Role of Nano-Size SiO_2 Additive on the Thermal Behavior of Cyanoacrylate Nanocomposite

Amir Yaghmaei, Mehrdad Kashefi Torbati, Seyyed Mojtaba Zebarjad
Department of Materials Science and Metallurgical Engineering, Faculty of Engineering,
Ferdowsi University of Mashhad, Mashhad, Iran

Nowadays, solvent-free, one-part cyanoacrylate adhesive is widely used in medicine and dentistry. According to a literature survey done by the authors, there are few papers concentrated on the role of nano-sized particles on the thermal behavior of cyanoacrylate glue. Thus the main goal of the current research focused on clarifying the role of nano-sized SiO_2 on the thermal behavior of cyanoacrylate. Thermal behavior of all materials including cyanoacrylate and its nanocomposites was studied by using Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods. The results of DSC analysis showed that an increase in the amount of nano-sized SiO_2 results in decreases in the duration of cyanoacrylate curing, energy release during polymerization, and incubation time of polymerization. Furthermore, the results of TGA tests illustrated that the weight loss of cyanoacrylate strongly depends on the contents of both caffeine and SiO_2. In fact, an increase in nano-sized SiO_2 content increases the degradation temperature of cyanoacrylate. J. VINYL ADDIT. TECHNOL., 16:204–208, 2010. © 2010 Society of Plastics Engineers

INTRODUCTION

Cyanoacrylate is a solvent-free, one-part adhesive that was first introduced to the industrial market in the 1950s [1]. Its ease of application, versatility, and solvent resistance make cyanoacrylate popular in industries. A wide variety of applications can be mentioned for cyanoacrylate including automotive [2], electrical and electronics [3], fingerprinting [4, 5], medicine, and daily uses.

The cyanoacrylate monomers can be polymerized by both free-radical and anionic mechanisms, but the latter hold much greater interest. This is mainly because for this mode of polymerization, they are among the most reactive monomers known and, as a consequence of this extreme reactivity, they are capable of initiation by relatively weak covalent bases [6]. This anionic reaction is inhibited at $pH < 5.5$ [6]; hence monomers are kept in their liquid form by the addition of a weak acid during storage and prior to use. Prior to polymerization, neutralization of the acids takes place. Any practical, weak-electron-donor base, such as moisture on the surface of a substrate, can trigger the polymerization reaction [7, 8]. Basic chemicals such as sodium carbonate, phosphates, amines, caffeine, or pyridine can be used to neutralize the stabilizer and so accelerate polymerization [2, 9, 10].

The lower members of the series are used for applications such as the assembly of delicate electronic components and household items. The higher homologues, i.e., butyl-, hexyl-, and heptyl-being wetted well by blood, are used in medicine, e.g., as tissue binders [11–16] and in drug delivery [17–21]. One of the most important applications of cyanoacrylate is in dentistry. This is because cyanoacrylates are bacteriostatic [22] and can adhere to a wide range of materials with rapid development of strength. Cyanoacrylate can be used in dentistry for tooth cavity treatment [23], tooth pit and fissure sealants [24], and tooth desensitizers [25]. As cyanoacrylates covalently bond to dentin [26] and make strong bonds, they are suitable in dental applications. As was mentioned, any practical, weak-electron-donor base, such as moisture on the surface of a substrate, can trigger the polymerization reaction. Thus, hydroxyl ions from the moisture of the dentin can cause rapid polymerization [26, 27] without losing a significant amount of water [27, 28].

Modifiers such as alumina, calcium carbonate, hydroxyapatite, and silicon dioxide are added to cyanoacrylate to improve its properties. Ridgway et al. [29] utilized cyanoacrylate and alumina powders to produce heart valves by a powder injection molding method. Leonard and Brandes [30] and Cijvan et al. [31] used cyanoacrylate/(calcium carbonate) composite as dental cement. Hydroxyapatite micro powders have been utilized by Bennetts et al. [32] and Tomlinson et al. [7] in cyanoacrylate in order to produce novel dental cements. Takeuchi [33, 34] and Chang and Joos [35] have also taken advantage of silicon dioxide micro powders in cyanoacrylate cements to use them in tooth cavity treatment and as sealants in dentistry. Silicon dioxide nano powders have been used as aerogels [36, 37] to improve cyanoacrylate coating properties by the chemical vapor deposition (CVD) method.

Correspondence to: S. M. Zebarjad; zebarjad@um.ac.ir

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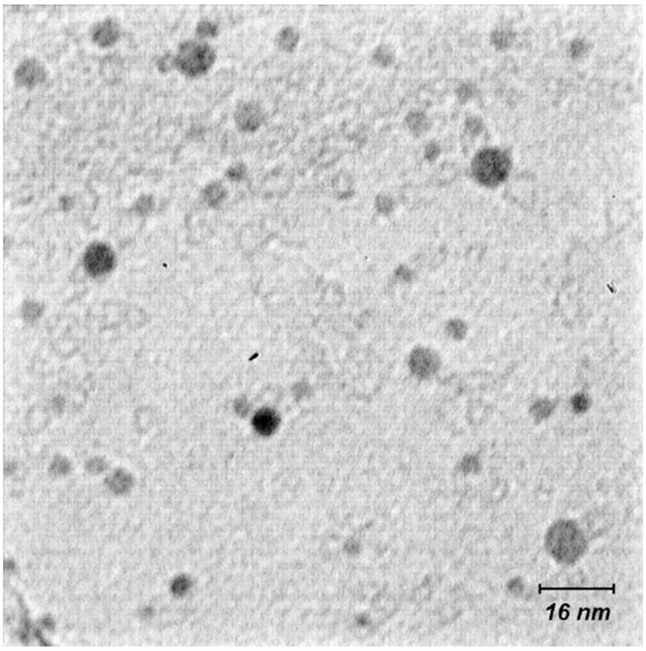

FIG. 1. TEM micrograph of nano-size silicon dioxide.

Also, some studies have concentrated on degradation behavior and glass transition temperature (T_g) of cyanoacrylate [38–43]. According to the literature survey done by the authors, there are no papers concentrated on the curing of cyanoacrylate under isothermal conditions. Besides, the role of nano-size silicon dioxide on the curing and thermal behavior of cyanoacrylate is still a subject of controversy among investigators. Thus the authors decided to fill the literature gap on this issue.

MATERIALS AND METHODS

Materials

Alkoxyethyl cyanoacrylate (Loctite 460, Henkel) with a molecular weight of 141 and a viscosity of 40 mPa.s and silicon dioxide nano powder (Nanolin, China) were used as matrix and reinforcement, respectively. Figure 1 shows a transmission electron microscope micrograph from nano-size silicon dioxide. These nano powders are polygonal in shape and 10–20 nm in size. The purity of the silicon dioxide nano powder used in this research is 99%.

As was mentioned before, in order to prevent polymerization, acids are added to cyanoacrylate. In this research *para*-toluenesulfonic acid (catalogue No. 814725, Merck), as suggested by other investigators [2, 11], was utilized. Neutralization should take place before polymerization, and caffeine (catalogue No. 119164, Merck) was used in the current research because of its biocompatibility.

Sample Preparation

To view nano-size silicon dioxide powders, transmission electron microscopy was utilized. For sample preparation, powders were first mixer-milled (Retsich MM400, Germany) for 10 min and then dispersed in ethanol and sonicated for 1 h. After that, the dispersed powders were placed on a grid and a transmission electron microscope (LEO 919 AB) micrograph was taken (see Fig. 1).

To prepare nanocomposite samples, first, 1 wt% of acid was dissolved in the cyanoacrylate. Without this amount of acid, polymerization occurs immediately upon addition of nano-sized silicon dioxide powders because of the moisture on their surface. In the next step, 1.5 wt% of caffeine was added to the mixture for acid neutralization and as a polymerization initiator. Without caffeine, polymerization will be retarded for several days. Minimum amounts of acid and caffeine were chosen after several experiments in order to investigate the role of silicon dioxide nano powders in the composite. The final step was addition of different amounts of silicon dioxide. To prevent agglomeration of the nano-sized powders, they were milled by a mixer-mill device (Retsich MM400, Germany) for 10 min prior to their addition to cyanoacrylate. During the addition of the SiO_2 powders, the mixture was under ultrasonic processing (Sonicator 3000, Misonix) in order to prevent agglomeration. All fabricated samples are listed in Table 1.

Chemical Structure Evaluation

In order to examine the chemical structure of the nanocomposite, FTIR spectra were recorded. They were obtained with a Shimadzu 4300 FTIR spectrometer by using KBr pellets.

Thermal Evaluation

Differential scanning calorimetry (DSC; DSC-60, Shimadzu, Japan) was utilized to calculate the energy released during polymerization and the setting time of the nanocomposite glue. For this purpose the test was done under isothermal conditions following the ASTM D3418 standard. Samples were kept in the device at room temperature until polymerization occurred.

In order to obtain the degradation temperature, thermogravimetric analysis (TGA; TGA-50, Shimadzu, Japan) was utilized according to the ASTM E2402 standard. Cured specimens were placed in the device and heated at the rate of 10°C/min up to 500°C.

TABLE 1. Nanocomposites produced.

Sample name	Polymer content (wt%)	Acid content (wt%)	Caffeine content (wt%)	SiO_2 content (wt%)
Cy/0% SiO_2	97.5	1	1.5	0
Cy/8% SiO_2	89.5	1	1.5	8
Cy/10% SiO_2	87.5	1	1.5	10
Cy/12% SiO_2	85.5	1	1.5	12

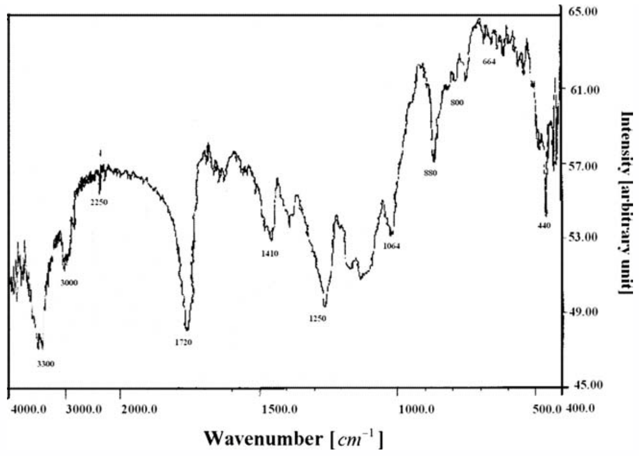

FIG. 2. FTIR spectrum (in KBr) for cyanoacrylate/SiO_2 nanocomposite.

RESULTS AND DISCUSSION

The infrared spectrum of a cyanoacrylate/SiO_2 sample is displayed in Fig. 2. Absorption bands for the solid-state vibrations in SiO_2 are at 440, 800, and 1064 cm^{-1}. Further bands can be seen at 1410 cm^{-1} for δ_{as} Si—CH_3 and 880 cm^{-1} for $\delta_{rocking}$ Si—C in —$Si(CH_3)_2$ [44]. Furthermore, vibrations for carbonyl groups and triply bonded carbon (—C≡C—) appear at 1720 and 2250 cm^{-1}, respectively, as well as a corresponding covalent vibration (≡C—H) at 3300 cm^{-1}. Other bands such as δ(N—H_2), δ(C—H), and δ(C—H) can be found at 664, 1250, and 3000 cm^{-1}, respectively [45].

The results of DSC analysis can be seen in Fig. 3. It is worth noting that because of the long periods of polymerization for 4 and 6% of SiO_2, results for these formulations do not appear in the figure. As indicated, incubation time and duration of polymerization depend strongly on nano-size SiO_2 content. When silicon dioxide is added to the mixture, both the energy released during polymerization and the maximum temperature decrease.

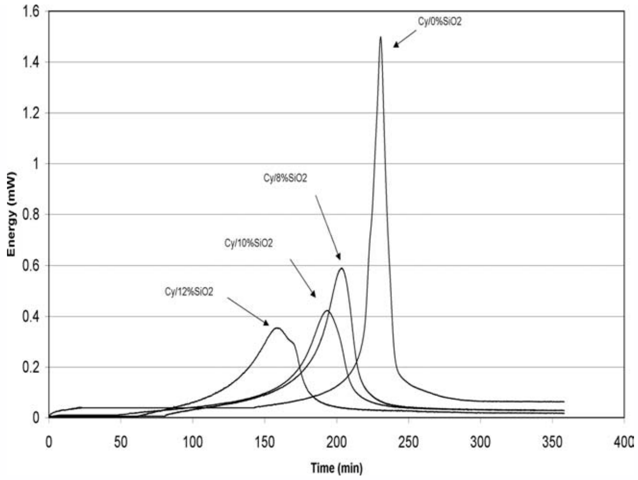

FIG. 3. DSC curves of cyanoacrylate and its nanocomposites.

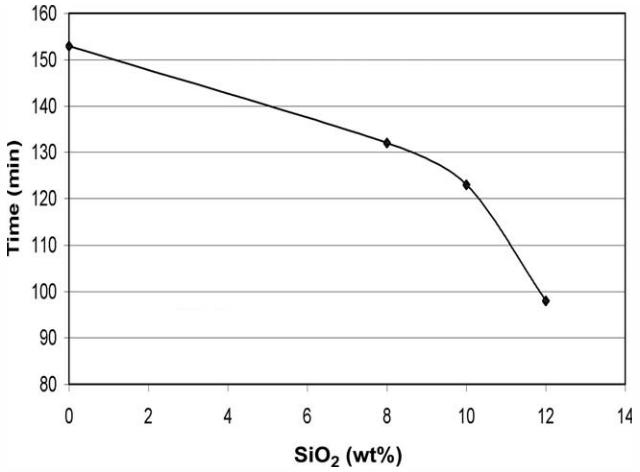

FIG. 4. Dependence of incubation time of cyanoacrylate polymerization on SiO_2 content.

It was indicated by the DSC curves that the incubation time of polymerization and its duration decreased upon increasing the silicon dioxide content. These trends can be seen in Figs. 4 and 5. They occur because of the moisture on the surface of the nano powders. This moisture can also reduce the propagation time of polymerization. Therefore, duration of setting is reduced by increasing the amount of nano powder. As mentioned before, moisture can trigger the polymerization of cyanoacrylate [7, 8]. It is worth noting that the reduction of setting time is important in many cases such as tooth cavity treatments.

The area beneath the DSC curves gives the energy released during polymerization. As shown in Fig. 6, the energy decreases as the SiO_2 amount increases. In fact, with a higher powder content in the glue, the amount of cured polymer will be decreased. Besides, other bonds (as mentioned before) are produced between silicon and polymer [36]. This is why the released energy decreases as nano-silica is added to the glue. The interesting result

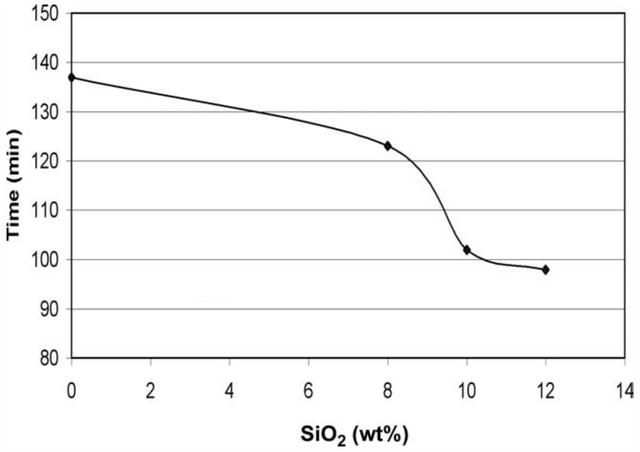

FIG. 5. Variation of duration of cyanoacrylate polymerization with SiO_2 content.

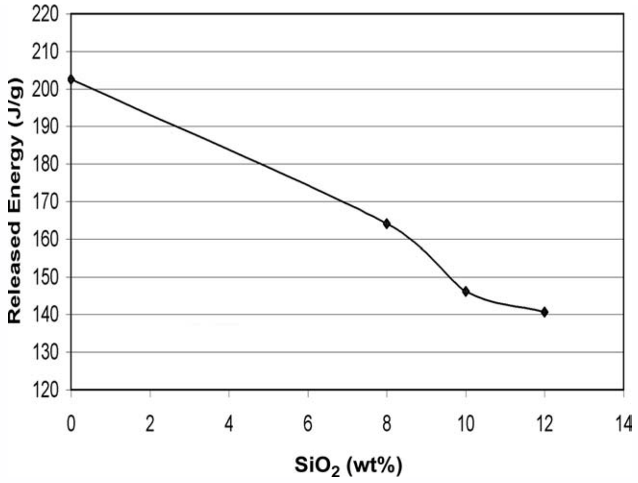

FIG. 6. Dependence of released energy on nano-size silicon dioxide content.

achieved in the current research is that the released energy increases the temperature during polymerization. This result is similar to what was proposed by Eriksson and Alberktsson [46]. They mentioned that releasing significant heat during polymerization that can increase temperature more than 10°C can damage surrounding tissues, so that the temperature should also be monitored. As can be concluded from DSC curves, the temperature rise from room temperature is decreased by increasing the SiO$_2$ powder content (see Fig. 7) because of the reduction in released energy. Therefore, changes in silicon dioxide content can reduce the rise in temperature below safety limits.

Thermogravimetric analysis results are shown in Fig. 8 and Table 2. The increase in SiO$_2$ amount leads to a slight increase in $T_{-10\%}$ (°C; the temperature of 10% weight loss) and a significant increase in $T_{-50\%}$ (°C; the temperature of 50% weight loss).

The TGA results demonstrate that the temperatures of 10% weight loss for four compositions are not significantly different but that an increase in the temperature of 50% weight loss can be observed. For comparison, the amounts of mass loss at 210–250°C are shown in Fig. 9. It can be observed that upon increasing the SiO$_2$ content, the amount of mass loss decreases. This effect occurs because the new bonds formed between silicon and polymer need a higher amount of heat to degrade. Thus, it can be concluded that silicon dioxide can increase the degradation temperature of nanocomposites-based cyanoacrylate.

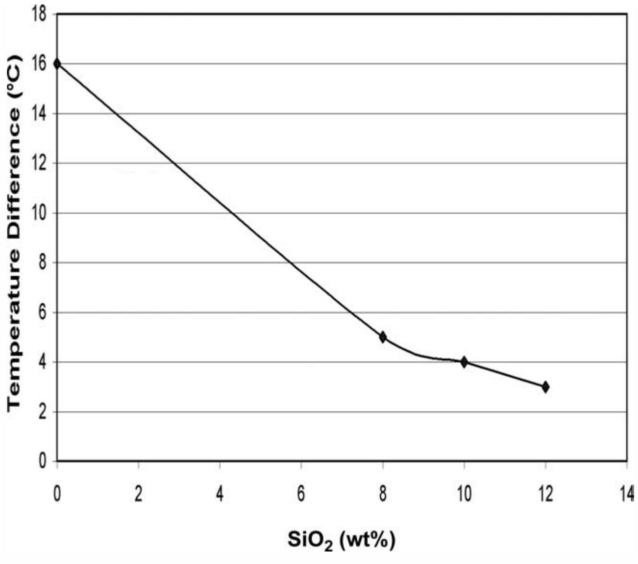

FIG. 7. Temperature difference (from room temperature) changes with increases in SiO$_2$ content.

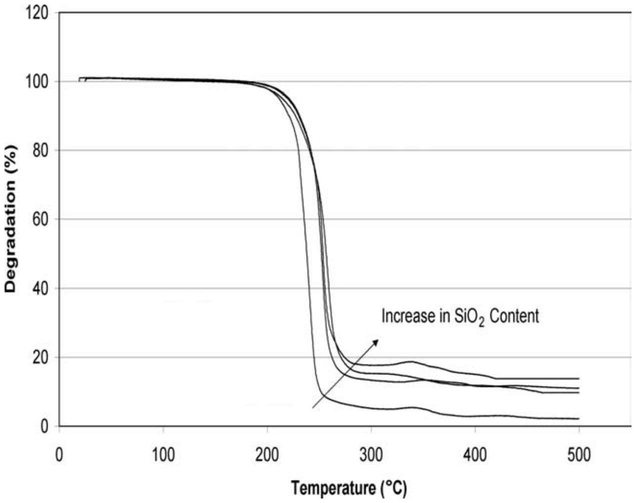

FIG. 8. TGA curves for cyanoacrylate and its nanocomposites.

CONCLUSIONS

Thermal behavior of cyanoacrylate in the presence of nano-sized SiO$_2$ was investigated. Differential scanning calorimetry was utilized to measure setting time and released energy of the cyanoacrylate. Thermogravimetric analysis was also utilized to determine the degradation temperature of the cyanoacrylate. It was found that the addition of silicon dioxide nano powder reduced the setting time, the energy released during polymerization, and the temperature rise resulting from this energy release. The degradation temperature of cyanoacrylate was increased by the addition of nano-sized SiO$_2$.

TABLE 2. Data extracted from DSC curves.

Sample name	$T_{-10\%}$ (°C)	$T_{-50\%}$ (°C)	Mass loss (210–250°C) (%)
Cy/0% SiO$_2$	219.3	237.1	84.1
Cy/8% SiO$_2$	220.1	240.2	73.8
Cy/10% SiO$_2$	220.6	242.3	67.8
Cy/12% SiO$_2$	221.2	245.1	67.5

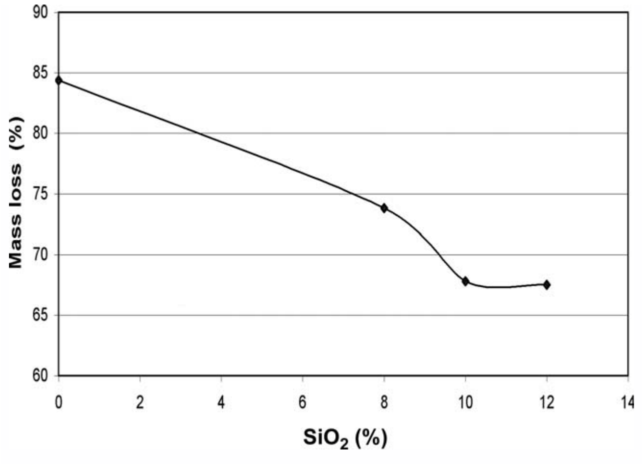

FIG. 9. Mass loss changes between 210 and 250°C.

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