Hindawi
Advances in Polymer Technology
Volume 2022, Article ID 6384600, 10 pages
https://doi.org/10.1155/2022/6384600

Research Article

Preparation and Characteristic of Polyurethane Powder Adhesives with Heating Resistance Modified by Nanosilica

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Received 5 January 2022; Revised 12 April 2022; Accepted 20 April 2022; Published 13 May 2022

Academic Editor: Sagar Roy

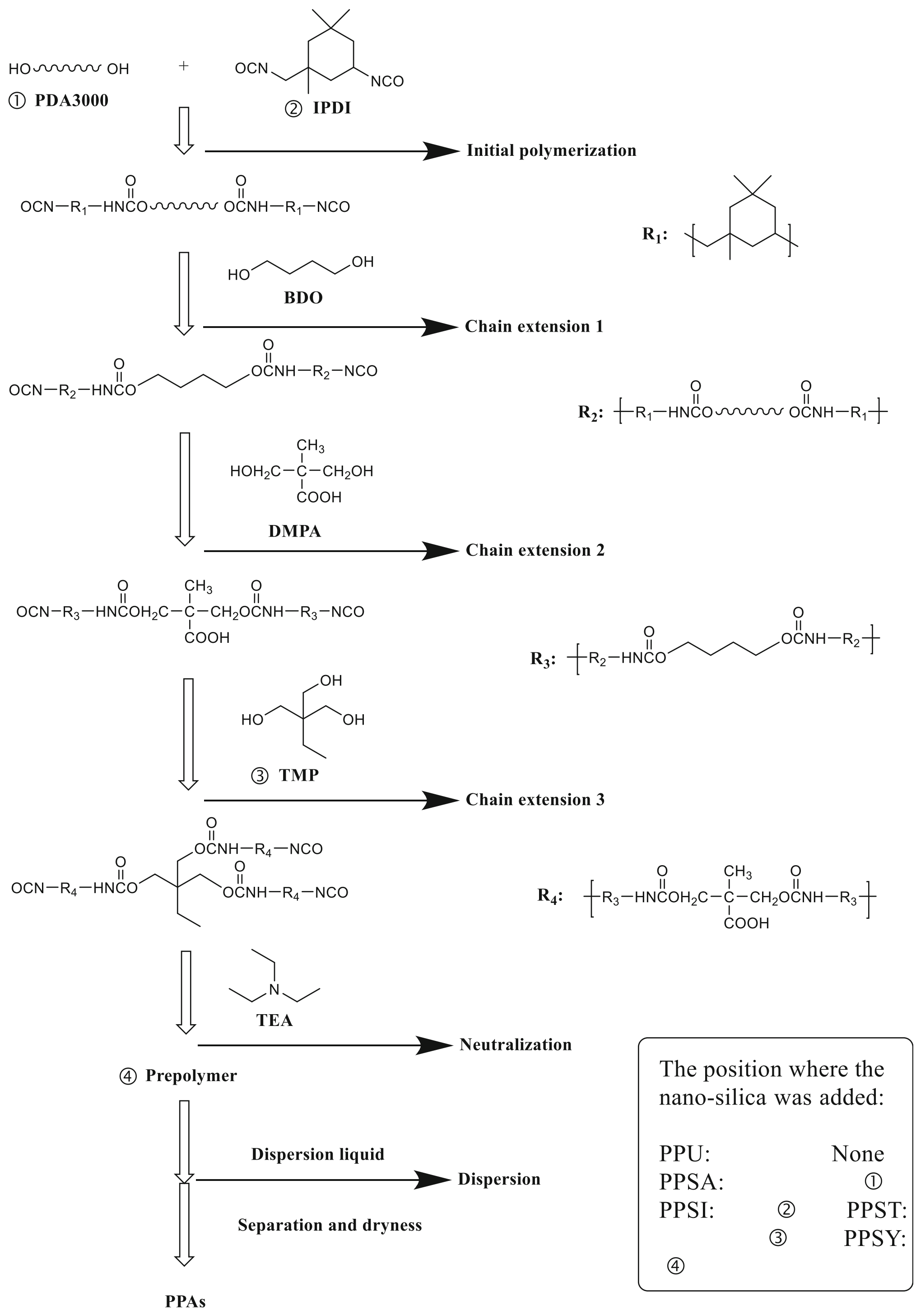
Polyurethane powder adhesives (PPAs) have a great application prospect in various areas. However, the weakly adhesion property at high temperature greatly hindered its application. In this study, nanosilica as reinforcing agent and dispersing agent has been introduced during the preparation of PPAs. A series of the polyurethane powder adhesives modified by nanosilica were prepared and the influence of adding order of nanosilica on the heat resistance and adhesive strength properties of PPAs has been investigated. The results showed that the T-peel strength of most samples after second heat (heated at 70°C for 24 hours) decreased about 60-80% comparing with the original T-peel strength. However, PPSY only decreased 17.5%, which indicated the nanosilica added after the chain extension reaction, in the prepolymer synthesis could increase the heat resistance performance of polyurethane powder adhesives. It also means the nanosilica was doped between the PU chains keeping the original form as enhancement reagent adding the nanosilica after the chain extension reaction. The excellent heat resistance performance of PPSY could meet the requirements of the industrial gluing in the fields of footwear.

1. Introduction

Polyurethane (PU) adhesives were a special group of polymeric materials which were in many ways different from most of the other plastic types [1–6]. Today, with continuous improvements in processing techniques, they were widely used in paints, liquid coatings, elastomers and insulators, foams, medical materials and so on [7–10]. The traditional PU adhesives were very popular because of the efficiency and convenience. But it caused a great impact on the environment. Especially the application of the solvent-borne PU commonly involves the evaporation of the volatile organic compounds (VOCs), such as acetone and dimethyl formamide (DMF) [11]. Polyurethane powder adhesives (PPAs) could avoid the environment pollution of the VOCs in the process of usage [12, 13]. The weakly adhesion property in the high temperature greatly limited its application yet. The addition of nanosilica could improve the thermal stability of the polymer [14–18]. It was found that the dispersion of nanosilica particles in coats prepared by in situ polymerization method was slightly better than that by blending method [19]. It also indicated that more polyester segments had reacted with silica particles during in situ polymerization than during the blending method [20]. The effect of different sizes of the nanosilica on the property of PU has been discussed [21–23]. However, the impact of nanosilica on the PPAs was barely reported.

To our knowledge, a vast amount of research has been done about the preparation of polyurethane powder for coating [24–26]. Farshchi and Gedan-Smolka [27] reviewed the most recent advances in the field of powder coating by focusing on polyurethane powder coating as a group of thermoset powder coatings. Shirkavand Hadavand et al. [28] used the electrostatic method on aluminum plates to get the powder coating. Yang et al. [29] found that there were two main methods for the production of powder coatings, dry and wet process production.

A simple, easy to operate, and low-cost granulation method for polyurethane powder adhesives has been given by our group [12]. In order to further improve the heat resistance of PPAs, a series of PPAs modified by nanosilica were



Scheme 1: Elementary steps for the preparation of PPAs with different addition orders of the nanosilica.

successfully synthesized on the basis of the solution polymerization. The prepared PPAs were investigated using different characterization techniques. The influence of adding order of nanosilica on the heat resistance and adhesive strength of PPAs was carried out. The optimal sequence of adding was after the chain extension reaction, during that the nanosilica was doped between the PU chains and kept the original form as enhancement reagent.

2. Experimental

2.1. Materials. Polyethylene adipate diethylene glycol diol with a molecular weight of 3000 (PDA3000), isophorone diisocyanate (IPDI), 1-methyl-2 pyrrolidone (NMP), and acetone were obtained from Guangdong Yutian Bali Technology Co., Ltd. (Zhuhai, China); 1,4-Butanediol (BDO) was purchased from Tianjin Chenfu Chemical

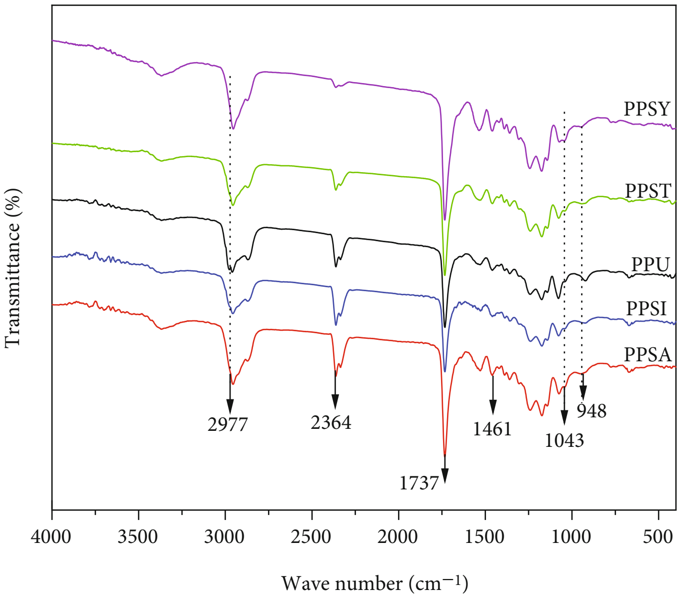


Figure 1: FTIR spectrum of the PPAs.

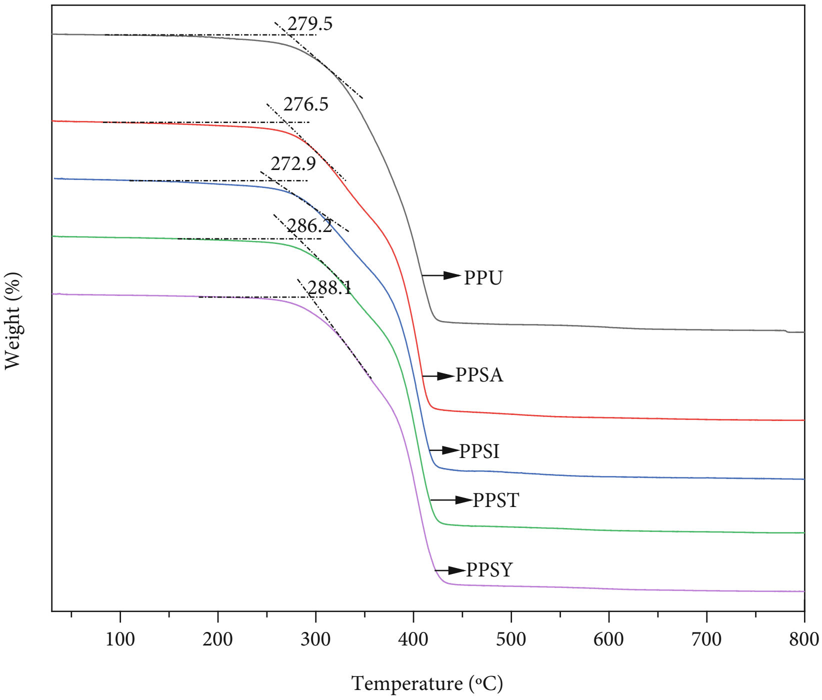


Figure 2: TGA curves of PPAs.

Reagent Company (Tianjin, China); 2,2-bis(hydroxymethyl) propionic acid (DMPA), dibutyltin dilaurate (DBTDL), and trimethylolpropane (TMP) were purchased from Aladdin (Shanghai, China); Triethylamine (TEA) was obtained from Guangdong Guanghua Technology Co., Ltd. (Guangzhou, China). Nanosilica (Mw = 60.09 g/mol, 99% purity) bearing surface silanol groups (18.7 mmol OH/g) were purchased from Zhengjiang Yuda Technology Co., Ltd. (Shangyu, China). The particle size was 10 nm.

2.2. Preparation of the PPAs. PPAs were prepared according to our previous reports [12]. Four approaches were adopted to introduce nanosilica to the PPAs as shown in Scheme 1. Before the nanosilica is incorporated into the synthesis system, the mixture of silica and acetone (mass ratio = 1 : 8 ~ 11) was sonicated for 30 min. A series of PU prepolymers were synthesized in a 250 mL four-necked flask equipped with a mechanical stirrer, condenser, thermometer, and nitrogen inlet. PDA3000 was heated at 105°C under vacuum for 1 ~ 2 h to

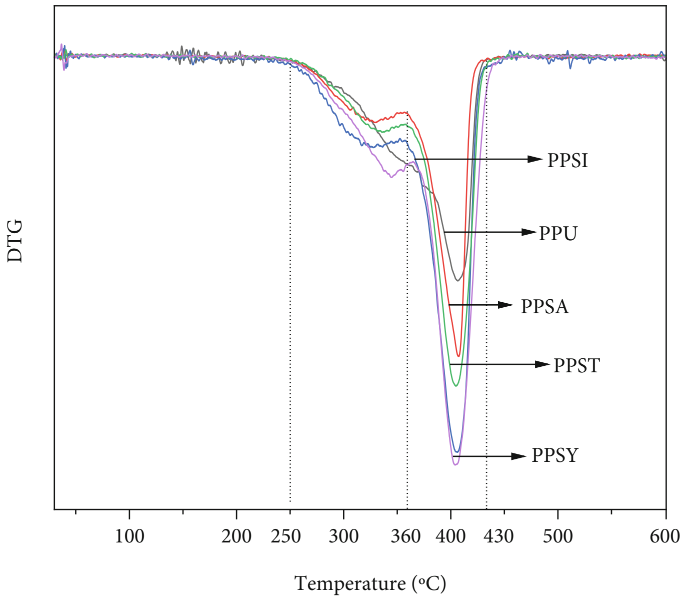


Figure 3: DTG curves of PPAs.

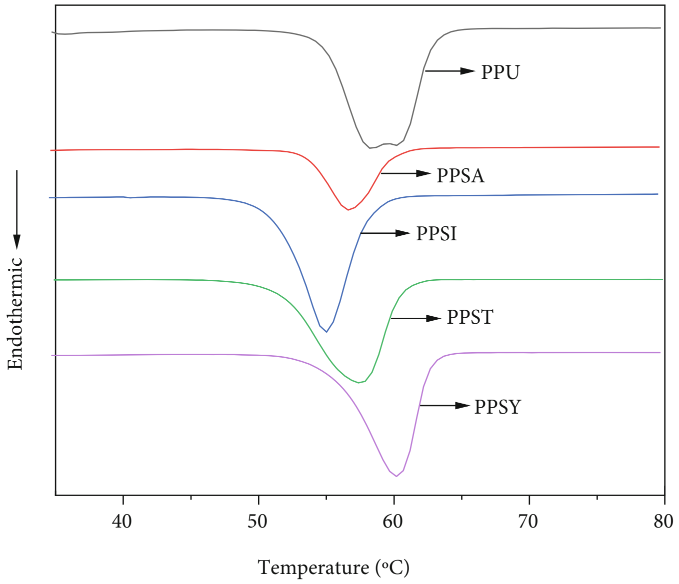


Figure 4: DSC curves of PPAs.

Table 1: The thermal properties.

Samples	$T_{5\%}$(°C)	$T_{50\%}$(°C)	$T_{\max}$(°C)	T_g (°C)
PPU	279.5	377.0	407.2	56.1
PPSA	276.5	386.6	408.0	55.2
PPSI	272.9	378.2	405.0	52.4
PPST	286.2	389.8	404.0	54.2
PPSY	288.1	390.4	404.8	57.1

remove moisture residue. The mixture of silica and acetone was fed to the four-necked flask equipped with PDA3000. Then, the four-necked flask was heated for 1 hour with a stirring speed of 400 rpm under nitrogen protection at 70°C. Then, the chain extender BDO was added into the above mixture which continued stirring for 1 hour. An appropriate amount of acetone was added to adjust the viscosity throughout. Then, mixture of DMPA and NMP of equal proportion was fed into the flask which continued reaction for 2 hours. TMP was added to the above mixture for further polymer. After reaction for 1 ~ 2 h, the PU prepolymer was cooled to the room temperature. TEA was added to neutralize the carboxylic acid for 1 hour. Next, the dispersion solution was added under a stirring speed of 1000-1500 rpm for about 2 hours. Finally, the white powder adhesives are obtained and labelled as PPSA. The other approaches to introduce nanosilica into the synthesis system were carried out using the same procedures.

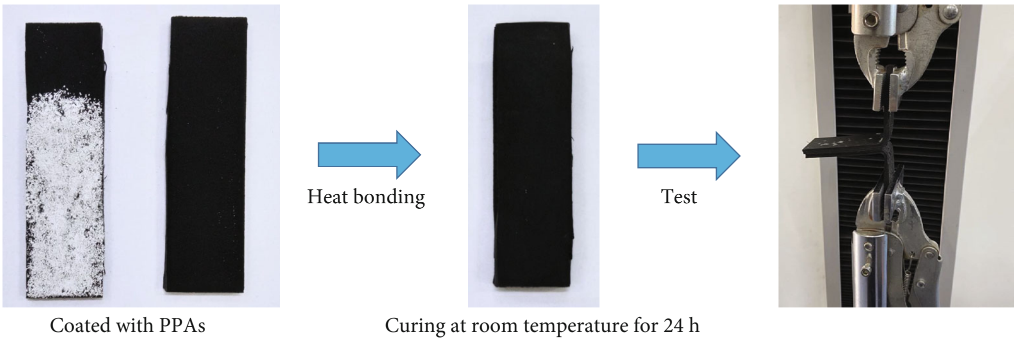


Figure 5: The T-peel strength testing.

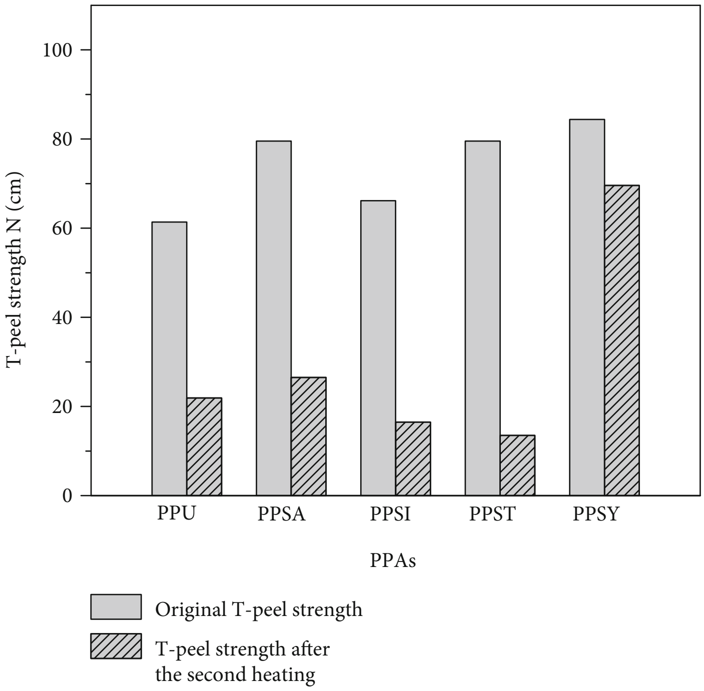


Figure 6: The T-peel strength of the PPAs.

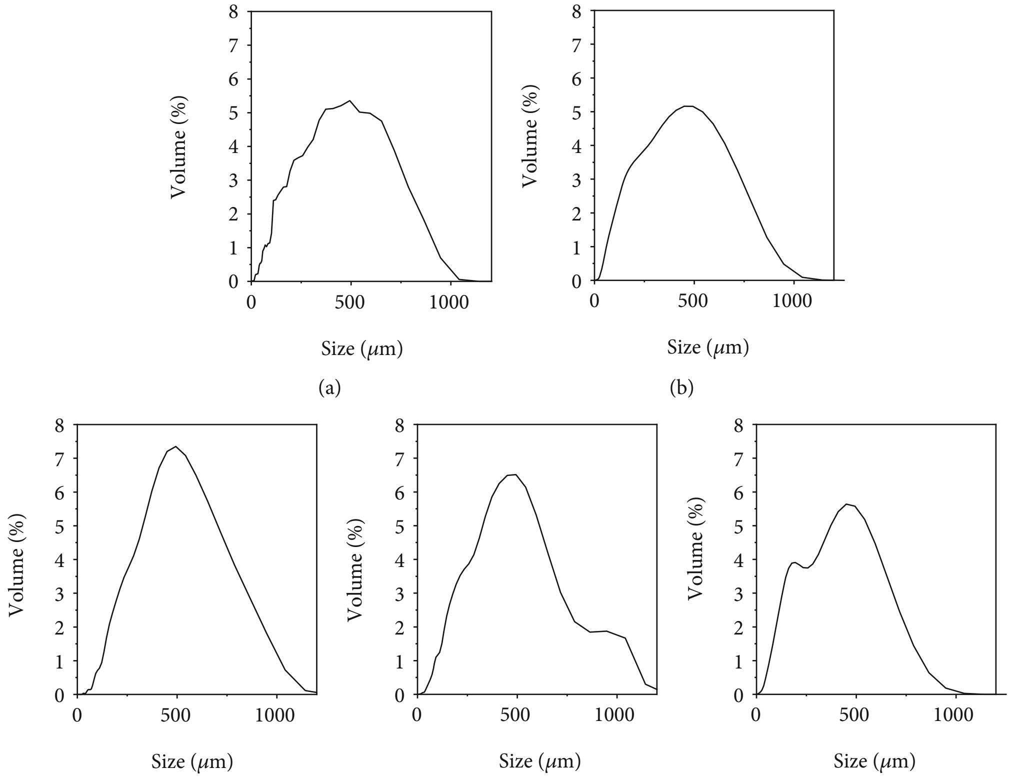
2.3. Measurements and Characterization

2.3.1. T-Peel Adhesion Strength. T-peel strength of the PPAs was measured in a material tensile machine (Haida, HD-B617-S, China) by referring to the Chinese national standard GB/T 532-2008 (Rubber, vulcanized, or thermoplastic—Determination of adhesion to textile fabric). The rubber strip (100 mm × 25 mm × 4 mm) was treated with rubber surface treatment agent first. Then, PPAs were tiled on rubber strips and melted at 140°C for 10 min and the rubber strips were fixed in contact at a pressure of 2 MPa for 30s. The original T-peel strengths were obtained 24 h after the joint formation (stored at room temperature). The T-peel strength of the second heat was tested after the rubber strips heated in the oven at 70°C for 24 h.

2.3.2. Scanning Electron Microscope (SEM). After the sample was dehydrated and dried in a vacuum drying oven of the microscope (Tescan, MIRA, Chech), a small amount of the sample was placed on the conductive tape, and then, the sample was gold-plated, the morphology is analyzed with a scanning electron microscope.

2.3.3. Differential Scanning Calorimetry (DSC). DSC analysis was performed under a nitrogen atmosphere from -20°C to 80°C, using a differential scanning calorimeter (Mettler, DSC1, Germany) at a heating rate of 10°C/min. The glass transition temperature is determined from the inflection point of the first heating cycle.

2.3.4. Thermogravimetric (TG). TG analysis was performed under a nitrogen atmosphere from -20°C to 80°C. It was performed using a differential thermal-thermogravimetry synchronous analyzer (Shimadzu, DYG-60H, Japan) at a heating rate of 10°C/min. In this case, about 5 mg of the sample was heated from 30°C to 800°C at the heating rate of 10°C/min.



(a) (b)

(c) (d) (e)

Figure 7: The particle size distribution of PPAs: (a) PPU, (b) PPSA, (c) PPSI, (d) PPST, and (e) PPSY.

2.3.5. Granulocometer Analysis. The particle size distribution of the powder was obtained in a nanoparticle size analyzer (Beckman, LS13320, America). Inclusion compound powder particle size analysis by using dynamic light scattering analyzer of solid test modules was measured at room temperature (25°C) and scattering angle 90°, using optical model (Fraunhofer. Rf780f).

2.3.6. Fourier Transform Infrared Spectroscopy (FTIR). FTIR of PPAs was determined with spectrometer (Shimadzu, IRprestige-21, Japan). After dissolving the powder with tetrahydrofuran, taking out a certain amount of solution and dropping it on the potassium bromide (KBr) wafer to make it into a thin film. The spectra were recorded by averaging 20 scans at a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}.

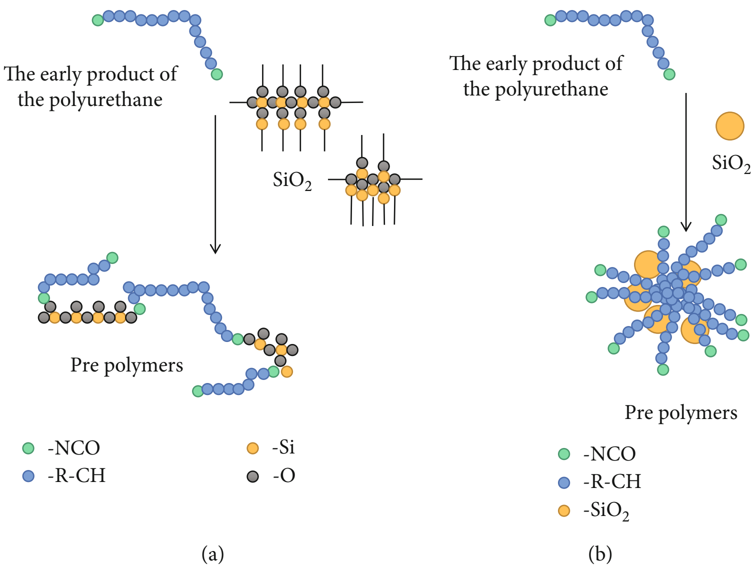
3. Results and Discussion

3.1. FTIR Characterization. The structures of the obtained samples were confirmed by FTIR spectra in Figure 1. The peak at 2977 cm^{-1} in PPU without nanosilica was assigned to the stretching vibration peak of the -CH$_3$ group. However, there was no same peak in the infrared spectra of PPA samples with nanosilica. It could be explained that nanosilica might affect the vibration of -CH$_3$. The peaks of the Si-O-Si at 1043 cm^{-1} and the Si-OH at 948 cm^{-1} in the PPAs were observed. Furthermore, the peak of PPSY is stronger than others, which indicates that nanosilica is mainly doped between the PU chains.

Table 2: The particle size distribution of PPAs.

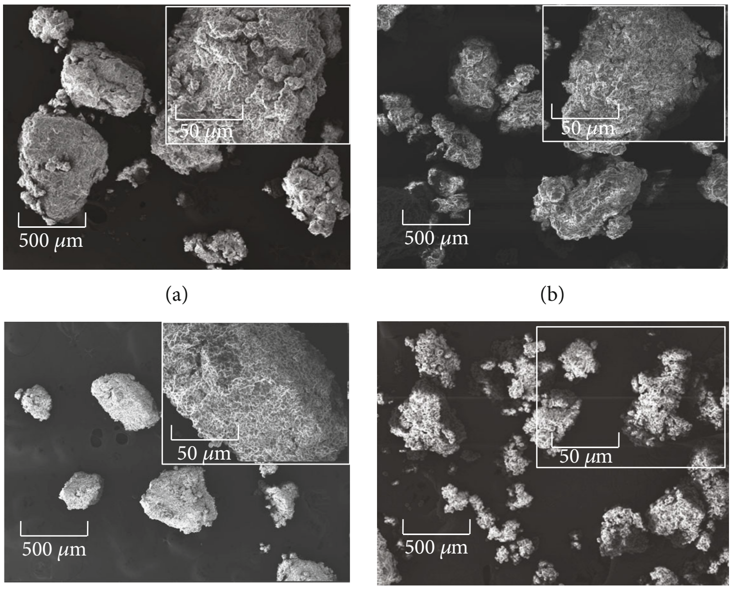
Samples	d_{10}(μm)	d_{50}(μm)	d_{90}(μm)
PPU	179	438	778
PPSA	107	318	693
PPSI	90	311	676
PPST	95	297	630
PPSY	86	329	701

3.2. Thermal Analysis. The effects of adding order of silica on the thermal properties of PPAs are shown in Figures 2, 3, and 4. From the TGA curves, the thermal decomposition temperature of PPSY is the highest. Besides, the thermal decomposition temperature of PPSY increased by nearly 10°C over PPU without nanosilica. This phenomenon indicated that the nanosilica hindered the thermal decomposition rate of hard segment decomposition in PU. PPAs showed two thermal degradation stages occurred in the DTG curves. The first slight degradation stage, from 250°C to 360°C, was attributed to the decomposition of the hard segments. And the second degradation stage, from 360°C to 430°C, was ascribed to the decomposition of the soft segments. As shown in Table 1 from the TGA, it can be seen that the glass-transition temperature (T_g) of PPSA, PPSI, and PPST is lower than that of PPU. The nanosilica in these samples was added into the PU chains, and this will increase the microphase separation of PU, which will lead to a decrease in T_g. However, a higher T_g was observed in PPSY.



(a) (b)

Figure 8: Schematic diagram of nanosilica/polyurethane: (a) hybridization and (b) doping.



(a) (b) (c) (d)

Figure 9: SEM images of the samples: (a) PPU, (b) PPSI, (c) PPST, and (d) PPSY. Scale bar is 500 μm.

It was explained that the nanosilica doped between the PU chains in PPSY restricted the molecular motion, and this will result in an increase in T_g. The melting peaks of PPA samples were given in DSC curves. There were obvious broad endothermic peaks in DSC, which further showed that the addition order of nanosilica had an effect on the melting properties of polyurethane powder adhesives.

3.3. T-Peel Strength. As shown in Figure 5, the T-peel strength test uses a material tensile to pull apart the substrate stained with powder adhesives. The T-peel strength test results of PPAs for the different adding positions of the nanosilica are shown in Figure 6. It was found the original T-peel strength of all samples with the nanosilica became higher relative to PPU. It may be due to the addition of silica making the polyurethane powder particle size generally smaller, which is conducive to the improvement of the T-peel strength. It could be clearly found that the size of PPAs with nanosilica was smaller than that of samples without

Table 3: The effect of nanosilica content on the T-peel strength.

Sample	Nanosilica (%)	T-peel strength (N cm^{-1})	
		Original	Second
PPU	0	61.4	21.9
PPSY1	1%	84.4	69.6
PPSY2	2%	73.2	53.6
PPSY3	3%	68.3	49.3

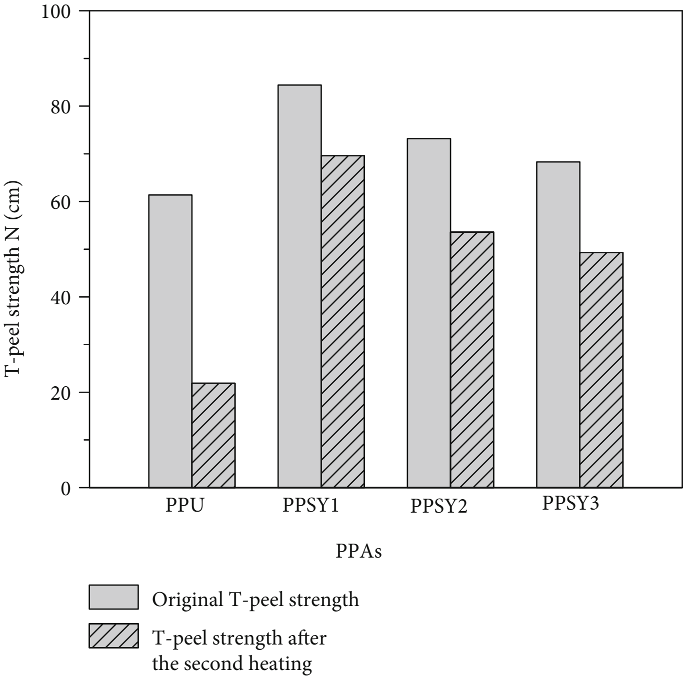


Figure 10: The effect of nanosilica content on the T-peel strength.

nanosilica in Figure 7 and Table 2. It suggested that the existence of nanosilica was promoted to prepolymer dispersed during particles forming.

As for the T-peel strength after second heating (heated at 70°C for 24 hours) in Figure 6, it could be seen that T-peel strength of most samples decreased about 60-80%, comparing with the original T-peel strength. However, PPSY only decreased 17.5%, which indicated the nanosilica added after the chain extension reaction, in the prepolymer synthesis could increase the heat resistance performance of polyurethane powder adhesives. It also means the nanosilica was doped between the PU chains keeping the original form as enhancement reagent.

In the synthesis of PPSA, PPSI, and PPST, the nanosilica was added during the chain reaction. It could react with isocyanate so that the nanosilica could form the hybridization with PU chains. Figures 8(a) and 8(b) showed a schematic diagram of nanosilica in polyurethane. The nanosilica existing in prepolymer as doping form could rise the heat resistance performance of polyurethane powder adhesives.

3.4. SEM Analysis. It could be seen that the size of PPAs with nanosilica appeared slightly smaller than that of samples without nanosilica in Figure 9. This may be caused that the addition of nanosilica was helpful for the dispersion of polymer powder and the forming smaller particles. Compared with the PPU, the surface of the samples PPSI and PPST exhibited to be more dense in Figures 9(b) and 9(c). It was explained that the nanosilica forms hybridization with the PU chains participating in the bonding process, so their shape was similar. The surface of the sample PPSY was partially loose in Figure 9(d), which was interpreted that the nanosilica was doped between the PU chains.

3.5. Effects of the Different Contents of Nanosilica on the Powder. As mentioned above, the properties of PPSY, that is, the nanosilica was added in the prepolymer after the chain extension reaction is the best optimum. On the basis of the same synthesis process as PPSY, the effect of silica content on the properties of the powder was investigated. Table 3 shows the impact of nanosilica content on the T-peel strength of the powder. Figure 10 shows the T-peel strength of PPSY1, PPSY2, and PPSY3. The adhesion properties of all the PPSYs were significantly improved when the content of nanosilica increases from 1.0% to 3.0%.

However, as the further increase of nanosilica content, the T-peel strength decreases significantly. The main reason may be that the excess of nanosilica caused the settlement phenomenon and thus reduced the adhesion of the PPSY. This trend was similar to the research of Guo [30]. Therefore, adding 1% content of nanosilica in polyurethane powder adhesives was the best.

4. Conclusions

In this paper, a series of PPAs modified by nanosilica with different adding orders were successfully prepared by the solution polymerization. The incorporation of nanosilica into the PPAs was confirmed by FTIR. The heat resistance and adhesive strength were investigated by TGA and material tensile machine. The results demonstrated that the adding order of nanosilica had a significant impact on these properties. The T-peel strength after second heat made known PPSY had the optimum heat resistance performance comparing with all other samples. The T-peel strength after the second heat of PPSY decreased 17.5% relative to the original T-peel strength, which could meet the requirements of the industrial gluing in the fields of footwear.

Data Availability

The authors declare that all data supporting the findings of this study are available within the paper and the Source Data file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research was financially supported by Guangdong Provincial Engineering Technology Research Center of the Green Polyurethane Adhesives, Zhuhai College of Science and Technology (Grant No. 2021GCZX010).

Supplementary Materials

Source data of Figures 1, 2, 4, 6, 7, 9, and 10 to this article can be found in the supplementary material. *(Supplementary Materials)*

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