3.1 Introduction

The first problem in preparing UV-cured composites is the filler transparency towards UV-light. Otherwise it will be a competition of the filler in absorbing the UV-radiation. In this work the influence of nanosilica on the curing reaction was investigated in order to verify if it can modify kinetics as well as total conversion of monomer during the UV-curing process and if the surface modification has any influence on the reaction\(^1,2\). Only nanosilica-filled systems were investigated, because its higher surface area should lead to more evident interaction effects in polymerization kinetics. In the following sections the results obtained on the filler/polymer systems are presented.

3.2 Experimental

UV-CURING

Different types of UV-lamps were used to cure the composites:

- Fusion lamp: thick (2 mm) samples, used for mechanical properties measurements, were irradiated for 21 s each side at \( I = 371 \text{ mW/cm}^2 \).
Helios Italquartz lamp: it was used for FT-IR kinetic measurements. The samples were put between two disks of KBr and irradiated for 5 s intervals at $I = 51$ mW/cm$^2$.

Photo-DSC lamp: samples were irradiated for 33 min. at $I = 0.58$ µW/cm$^2$ (total time run = 36 min). The optimal operative conditions for these systems were established with tests at different wavelengths, with different sample weights and different amounts of treated/untreated nanofillers; the obtained conditions, reported Tab. 3.1, were used for all the experiments.

| Tab. 3.1: Operative conditions for photo-calorimetric experiments. |
|-------------------------|-------------------------|
|                         | CE                      | CE + 10% w/w silica    |
| optimal weight (mg)     | 0.390                   | 0.370*                  |
| optimal wavelength (nm) | 280-290                 | 280                     |
|                         | DGE                     | DGE + 10% w/w silica    |
| optimal weight (mg)     | 0.400                   | 0.400*                  |
| optimal wavelength (nm) | 300                     | 300                     |

The weight values indicated with * represent the total weight of the sample present in the DSC aluminum pan; all the $\Delta H$ values obtained during experiments with nanofillers have been corrected to taking into account the presence of silica.

Several experiments were done for each concentration to control their reproducibility.

FT-IR and photo-DSC techniques were used to follow the reaction kinetics of the reactive systems filled with different amounts of nanosilica concentrations.

FT-IR measurements

FT-IR instrument was used to follow the reaction kinetics by measuring the decrease of the band at 750 cm$^{-1}$ due to the epoxy group polymerization. The measurement was discontinue; irradiation was performed for 5 s at the beginning and for 10 s until the end of the reaction. The absorbance data were plotted against the reaction time.
Photo-DSC measurements

Photo-DSC was used to follow the reaction through a real-time measurement. Each experiment was done at 30°C with an isothermal analysis, so that the ΔH curve was obtained as a function of time. ΔH is related to the heat developed during the polymerization reaction.

3.3 Reaction kinetics: Results and discussion

FT-IR RESULTS

The reaction kinetics were followed by monitoring the decrease of the epoxy band at 750 cm\(^{-1}\) (Fig. 3.1); normalization was made using the C=O band at 1730 cm\(^{-1}\).

In Fig. 3.2 examples of the data obtained for kinetic curves by using CE system are reported. They concern the pure monomer and its mixtures with 10% w/w of treated silica and with 10% w/w of untreated silica.
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Fig. 3.2: FT-IR kinetic curves of CE system filled with untreated or treated silica
($I = 51 \text{ mW/cm}^2$).

A decrease of both kinetic and total conversion values when treated/untreated silica is added to the photopolymerizable system is evident. The grafting of silica seems not to have an important effect on the UV-curing reaction kinetics.

As far as the DGE system is concerned (Fig. 3.3), similar results were obtained when DGE is photopolymerized with 5% w/w of untreated silica\(^3\).

Fig. 3.3: FT-IR kinetic curves of unfilled and silica filled DGE system\(^3\)
($I = 8 \text{ mW/cm}^2$).
The first explanation proposed for the effect of silica on the photopolymerization kinetics could be the scattering of the UV radiation by silica particles.

In typical experiments, in the presence of 5% w/w of silica, the light transmittance curve of the mixture decreases of 15%. When the photopolymerization was performed reducing the intensity of the emitted light of this value, a very small variation of the kinetic was observed. Therefore the scattering of UV-light by the dispersed silica particles does not justify the modification of the curing process.

Taking into account the high specific surface of silica (200 m² g⁻¹), we suggest that the particles could adsorb the cationic species of the photoinitiator molecules, thus decreasing their activity in the photopolymerization. In fact the photoinitiator species are polar molecules which can strongly interact with the silica surface.

In order to check this possibility, UV measurements were performed on solutions of the cationic photoinitiator in the presence of silica. The photoinitiator was dissolved in propylene carbonate and its absorbance at 300 nm was evaluated. 5% w/w of treated and untreated nanosilica was added to the solution. The mixture was centrifuged in order to separate silica particles and the solution was examined by UV spectroscopy. Results are collected in Tab. 3.2.

Tab. 3.2: Results of UV absorptions on photoinitiator-silica systems at 300 nm.

<table>
<thead>
<tr>
<th>sample</th>
<th>Abs₃₃₀ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>photoinitiator*</td>
<td>0.713</td>
</tr>
<tr>
<td>photoinitiator* added of 5% w/w untreated silica</td>
<td>≈ 0</td>
</tr>
<tr>
<td>photoinitiator* added of 5% w/w treated silica (CETS)</td>
<td>≈ 0</td>
</tr>
<tr>
<td>photoinitiator* added of 5% w/w treated silica (GPTS)</td>
<td>≈ 0</td>
</tr>
</tbody>
</table>

*Ph₃S⁺SbF₆⁻, 5.56 × 10⁻³ M in propylene carbonate.

The results above reported indicate that silica interacts deeply with the cationic photoinitiator by adsorbing it on its surface. The adsorbed photoinitiator could have lower activity under UV-irradiation. In this way, we can explain the decrease of the photopolymerization kinetics in the presence of silica. The photoinitiator-silica interaction will be further study in depth.
It should be noticed that in radical systems, no decrease of UV-curing kinetics in the presence of silica was observed\textsuperscript{4}.

PHOTO-DSC RESULTS

Examples of typical photo-DSC curves for the systems based on CE and DGE are presented in Fig. 3.4 and Fig. 3.5.

In each figure are reported two different thermograms: one is related to the polymerization of the pure monomer and the other to the polymerization of the monomer filled with 20% treated silica.

Even if the most part of the photopolymerization occurs in few minutes; the samples were irradiated for 33 minutes to assure the completion of the reaction.

![Photo-DSC traces of neat CE and CE monomer filled with silica (treated CETS 1\% v/v).](image-url)
To obtain the ΔH (J/g) values of each UV-DSC trace, integration of the area below the base line (Fig. 3.6) was made. The integration limits were chosen in correspondence of the switch on/off of UV lamp. The obtained value was corrected in the case of composites, taking into account the different percentages of silica added to the sample.
In Fig. 3.7 and Fig. 3.8 the results obtained in the kinetics experiments on CE and DGE in the presence of treated or untreated silica are reported (for each concentration three $\Delta H$ values were considered).

The figures indicate for both CE and DGE system a decrease of $\Delta H$ of polymerization in the presence of different amounts of silica. Moreover the results indicate no clear influence of the surface treatment of grafting on the photopolymerization reaction.

Fig. 3.9 reports the kinetic curves calculated from the thermograms obtained using CE added of different percentages of treated silica: they show the decrease of the $\Delta H$ values when the amount of silica present in the system is increased.

The results of photocalorimetric experiments fully confirm those obtained by FT-IR measurements indicating a decrease of the rate of reaction and of the final conversion in the presence of silica nanoparticles.

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![Graph](image-url)

*Fig. 3.7: $\Delta H$ of reaction as a function of percentage of silica introduced in the CE monomer.*
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**Fig. 3.8:** $\Delta H$ of reaction as a function of percentage of silica introduced in the DGE monomer.

**Fig. 3.9:** Dependence of polymerization of CE monomer filled with various percentages of grafted silica.
3.4 Conclusions

FT-IR and photo-DSC measurements indicate that the addition of nanosilica leads to a modification of the photopolymerization reaction and to a decrease in both kinetics and total conversions of reactive groups.

As far as the influence of the surface treatment is concerned, the results obtained do not indicate a clear influence on the photopolymerization reaction.

We explain the observed decrease of the photopolymerization kinetics in the presence of silica on the basis of the interaction between photoinitiator and silica, as previously reported in this chapter. In fact, such nanofillers display a large amount of interface as the specific surface of silica is very important. One can aspects a minor effect on the polymerization kinetics for the fiber-based composites, as the surface displayed by the filler is very low compared to nanosilica.