In-situ Polymerization and Characterization of Poly (ε-caprolactone) Urethane/SiO\textsubscript{2} Nanocomposites

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Abstract. Nanocomposites of poly(ε-caprolactone) (PCL) castable polyurethane elastomer (CPUE) with nano-SiO\textsubscript{2} particles of different surface properties were prepared via in-situ polymerization. An electromechanical universal testing machine, a durometer, a rubber resilience experimental machine, a dynamic-mechanical analyzer, a thermogravimetric analysis and a scanning electron microscope were used to investigate the macro-static/dynamic mechanical properties, micro-dispersed state and thermostability. The results showed that the modulus at 100% and 300%, elongation at break, tensile strength and tear strength of poly(ε-caprolactone) urethane nanocomposites were increased by introducing a certain amount of nano-SiO\textsubscript{2}. Especially the tensile strength and tear strength at 100°C of the PCL CPUE with 5% nano-SiO\textsubscript{2} pretreated by γ-glycidochloropropyl methyl trimethoxy silane (trade name A-187) were 1.50 and 1.94 times than those of the pure PCL CPUE, respectively. The addition of the nano-SiO\textsubscript{2} had little effect on the hardness, but the impact resilience decreased slightly. The loss factor peaks of two nano-SiO\textsubscript{2} polyurethane composites were higher obviously than the pure PCL CPUE and the glass transition temperature (T\textsubscript{g}) of the two nano-SiO\textsubscript{2} polyurethane composites increased to higher temperature region. The surface treatment by the optimum silane coupling agent influenced the dispersibility of nano-SiO\textsubscript{2} in the PCL CPUE distinctly. The agglomerating phenomenon, and even some nano-agglomerates with more than 1 μm diameter can be observed in the PCL CPUE with 5% untreated nano-SiO\textsubscript{2}, but the nano-SiO\textsubscript{2} pretreated by A-187 was dispersed in the PCL CPUE at nano-scale.

Introduction

The preparation methods of polymer/inorganic nano-particle composites are sol-gel method, intercalation method, melt-compounding method and \textit{in-situ} polymerization process\textsuperscript{1-5}. Here the \textit{in-situ} polymerization process is defined that the monomers dispersed with nano-scale inorganic powders can bulk polymerize and a certain nano composites are obtained. It is benefit for the dispersion of nano-scale inorganic powders in polymer matrix by using this method, and the obtained composites usually feature outstanding processing properties. At the same time, silane coupling agents with active groups are employed widely in the surface treatment of nano-scale inorganic powders, especially for those powders with hydroxyl groups on their surface. The alkoxy groups of silane coupling agents can be hydrolyzed and form chemical bonding with the surface of inorganic powders and the active groups can generate chemical bonds with polymer matrix. Then the interfacial bonding of inorganic powders and polymer matrix can be improved, also a high performance composite can be obtained\textsuperscript{1}.

Castable polyurethane elastomers (CPUEs) have been applied widely in national defense, metallurgical industry, mining, electro-machinery vocation, textile industry, shoemaking and automobile fields. But the application of the traditional CPUEs is still unsatisfied in some tough circumstance because there are some disadvantages such as high heat generation and poor heat
Many engineers are working hard to find a solution for this problem and promoting new applications for the CPUEs.

Polymer nanocomposites exhibit many outstanding properties when compared with the universal materials with micrometre fillers, this point attracts attention of the world. The most prominent feature is that the introduction of a small amount of nano-scale fillers can modify the mechanical properties of the nanocomposites significantly. So many studies have been carried out on the polymer nanocomposites. As an increasingly advancing material, polyurethane is a focus what has been developed for several decades. According to the search data, more than one hundred papers had been adopted by SCI after the first thesis of polyurethane nanocomposites was published in 1998.

The research field is mainly concentrated on the structure and properties of polyurethane/surface modified nano clay composites, and different research teams obtained different conclusions. Tien and Wei found that the young's modulus and the elongation at break increased substantially, while Zilg et al. reported an improvement of elongation at break, but a reduction in the young's modulus. Han et al. obtained a result that the dynamic tensile modulus decreased, however, the elongation at break decreased. Xia et al. found that the tensile strength and modulus increased, whereas the elongation decreased with the increasing of the exfoliation degree. Zheng et al. not only carried out the study on the polyurethane nano clay and nano Al₂O₃ composites, but also discussed the polyurethane/ZnO nanocomposites. The experiments presented some surprising results: the introduction of nano-scale fillers resulted in a decrease both in the modules and the elongation at break, also the decline amplitude was variable with the different kinds of nano-scale fillers. The modification of the nano SiO₂ on the polyurethane has become the hot topic in recent years. Park prepared the polyurethane acrylate anionomer /silica composites by the sol-gel reaction. The mechanical properties of the composites were enhanced drastically. Other researchers worked hard on the preparation of polyurethane/SiO₂ nanocomposites used as adhesives & coatings via the solvent method to improve the hardness, abrasion resistance, surface free energy and tensile properties of the polymer films. It is interesting that few studies are concerned with the preparation of castable polyurethane/SiO₂ nanocomposite elastomers via in-situ bulk polymerization and the investigation of the micro-dispersibility of nano-scale SiO₂ with different surface characteristics in prepolymers & CPUEs and the influence mechanism of nano-scale SiO₂ on the mechanical properties.

Nano-scale SiO₂ fillers are ultrafine SiO₂ powder obtained by the pyrohydrolysis of silicon/organosilicon chloride and within hydroxyl groups/adsorption water on the surface. They exhibit the characteristics such as small particle size (<100nm), huge specific surface area (>100m²/g), high chemical purity and good dispersibility. They have been employed extensively in the rubber, coatings, medicine and papermaking because of their excellent stability, reinforcement, thickening and thixotropic properties. The tensile/ tear strength, wear resistance, aging characteristic and thermostability of the modified rubber with nano-scale SiO₂ fillers are all improved.

Poly (ε-caprolactone) polyurethane/SiO₂ nanocomposites were prepared via in-situ polymerization and characterized by a scanning electronic microscope, an electronic universal testing machine, a thermogravimetric analyzer and a dynamic thermomechanical analyzer. The surface treatment effect of coupling silicone agent on the nano-scale SiO₂ and its effect on the properties of CPUE composites were investigated. It is believed that this work can provide some thoughts for the design of novel materials.

1. **Experimental**

1.1. **Raw materials**

ε-caprolactone monomer, purchased from Chunshin Chemical Co., Ltd, was stored below 5°C in nitrogen atmosphere and purified by distillation before usage. 1, 5-pentanediol, supplied by Nanjing Oriental Pearl Industry & Trade Co., Ltd, was distilled under reduced pressure before use. Tetraisopropyl orthotitanate, the catalyst for ring-opening polymerization, was used as received. Nano-scale SiO₂ (trade mark SS1) spherical particles of Zsmrnmclgs production, with a mean particle size
from 20 to 50 nm and a purity of more than 99.5%, was stored in a desiccator. Its specific surface area was 160±20m²/g and hydroxyl group content was more than 19%. \( \gamma \)-glycidochloropropyl methyl trimethoxy silane, with a trade name of A-187, was produced by American Union Carbide Company.

2, 4-toluene diisocyanate (TDI), manufactured by Bayer, was used as reviewed. The production of Albemarle Corporation, 3, 5-dimethylthiotoluene diamine, was dehydrated before use.

1.2. Synthesis of poly(\( \varepsilon \)-caprolactone) glycol

Nitrogen was imported into a 500ml glass reactor equipped with a stirrer, a thermometer and a reflux condenser. Stoichiometric quantities of \( \varepsilon \)-caprolactone monomer and tetraisopropyl orthotitanate were added, then 1, 5-pentanediol, used as the initiator, was introduced and the mixture was heated with an intensive stirring. The polymerization was carried out under nitrogen atmosphere for 48h at 140 to 160°C. After reaction, the mixture was vacuum-evaporated at 120 to 140, and the unreacted monomer was removed. A milk-white solid was obtained and stored in a desiccator after cooled. The polymerization process is presented in Formula 1 and the mean molecular weight was determined before the preparation of prepolymer.

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0 \xrightarrow{\text{Catalyst}} \varepsilon-\text{caprolactone} + \text{CH}_2=\text{CH}-\text{OH} \xrightarrow{\text{Heat}} \text{NCO} + \text{CH}_2=\text{CH}-\text{OH} \]

1.3. Preparation of CPUE

1.3.1. Surface treatment of nano-scale SiO\(_2\) particle
\n\( \gamma \)-glycidochloropropyl methyl trimethoxy silane (A-187) was added into acetone solvent and dispersed via ultrasonic wave for 10 minutes to form a solution with 20% content. Nano-scale SiO\(_2\) particles were added into the solution and mixed uniformly. Then the mixture was treated via ultrasonic wave for 30 minutes and coupling-reacted for 2 hours, and the solvent was distillated and recycled. The obtained nano-scale SiO\(_2\) particles were desiccated and ready for next operation.

1.3.2. Synthesis of NCO terminated prepolymer
Poly (\( \varepsilon \)-caprolactone) glycol was melted and the nano-scale SiO\(_2\) particles were added with high speed stirring. Nano SiO\(_2\)/polylol dispersion was formed after 15 to 30 minutes stirring with the speed of 4000 to 5000 rpm. The dispersion was heated to 100 to 120°C and dehydrated at vacuum for 2 to 3 hours. After cooled to 60°C, the dispersion was mixed with a stoichiometric quality of diisocyanates and maintained the temperature at 80°C for 3 hours. The reactant was degassed after the concentration of isocyanate groups was determined by the amine equivalent method.

1.3.3. Preparation of polyurethane elastomer
In this stage, the precisely dehydrated 3, 5-dimethylthiotoluene diamine was poured into the NCO terminated prepolymer at 80°C at the quantity which was obtained from the designed molar ratio (NH/NCO group=0.88). After 1 min of intensive stirring, the mixture was poured into a mold which had been placed on a vulcanizing press and preheated up to 100°C. The mold was locked while the mixture initially formed a gel. A piece of 2mm thick test plate was obtained after 30 min curing period and demolded from the mold. The elastomer samples were subjected to the tests after vulcanized in an oven at 120°C for 24 hours and stored at room temperature for a week.

2. Test and characterization

2.1. Determination of the mean molecular weight of poly(\( \varepsilon \)-caprolactone) glycol
The mean molecular weight of poly (ε-caprolactone) glycol was determined via a Knauer vapour pressure osmometer (model: K-7000) by using toluene as solvent. The test temperature was 37±0.01℃. The test method was based on the Ragout’s law. At the same time, it was also measured by testing the terminated hydroxyl groups via the phthalic anhydride-pyridine acylation method.

2.2. Characterization of the dispersity and storage stability of nano-scale SiO₂ in the poly(ε-caprolactone) prepolymer
The melting prepolymer was casted on the 0.2mm thick glass slide and formed a film, then the film was observed by a Nikon YS100 optical microscope after stained by KMnO₄ solution. And the storage stability can be judged by the appearance of the prepared prepolymer and the state after long time storage.

2.3. Characterization of the dispersity of nano-scale SiO₂ in CPUE
The CPUE samples were fractured in liquefied nitrogen. The brittle fractured surface was sputtered with gold. The morphology of sample surface and the dispersity of nano-scale SiO₂ in CPUE were observed via a Philip XL30 scanning electron microscope (SEM).

2.4. Properties determination

2.4.1. mechanical properties
The mechanical properties of CPUE samples were tested via an electronmechanical universal testing machine (INSTRON Co. LTD, Model 5566, USA). The test of tensile strength was based on ASTM D412-1998A named “Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers Tension”. And the tear strength was tested based on ASTM D624-00e1 named “Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers”.

2.4.2. Hardness
A LX-A durometer made by ShangHai HongSheng Instrument Co., Ltd. was utilized to determine the sample hardness according to ASTM D 2240 named “Standard Test Method for Rubber Property—Durometer Hardness”.

2.4.3. Resilience
A rubber resilience experimental machine made by ShangHai Chemical Machinery Company was used for testing the impact resilience of samples and ASTM D 1054-2002 Standard titled “Test Method for Rubber Property - Resilience Using a Goodyear-Healey Rebound Pendulum” was the basic method.

2.4.4. Characterization of the thermostability of samples
Thermogravimetric analysis (TGA) was carried out on a NETZSCH Instruments analyser TG209 in nitrogen atmosphere. All samples were heated from 25 to 500℃ at a heating rate of 10℃/min.

2.4.5. Characterization of the dynamic mechanical properties of samples
A NETZSCH Instrument, Dynamic-Mechanical Analyzer DMA242, was employed to determine the dynamic properties of the sample which was cut as following size: 2.0×5.8×10.0mm. The test was carried out at 10 Hz frequencies, ±2N maximum dynamic stress, ±40μm maximum deformation amplitude. The temperature range was -100～150℃ and the heating rate was 5℃/min.

3. Results and discussion

3.1. The dispersity and storage stability of two sorts of nano-scale SiO₂ in PCL prepolymer
A key technique of nano-scale particle modification on CPUE is how to disperse the nano-scale particle into material matrix with nanometer grade successfully. At the same time, the storage stability is a great factor on the manufacturability of prepolymer. First of all, it is necessary to investigate the dispersing state and storage stability of nano-scale SiO$_2$ in the prepolymer.

![Image of optical micrographs](a) pure prepolymer, (b) PCL based prepolymer with 5% untreated nano-SiO$_2$ and (d) PCL based prepolymer with 5% nano-SiO$_2$ pretreated by A-187(1000×)

The films of two types of prepolymer, the PCL based prepolymer with 5% untreated nano-SiO$_2$ and the PCL based prepolymer with 5% nano-SiO$_2$ pretreated by A-187, were observed and different images were obtained. In order to get a comparison, an image of the pure prepolymer was also captured and listed in figure 1. It was obviously that the nano-SiO$_2$ pretreated by A-187 formed a homogenizing-dispersion, while the untreated nano-SiO$_2$ aggregated and even formed some agglomerates within 1 μm diameter because of the incompatibility caused by the polarity difference between two components.

**Table 1.** Storage stability of two sorts of nano-scale SiO$_2$ in PCL prepolymer

| Prepolymer sample                              | Storage stability                                      |
|------------------------------------------------|-------------------------------------------------------|
| PCL based prepolymer with 5% untreated nano-SiO$_2$ | White subtransparent liquid with some deposition after 48 hours storage at room temperature |
| PCL based prepolymer with 5% nano-SiO$_2$ pretreated by A-187 | Colourless transparent dispersion without any change during storage life (30d) |

As shown in table 1, the untreated nano-SiO$_2$ with 5% content was dispersed in PCL based prepolymer, and a white subtransparent liquid was obtained. After stored for 48 hours in room temperature, there was some deposition in this system because of the poor interface compatibility between the untreated nano-SiO$_2$ and the prepolymer matrix. While the nano-SiO$_2$ pretreated by A-187 with 5% content was dispersed uniformly and a colourless transparent homogeneous system was obtained. It was so stable that there was no change during 30 days of storage. This phenomenon also confirmed the micro-dispersing difference between two systems.

3.2. The dispersity difference of two sorts of nano-scale SiO$_2$ in PCL CPUEs

The SEM fractographs in figure 2 present the surface morphology of three samples. After compared the fractographs, a conclusion can be made that there are obvious differences in the dispersibility of two sorts of nano-scale SiO$_2$ in the PCL CPUEs. The surface of the Pure PCL CPUE is smooth and clear, whereas both the polyurethane/nano-scale SiO$_2$ composites have rough surface. It could be contributed that the difference in surface recovery capability what is depended on the soft segment mobility. The soft segments within low glass transition temperature (Tg) and low surface energy could move and minimize the surface area. In the nanocomposites, the soft segment could not
effectively migrate and was unable to recover surface because it was restricted by the interfacial interactions between the polymer matrix and the nano-scale particles\textsuperscript{19}. This explanation also confirmed by the comparison of the DMA curves of the samples in figure 5. On the other hand, the polarity difference between two components resulted in different dispersion states of polyurethane/nano-scale SiO\textsubscript{2} composites. In the PCL CPUE with 5\% untreated nano-SiO\textsubscript{2}, there existed agglomerating phenomenon, and even formed some nano-agglomerates having more than 1 \( \mu \)m diameter. But the stable and homogeneous nano-dispersion of nano-scale SiO\textsubscript{2} in the PCL CPUE was achieved because of the surface modification on nano-scale SiO\textsubscript{2}. This phenomenon corresponded well with the dispersion states of two nano-scale SiO\textsubscript{2} in the PCL prepolymers.

![Figure 2](image_url)

**Figure 2.** SEM fractographs of (a) Pure PCL CPUE, (b) PCL CPUE with 5\% untreated nano-SiO\textsubscript{2} and (c) PCL CPUE with 5\% nano-SiO\textsubscript{2} pretreated by A-187 (10000\( \times \))

3.3. The thermostability difference of two sorts of nano-scale SiO\textsubscript{2} in PCL CPUEs

In figure 3, the comparison of three TGA curves can indicate remarkably that the introduction of nano-scale SiO\textsubscript{2} in the PCL CPUE via in-situ polymerization increased the initial thermal degradation
temperature, moreover, the PCL CPUE with 5% nano-SiO₂ pretreated by A-187 exhibited better thermostability than the PCL CPUE with 5% untreated nano-SiO₂ because more efficient chemical bonds could be found due to the reactive groups on the surface of nano-SiO₂ pretreated by A-187.

![Figure 3. TGA thermograms for (1) Pure PCL CPUE, (2) PCL CPUE with 5% untreated nano-SiO₂ and (3) PCL CPUE with 5% nano-SiO₂ pretreated by A-187](image)

3.4. Effect of nano-scale SiO₂ on the mechanical properties of PCL CPUEs

| Sample                  | Hardness (Shore A) | Modulus 100% MPa | Modulus 300% MPa | Elongation at break, % | Tensile strength, Mpa Ambient temperature 100℃ | Tear strength, KN/m Ambient temperature 100℃ | Resilience, % |
|-------------------------|--------------------|------------------|-------------------|------------------------|-----------------------------------------------|-----------------------------------------------|--------------|
| Pure PCL CPUE           | 83                 | 4.33             | 8.23              | 582.0                  | 39.24                                         | 8.48                                          | 79.5         | 41.0         | 51          |
| PCL CPUE with 5% untreated nano-SiO₂ | 83                 | 4.58             | 8.51              | 597.1                  | 40.70                                         | 9.43                                          | 85.7         | 68.7         | 50          |
| PCL CPUE with 5% nano-SiO₂ pretreated by A-187 | 84                 | 5.22             | 10.46             | 622.5                  | 46.39                                         | 12.72                                         | 99.7         | 79.5         | 48          |

Note: All the CPUE samples were prepared by PCL and TDI, the content of NCO group was 3.4%, the chainextender was DADMT, and crosslinking ratio was 0.88.

From the data in table 2, a conclusion could be made that the introduction of two sorts of nano-SiO₂ increased the modulus at 100% and 300%, elongation at break, tensile strength and tear strength. What should be specially noted was that the improvement of the tensile strength and tear strength at 100℃ of the PCL CPUE with 5% nano-SiO₂ pretreated by A-187 was the best. When compared with the data of the pure PCL CPUE, they were increased by 1.50 and 1.94 times, respectively. At the same time,
the introduction of nano-SiO$_2$ via in-situ polymerization had little influence on the hardness, but the impact resilience of nano composites decreased slightly.

These results are understandable according to the systematical analysis on the nature of the nano composites. The dispersion state of nano-SiO$_2$ in the polyurethane matrix played an important role when the elastomer materials were impacted by an external force. The nano fillers could improve the tension resistance effectively because they acted as crosslinking points. It was remarkable that the optimum coupling agent, $\gamma$-glycidochloropropyl methyl trimethoxy silane (A-187), not only formed hydrogen bonds with polar groups contained by soft/hard segments of polyurethane, but also ring-opening reacted with isocyanate groups & hydroxyl/amine groups during the preparation process by the terminated epoxy groups and achieved stable chemical bonds. This was favorable for the modification of the mechanical properties, especially for the performance at the elevated temperature of the CPUEs.

![Molecular structure of $\gamma$-glycidochloropropyl methyl trimethoxy silane (A-187)](image)

Figure 4. Molecular structure of $\gamma$-glycidochloropropyl methyl trimethoxy silane (A-187)

3.5. Effect of nano-scale SiO2 on the dynamic mechanical properties of PCL CPUEs

As shown in figure 5, $T_g$ of two nano-SiO$_2$ polyurethane composites increased to higher temperature region than the pure PCL CPUE. $T_g$ of the PCL CPUE with 5% untreated nano-SiO$_2$ increased about 2.5 $^\circ$C and that of the PCL CPUE with 5% nano-SiO$_2$ pretreated by A-187 increased about 7.5 $^\circ$C. And the loss factor peaks of the two nano-SiO$_2$ polyurethane composites were higher obviously than that of the pure PCL CPUE. In addition, the loss factor (Tan$\delta$) of the PCL CPUE with 5% nano-SiO$_2$ pretreated by A-187 was the biggest one among the three samples. This may be explained by the differences in the microphase separation degree caused by the modification of nano-SiO$_2$ on the CPUEs. More hard segments were dispersed in the soft matrix, which can restrict the movement of soft chain and result in the migration to higher temperature zone of $T_g$. At the same time, the material hysteresis became bigger. This phenomenon was correlated to the decrease in the resilience of the two nano-SiO$_2$ polyurethane composites.
Figure 5. DMA curves for (1) Pure PCL CPUE, (2) PCL CPUE with 5% untreated nano-SiO$_2$ and (3) PCL CPUE with 5% nano-SiO$_2$ pretreated by A-187

Conclusion

The following conclusions can be made according to the investigation on the two nano-SiO$_2$ polyurethane composites.

(1) The surface treatment by the optimum silane coupling agent influenced the dispersibility of nano-SiO$_2$ in the PCL CPUE distinctly. The agglomerating phenomenon, and even some nano-agglomerates with more than 1 μm diameter can be observed in the PCL CPUE with 5% untreated nano-SiO$_2$, but the nano-SiO$_2$ pretreated by A-187 dispersed in the PCL CPUE in the nano-scale degree.

(2) The introduction of a certain amount of the nano-SiO$_2$ in the PCL CPUE via in-situ polymerization improved the initial thermal degradation temperature. And for the PCL CPUE with 5% nano-SiO2 pretreated by A-187, it was boosted close to 30°C compared with the data of the pure PCL CPUE.

(3) The introduction of a certain amount of the nano-SiO$_2$ via in-situ polymerization intensified the modulus at 100% and 300%, elongation at break, tensile strength and tear strength. The most remarkable fact is that the tensile strength and tear strength at 100°C of the PCL CPUE with 5% nano-SiO$_2$ pretreated by A-187 were 1.50 and 1.94 times than those of the pure PCL CPUE, respectively.

(4) Hardness of the nanocomposites had nothing to do with the addition of nano-SiO$_2$, but the impact resilience decreased slightly.

(5) $T_g$ of the two nano-SiO$_2$ polyurethane composites increased to higher temperature region compared to the pure PCL CPUE. Here, $T_g$ of the PCL CPUE with 5% untreated nano-SiO$_2$ increased about 2.5°C and that of the PCL CPUE with 5% nano-SiO$_2$ pretreated by A-187 increased about 7.5°C.

(6) The loss factor peaks of two nano-SiO$_2$ polyurethane composites were higher obviously than that of the pure PCL CPUE. In addition, the loss factor (Tanδ) of the PCL CPUE with 5% nano-SiO$_2$ pretreated by A-187 was the biggest one among the three samples.

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