

A Designed Surface Modification to Disperse Silica Powder into Polyurethane

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ABSTRACT: Nanoparticles of silica powder were modified by grafting polyurethane (PU) short chains or oligomers using surface-started condensation reactions of various di- or tri-ols and di-isocyanates in step-by-step. Surface density of NCO-groups, introduced by an autoclave method and ready for starting of subsequent reactions, was adjusted by amount of 3-isocyanatepropyltriethoxysilane (ICPTES). Length of grafted oligomers was determined by reaction steps. TG/DTA measurements demonstrated a gradual increase of NCO-groups density with the amount of modifier input. FTIR spectra and thermal weight loss analyses confirmed the occurrence of reac-

tion in each step and the growth of grafted oligomer. SEM images of particles dispersed in *N,N*-dimethylacetamide or in prepolymer of PU indicated an improved dispersion. Moreover, when as-modified particles were incorporated in PU prepolymer, the resultant hybrid films displayed an enhanced optical property, thermal stability, and Vicker's hardness, suggesting a better dispersion of modified particles. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

Key words: silica nanoparticle; surface modification; dispersion; polyurethane

INTRODUCTION

Polymer/silica nanocomposite materials have attracted both academic and industrial interest for several decades because of their unique synergistic properties, advantages of availability and inexpensiveness, and potential applications in various fields.^{1–9} However, a well-defined dispersion of silica powder nanoparticles (NPs) in polymer matrices is still a pursuing issue, as the enough strong interactions at interface between polymer matrices and inorganic NPs is intrinsically hard to achieve.¹⁰

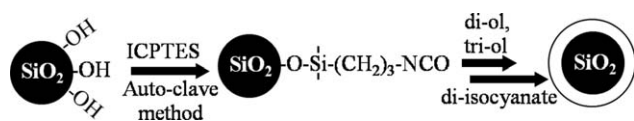
Up to now, extensive research works have been done to mitigate the self-aggregation of inorganic NPs derived from Vander Waals attractions, and thus to improve the compatibility of inorganic NPs with an organic phase.^{11–13} Among them, surface initiated control/living radical polymerizations^{10,14–16} are considered to be effective techniques to firmly control parameters including graft density, molecular weight, and chemical composition of graft and matrix polymers, etc.^{17–19} to enhance the dispersion of inorganic NPs.¹⁹ Usually, dense and long grafted chains were prerequisite to achieve complete isolation of NPs in homo- or block-polymer matrices¹⁹ to take full advantage

of large specific surface/interface area of NPs. Sometimes, particles grafted with relative sparse and short chains also brought about an effective dispersion, and their self-assembly into highly anisotropic structures led to a pronounced enhancements in mechanical property of resultant nanocomposites.^{10,17,19}

In addition, condensation reactions initiated from a solid surface provide an alternative to covalently immobilize linear or branched functional copolymer chains on particles, and hence to facilitate the dispersion of inorganic NPs. Some of investigations on surface-started condensation polymerization have been performed to create highly advanced organic/inorganic nanocomposites,²⁰ for example, Chen et al.²¹ prepared polyurethane (PU)/silica hybrid nanocomposites by incorporation of inorganic nanosized silica building blocks into PU matrix via a two step functionalized reaction including encapsulation of 3-aminopropyltriethoxysilane (APTS) and tether of PU shell on silica surface. In previous works, elaborate control of grafting of PU chains onto silica powder particles, such as manipulation of surface density, grafted chain length, and structure, by condensation reactions started from particle surface, was seldom involved in, and a better dispersion of silica powder in matrix of PU is still needed.

It is known that PU can be manufactured by condensation polymerization of di-isocyanates and di- or tri-hydroxyl compounds (di-ols or tri-ols). The employment of multifunctional monomers would

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Scheme 1 Representation of surface modification of silica NPs with ICPTES, and further reactions with di-, tri-ol, or di-isocyanate.

make the grafting of PU on particle surface more complex in comparison with the grafting of homopolymers such as polystyrene (PSt), or poly(methyl methacrylate) (PMMA) by free radical polymerizations. Especially, when surface condensation reactions start from large aggregated silica particles, rather than from individual NPs dispersed homogeneously in a good solvent or media, it is not easy to achieve dense and long linear grafted chains because of high reactivity of multifunctional monomers. Furthermore, the dispersing behavior of as-grafted NPs in PU is supposed to be dissimilar to that of silica NPs attached homopolymer in analogous matrices of homopolymer, block copolymer¹⁶ or miscible blends of polymers¹⁹. Accordingly, further investigations on the grafting of PU on particle surface by condensation reaction to disassociate silica power in PU are demanded.

In our group, surface designed reactions were proposed to shield silica particle surface with densely grafted functional polymers to achieve a good dispersion in polyimide (PI) or in slurry.^{22,23} Herein, with the aim to improve the dispersibility of silica powder in PU matrix, oligomer, or short-chain of PU was devised to incorporate onto particles by an autoclave method under supercritical hexane using 3-isocyanatepropyltriethoxysilane (ICPTES) as a modifier agent, and followed by graft condensation reactions of surface-coupled isocyanate groups (NCO—) with di-, tri-ols, and di-isocyanate, as shown in Scheme 1. Surface density of initial functional groups (NCO—), which indicated the surface grafting density of oligomers on silica particles, was adjusted by modifier agent input and evaluated by TG/DTA measurements. Graft chain length of PU oligomers, demonstrated by FTIR spectra analysis, and TG/DTA measurements, was thought to be manipulated by further grafting reactions of di- or tri-ols, and di-isocyanate in step by step. Furthermore, hybrid thin films with modified silica particles dispersed in PU were prepared by a controlled roller coating and thermal curing, and their optical properties, thermal, and mechanical properties were examined.

EXPERIMENTAL

Materials

Silica powder (Aerosil OX 50, average particle size of 40 nm, specific surface area 50 m²/g, supplied by

Nippon Aerosil) was dried at 130°C in a vacuum oven for at least 48 h and stored at room temperature (RT) with a relative humidity (RH) of 34%. Modifier agent ICPTES (Shin-Etsu Silicone, KBE 9007, 99.7%, purchased from Shin-Etsu Chemical), poly-ols including polyethylene glycol (PEG, $M_W = 400, 2000, 99\%$), triethylene glycol (TEG, $M_W = 150.17, 99.8\%$), diethanolamine (DEOA, $M_W = 105.14, 99.8\%$), *tris*-(hydroxymethyl)aminomethane (TOAM, $M_W = 121.14, 99.8\%$), and 4,4-Diphenylmethane diisocyanate (MDI, 99.7%), etc., from Shin-Etsu Chemical, were used without further purification. Solvents such as *N, N*-dimethylacetamide (DMAc) and acetone, etc., were used as received.

Modification of silica particles with ICPTES

The chemical reaction of ICPTES with hydroxyl groups of silica (density of OH— groups: 2.8/nm²) was carried out using an autoclave method as described previously.²² The amount of modifier applied was referred to mole ratio of NCO-group to silanol groups (NCO—/OH in moles) on silica surface. The surface density of modifier, noted as surface density of NCO-groups (d_M , NCO— nm²) on particles, was determined with weight loss data from TG/DTA analysis and calculated according to the following equation²³:

$$d_M(\text{NCO—}/\text{nm}^2) = \frac{(\Delta W_{\text{CH}} - \Delta W_{\text{OH}})N_A}{M_W S_{N_2}}$$

where ΔW_{CH} is the weight loss ratio of modified silica particle, ΔW_{OH} is that of pristine one, N_A is the Avogadro number, M_W is the molecular weight of modified group (84), and S_{N_2} is the specific surface area of silica powder used (50 m²/g).

Surface grafting by condensation reactions

In a 100 mL, 4-neck bottom flask equipped with condenser, thermometer and N₂ inlet, the modified particles (Si—NCO) were suspended into DMAc with aids of a magnetic stirrer, and then di- or tri-ols, or MDI was introduced into the suspension in step by step. The condensation reaction was performed usually under a small N₂ flow at 25°C for 3 h.

After cycles of reaction of diisocyanate and poly-ols, particle surface was coated with oligomers of PU. Sample produced in each step was isolated by centrifugation, washed with DMAc, and acetone for at least 3 cycles, and then dried under vacuum.

Preparation of hybrid films

Pristine or surface-modified silica particles (5 wt %) were ultrasonically dispersed in 2 mL of a mixture

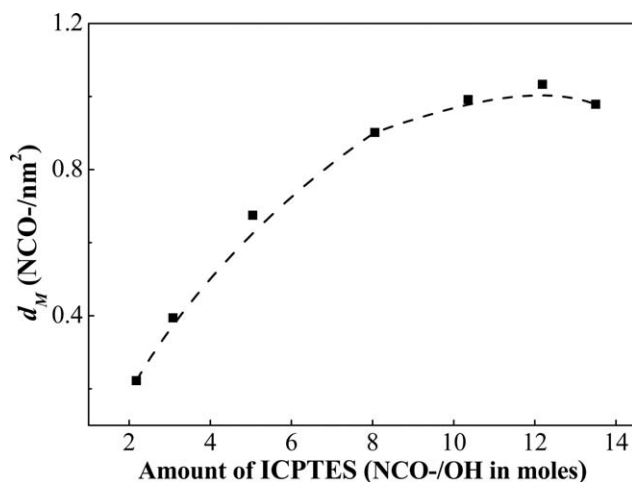


Figure 1 Surface density of NCO-groups on silica particles modified with various ratio of NCO-/OH.

of PEG400 (3×10^{-3} mol), MDI (3×10^{-3} mol) and DMAc. 0.05 mL or 0.5mL of the as-produced dispersion was coated on a piece of quartz or pyrex glass using a K101 Control Coater (RK Print Coat Instrument, UK), and then cured at 70°C for 12 h to get a thin or thick film.

Characterization

Weight loss data: determined on a Thermo Plus TG8120 analyzer (Rigaku, Japan) under O₂ atmosphere with a flow rate of 500 mL/min, heating rate of 10°C/min, from room temperature to 700°C.

Grafted chains analysis: done on a FTIR 6200 spectrometer (Jasco, Japan) using KBr pellets.

Morphology of particles: observed on a JSM-7000F Scanning Electron Microscope (SEM, Jeol, Japan), under an accelerating voltage of 10 kV. Samples were prepared by dropping suspension of silica particles in DMAc on a small piece of cover glass and evaporating at room temperature, or by spin-coating the mixture of silica particles, PEG, MDI, and DMAc on a glass and then drying under vacuum at 70°C for 8 h. Before SEM observation, samples were coated with osmium (OsO₄).

Particle size and its distribution: evaluated by Zetasizer Nano Series (Malvern Instrument) in a solvent of DMAc.

Transmittance of hybrid films: measured on a UV-VIS-NIR spectrophotometer, UV3150 (Shimadzu, Japan) in wavelength range of 190–900 nm.

Vicker hardness of hybrid film: estimated on a HMV-2T micro-hardness tester (Shimadzu, Japan), and for each sample, at least four points was measured to get an average value.

RESULTS AND DISCUSSION

Surface-initiated condensation reactions and structure analysis

An autoclave method was used to allow the surface —OH groups react efficiently with silane coupling agent^{22,23} due to —OH groups in silica powder are not easy to be fully exposed on surface. Surface density of NCO-groups (d_M) introduced firstly onto particle, approximating the graft density of PU oligomer or short chain in subsequent process, could be controlled by varying ICPTES input in system and evaluated by TG/DTA analysis. As plotted in Figure 1,

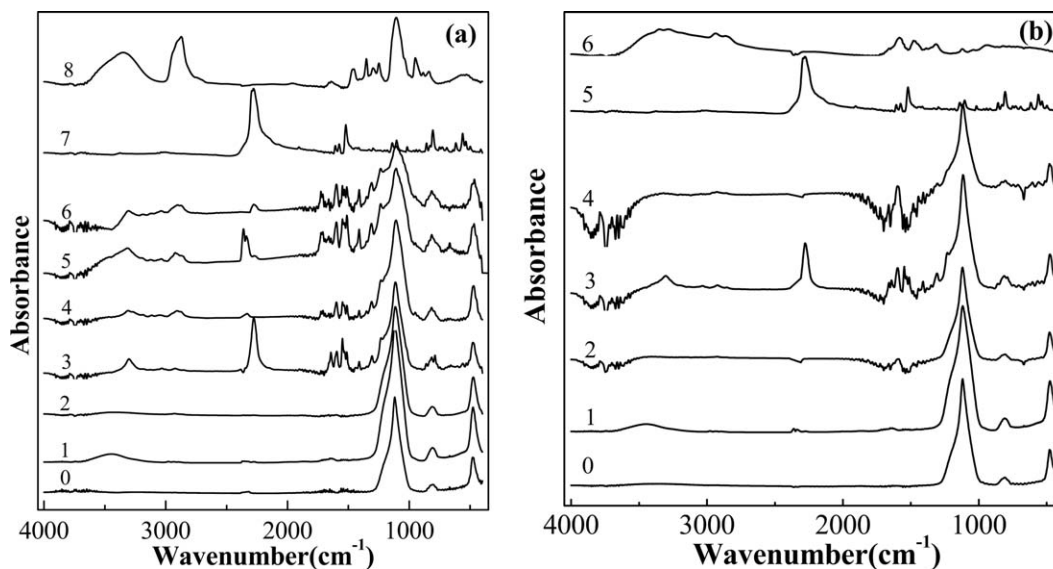


Figure 2 FTIR spectra analysis of silica particles and materials, 0: pristine particles, 1: Si-NCO particles, 2,4,6 (a) particles produced after reaction with PEG (a) or DEOA (b), 3,5 (a) particles produced after further reaction with MDI. 7(a), 5(b): MDI, 8(a): PEG, 6(b) DEOA.

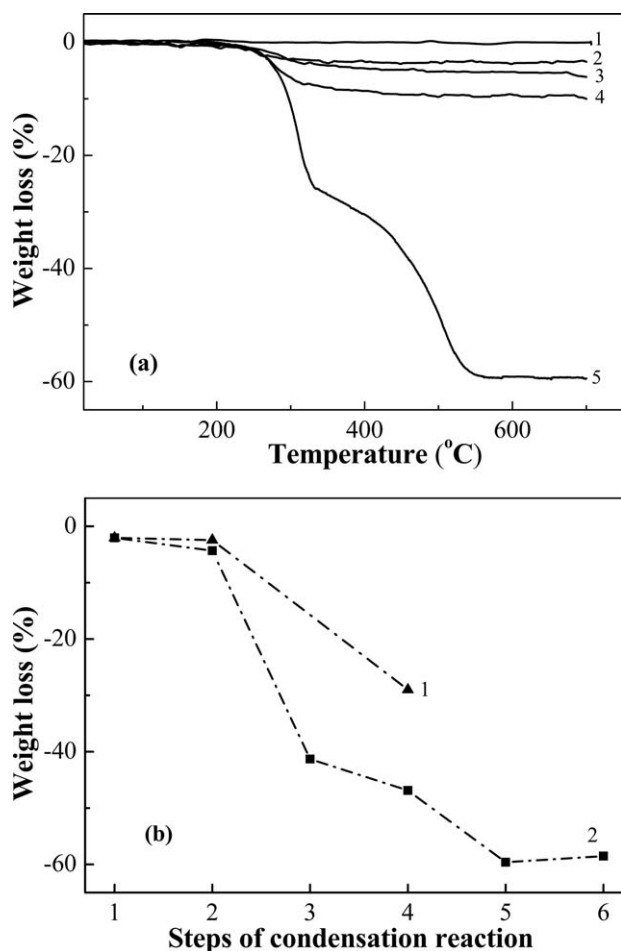


Figure 3 (a) Typical TG curves of silica particles: pristine particles (1), Si-NCO particles (2), modified silica particles after reaction with TEG (3), and then with MDI repeatedly at 0°C (4) or 25°C (5) for 5 steps. (b) Condensation reaction of Si-NCO particles with PEG (1) or DEOA (2), and then with MDI in multisteps, $W_{\text{Si-NCO}} = 0.2$ g, $M_{\text{PEG or DEOA}} = M_{\text{MDI}} = 3 \times 10^{-3}$ mol, $V_{\text{DMAc}} = 30$ mL.

d_M improved along with increase of modifier amount, confirming the successful incorporation of NCO-groups on particle surface. When mole ratio of NCO-/OH was increased up to 12.2, surface density of about 1.14 NCO-groups/nm² was achieved, and then a slight change of coupling of NCO-groups displayed at a higher mole ratio of NCO-/OH.

In the present experiments, values of d_M were lower than that achieved previously^{22,23} and far less than theoretical one of 2.8-OH/nm^{2,23}. This case would cause some difficulties in detecting the pres-

ence of NCO-groups by FTIR analysis (Figure 2, curve 1). The aggregation of silica particles in powder (could be at around 600–1700 nm, evaluated by dynamic light scattering, DLS) might screen some free -OH groups on surface and limit their reaction with modifier of ICPTEs, leading to a low coupling degree of NCO-groups. In addition, the possible reaction of NCO-groups of ICPTEs with OH-groups on particle surface might also be negative to the coupling of NCO-groups.

When poly-ols such as PEG or DEOA were charged into reaction system to start condensation reaction with pristine particles, and MDI was added in subsequent step, the obtained particles showed no distinct FTIR absorptions and marked weight loss differing from those of pristine particles. In system contained particle with NCO-groups coupled on surface in a density of 1.14/nm², FTIR analysis indicated that in the first step, with poly-ols such as PEG or DEOA charged, no significant variations was discerned (Figure 2, curve 2). While, with MDI segments incorporated onto particle surface, characteristic absorption of NCO-group at 2279 cm⁻¹ was observed clearly (Figure 2, curves a3 and b3). This phenomenon implied that more NCO-groups could be combined because of the possible reaction of MDI with surface free -OH groups freshly exposed due to a gradually improved dispersion. The above results further verified the successful introduction of original NCO-groups, and revealed that it was enough to start condensation reactions from particles surface with NCO-groups in a low density, allowing to graft sparse and enough long polymer chains on surface to improve the dispersion of particles.

As seen in Figure 2, absorption at 1720 cm⁻¹ could be assigned to -C=O group come forth with the addition of MDI. Absorption at 1650 cm⁻¹ could be ascribed to amide groups -CO-NH-, and absorptions at 1705, 1632 cm⁻¹ could be attributed to carbonyl groups of urethano units (-NHCOO-). Absorptions at 1600, 1560, 1514, 1423 cm⁻¹ were aromatic characteristic peaks. When reaction with PEG or DEOA occurred again, the characteristic absorption of NCO- at 2279 cm⁻¹ was disappeared almost completely (Figure 2, curves a4 and b4), and absorptions arising from -CH₂ symmetric stretching vibration at 2890 cm⁻¹, N-H stretching vibration at about 3300 cm⁻¹ were detected apparently. Similar

TABLE I
Grafting of Short Chains or Oligomers Through Condensation Reactions in Multisteps

Composition of grafted chains	Si-NCO-TEG	Si-NCO-PEG400	Si-NCO-PEG2000	Si-NCO-TEG-MDI-TEG-MDI-TEG	Si-NCO-TOAM	Si-NCO-DEOA	Si-NCO-DEOA-MDI-DEOA
Weight loss%	-3.83	-4.32	-5.15	-5.26	-4.74	-4.94	-9.15

Reaction time: 6 h; temperature: 0°C; $W_{\text{Si-NCO}} = 0.2$ g; $M_{\text{ols}} = M_{\text{MDI}} = 3 \times 10^{-3}$ mol; $V_{\text{DMAc}} = 30$ mL.

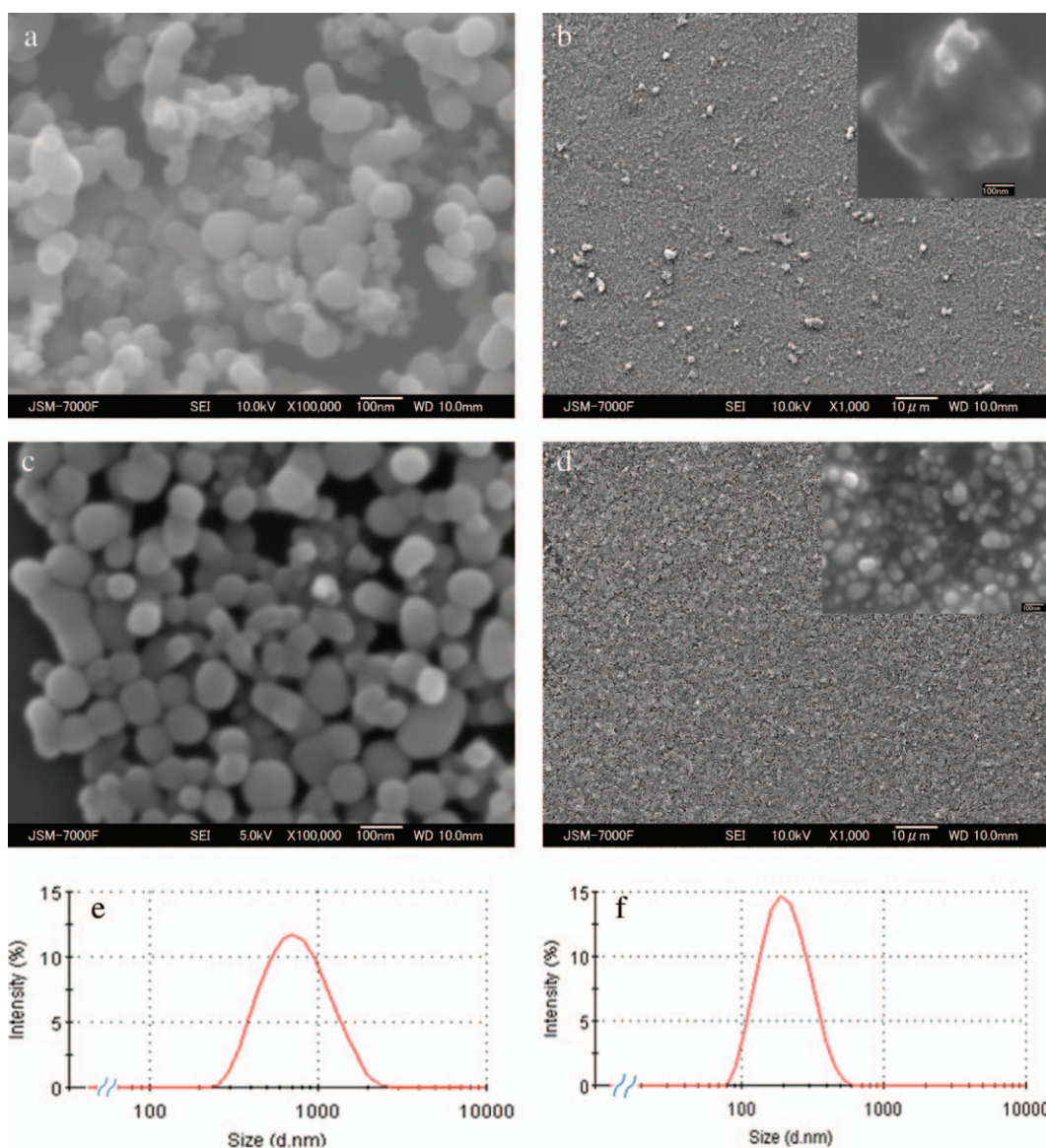


Figure 4 SEM images of pristine (a, b) and modified (c, d, weight loss 4.5%) particles dispersed in DMAC or in prepolymer of PU, and pristine (e) or modified (f) particle size distribution by intensity in DMAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observations were presented after repeated reaction with PEG and MDI in cycles (Figure 2, curves a5 and a6). The above described FTIR analysis demonstrated the occurrence of grafting condensation reaction and implied the growth of grafting chains in each step.

Typical TD/DTA measurements under an O_2 atmosphere indicated that started from surface NCO-groups, condensation reactions with TEG and then MDI repeatedly led to a gradual increase of weight loss [Figure 3(a)], suggesting a growth of grafted chains. This phenomenon was further confirmed by weight loss data against reaction steps [Figure 3(b)] with various di-ols selected as a monomer.

It could be noted that from Figure 3(a), curve 4 and 5, the loading amount of PU oligomers obtained at reaction temperature of 25°C , was much greater than that achieved at 0°C , and TG curve of resultant sample appeared two distinct regions of weight loss started from about 200 and 330°C , respectively, analogous to a typical TG curve of PU as reported.²⁴ It is known that PU is commonly composed of hard and soft segments. The first region was related to thermal degradation of hard segment of grafted chains due to low thermal stability of urethane groups,²⁵ while the second region was associated to the soft segment decomposition.²⁶ Weight losses for the first and second regions were 27 and 34%, respectively. Using weight loss at each region as an approximately quantitative indication²⁵ of hard

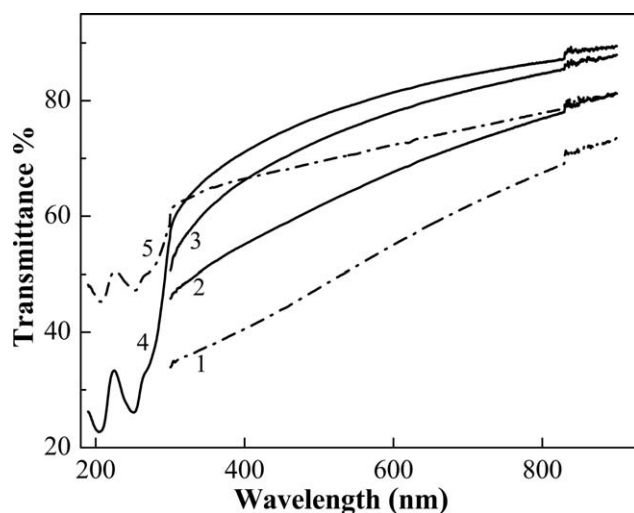


Figure 5 Transmittance of hybrid films impregnated with pristine particle (1, 5), and modified particles (2, surface attached with PEG400 segment, weight loss 4.4%; 3, 4, surface grafted with PU oligomer composing of TEG and MDI segments, weight loss 5.6%).

and soft segment content in grafted PU chains, one could find that the content ratio of hard and soft segment was close to feed mole ratio of MDI to TEG (2/3) in reactions.

Moreover, compared with reactions occurred at a lower temperature, or reactions performed only one or two steps, samples generated at a higher temperature and for more than three steps displayed extremely great weight loss percents, which might not be reasonably attributed to the lengthened grafting chains. Some free oligomer might be generated accompanying the growth of grafted chains and responsible for this exaggeration in weight losses, because of high reactivity of isocyanate and its complexity in reaction with poly-ols.^{27,28}

To alleviate the formation of free oligomer, reactions were carried out in low temperature for long time, and various types of poly-ols were selected to deal with particles. As summarized in Table I, using a diol having a high molecular weight, long chains could be attached onto particle surface, as indicated by the increased weight loss. Multi-step reactions could also be favorable for the lengthening of tethered chains. Especially, the employment of CB_n -type poly-ols permitted the covalent incorporation of branched oligomer on particle surface, which would be advantageous to make grafted chains spread into a larger area as it moved away from a curved surface, and result in a broader grafted chain/matrix interface and favorable grafted chain/matrix interactions. On the other hand, more functional groups introduced onto particle surface by application of CB_n -type polyols could give more possibility to interact with groups in PU matrix, and thus be positive to the dispersion of particles.

Dispersion of modified particles

When pristine silica particles were dispersed in DMAc, compact aggregate was observed from SEM image [Figure 4(a)], even DMAc is a solvent in which silica particles could be electrostatically stabilized.²⁹ Also, it was seen that at a low magnification, pristine silica particles could not be homogeneously dispersed in prepolymer of PU [Figure 4(b)], and at a high magnification, great assemblies of silica particle were found [Figure 4(b), inserted]. When silica particles were subjected to surface grafting modification, large aggregation was disappeared, only some particles still congregated [Figure 4(c)]. At a low magnification, almost uniform dispersion of modified particles could be observed [Figure 4(d)], and separated particles in prepolymer of PU were presented [Figure 4(d), inserted]. These observations indicated that the grafting of polymer chains indeed improved the dispersion of particles in DMAc and prepolymer of PU, and this effect became greater in prepolymer of PU due to stronger interactions between functional groups. DLS measurement further confirmed the decrease in particle size and its distribution [Figure 4(e,f)].

Properties of hybrid films

When pristine particles were impregnated in prepolymer of PU, the prepared film had a transmittance of around 35–70% in wavelength of 300–900 nm using a piece of pyrex glass as reference (Figure 5, curve 1). When modified particles were immersed in prepolymer of PU, the hybrid film showed a transmittance of about 45–80% (Figure 5, curve 2), or 50–88% (Figure 5, curve 3). Silica particles immobilized longer oligomer on surfaces (indicated by the greater

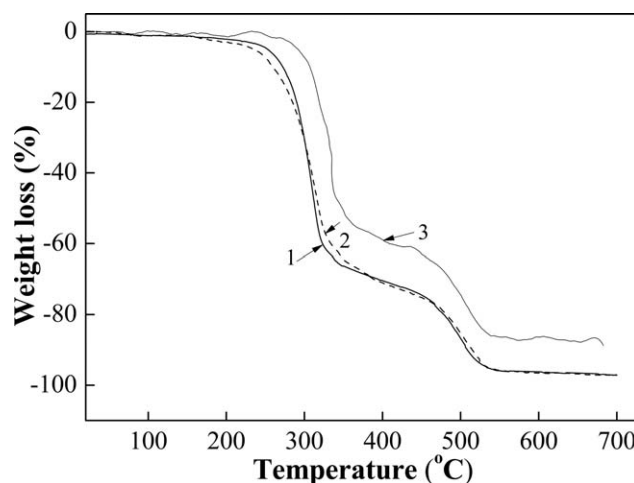


Figure 6 TG curves of hybrid films contained pristine (1), modified particles attached PEG400 segment (2, weight loss 4.4%) or PU oligomer composing of PEG400 and MDI segments (3, weight loss 6.3%).

TABLE II
Vicker's Hardness of Hybrid Films

Si NPs	Pristine	Si-NCO-PEG400	Si-NCO-PEG400-MDI-PEG400-MDI-PEG400
Weight loss%	–	–4.3	–6.5
Average hardness (loading)	24 (98.07 mN)	71 (245.2 mN)	554 (1.961 N) ^a

Formulation of hybrid film: Si NPs: 5 wt %, M_{ols} , M_{MDI} : 3×10^{-3} mol, V : 2 mL.

^a Time: 10 s.

weight loss %) were more favorable for preparing a transparent hybrid film. Using a piece of quartz glass as reference, the transmittance of hybrid film was improved from 60–80% (Figure 5, curve 5) to 58–90% (Figure 5, curve 4), closing to the transmittance (\approx 80–90%, 300–900 nm) of PU film synthesized with PEG and MDI under similar conditions. This enhanced transmittance of hybrid films also evidenced the improvement in particles dispersion.

On the other hand, Figure 5 shows that in wavelength range of 190–300 nm, hybrid films appeared marked absorptions, which could be attributed to aromatic and carbonyl structures of PU, and the presence of particle attached PU oligomer seemed to strengthen this UV absorption. This phenomenon might be reasonable because of stronger interaction of modified particles with PU prepolymer, which might afford stretched grafted oligomers into matrix and hence make a contribution to UV absorption.

TG/DTA measurements on hybrid films indicated that with modified particles (presenting greater weight loss) dispersed in matrix of PU prepolymer, the as-prepared hybrid films exhibited a higher starting thermal decomposition temperature (T_d) (Figure 6, curve 3), while film contained particles providing lower weight loss showed no significant divergence in T_d with that one impregnated pristine particles (Figure 6, curves 2 and 1). The end residue of hybrid film after a TG/DTA run (Figure 6, curve 3) seemed to be somewhat greater than silica content (5 wt %), which might be ascribed to the trapping of polymer moiety in inorganic matrix.³⁰ The aforementioned thermal behaviors suggested an improvement of thermal stability through incorporation of modified particles. The covalently anchored functional groups on particle would cause more surface binding sites with matrix, thus enhancing interfacial interaction with matrix and compatibility with organic phase, and resulting in a greater thermal stability.

Vicker's hardness of prepared hybrid films measured by a micro-controlled tester further proved the compatibility enhancement derived from good disper-

sion of modified particles. As shown in Table II, with particles giving greater weight loss, the resultant hybrid film demonstrated an extremely high hardness.

As reported by Smith and Bedrov,¹⁷ dense and long polymer brushes were not always necessary for achievement of well-defined dispersion and profound improvement of properties of composite containing inorganic NPs. Here, our results provided another example to confirm this point by introducing sparse and long grafted chains to particles surface. Probable reactions of functional groups and stronger interactions between the grafted oligomer and prepolymer of PU could contribute to the dispersion.

CONCLUSIONS

Using surface-emanated condensation reactions of di- or tri-ols with di-isocyanates in steps, dispersion of silica powder in PU was improved greatly, which was demonstrated by SEM observations, DLS measurements and improvements in properties of hybrid films. As for the modification of silica particles, the graft density could be controlled by amount of modifier agent used in planting NCO-groups onto surface, and composition, length of grafted chains could be devised by selecting types of di- or tri-ols and reaction steps.

Reactions occurred between functional groups on particles surface and matrix of PU, and strong interactions between modified particles and matrix could be advantageous to the improvement of dispersion of particles and properties of hybrid films, in despite of that the density and length of grafted chains were not so high.

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