetic leather was prepared by transfer coating method with ^{vi}PDMS^{vi} as basic polymer, PMHS as a crosslinking agent, platinum complex as catalyst, ^{vi}PMVS^{vi} as a reinforcing agent, and silica as reinforcing filler. Through the study of the structure–activity relationship, the optimized formula is as follows: the mass ratio of η-10,000 and η-80,000 ^{vi}PDMS^{vi} is 1:1, the molar ratio of vinyl groups to active hydrogen is 1:2, the amount of reinforcing agent ^{vi}PMVS^{vi} is 7 wt%, and the amount of silica is 40 wt%. The PDMS film prepared by in situ hydrosilylation in presence of the thermally induced catalytic system shows 5.96 MPa tensile strength and >480% elongation at break. In comparison with PU or PVC based synthetic leather coating, the as-prepared PDMS synthetic leather coating shows excellent low-temperature flexibility, abrasion resistance together with hydrophobicity and anti-graffiti. The organosilicon material is applied to synthetic leather coating to realize the substitution of silicon for carbon, which provides a new path for carbon emission reduction and carbon peak strategy.

Abbreviations

^{vi}PDMS^{vi}: Divinyl-terminated polydimethylsiloxane; PMHS: Poly(methylhydrosiloxane); ^{vi}PMVS^{vi}: Divinyl-terminated polymethylvinylsiloxane; PDMS: Polydimethylsiloxane; PU: Polyurethane; PVC: Polyvinyl chloride; RIM: Reaction injection molding; VOCs: Volatile organic compounds; FT-IR: Fourier transform infrared; DSC: Differential scanning calorimeter; T_g: Glass transition temperature; T_c: Crystallization temperature.

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Author contributions

WW: Conceptualization, Methodology, Formal analysis, Writing—original draft. HF: Writing—review and editing, Supervision. LS: Writing—review and editing, Investigation. ZW: Data curation, Formal analysis. HL: Validation, Investigation. JX: Writing—review and editing, Validation. QH: Validation. XC: Visualization. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this manuscript and the additional file. The authors declare that the data in this article are reliable.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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