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Photocurable methacrylate/nanosilica composites

RAPID COMMUNICATION

Abstract — Two types of photocurable systems containing triethylene glycol dimethacrylate (TEGDM) and 3—15 wt. % of nanosilica were prepared and investigated. The silicas used were structure modified fumed silicas aftertreated by methacrylsilane. The obtained dispersions were characterized by mean particle size (Z-average diameter), polydispersity index (*PDI*), Zeta potential and by the viscosity of the system (η). It was found that the maximum polymerization rate R_p^{max} and double bond conversion p increase with silica concentration up to 5 or 4 wt. %, depending on silica type; further increase in silica content reduces both R_p^{max} and p. This result correlates well with the stability of the dispersion as measured by its Zeta potential value. The lowest Zeta potentials were obtained for composites showing the highest R_p^{max} values.
Key words: nanosilica, methacrylate, composites, photopolymerization, Zeta potential.

FOTOUTWARDZALNE KOMPOZYTY METAKRYLAN/NANOKRZEMIONKA
Streszczenie — Otrzymano i zbadano dwa rodzaje kompozycji fotoutwardzalnych zawierających dimetakrylan glikolu trietylenowego oraz nanokrzemionkę w ilościach 3—15 % mas. Zastosowano nanokrzemionki pirolityczne modyfikowane strukturalnie oraz powierzchniowo. Otrzymane dyspersje scharakteryzowano poprzez średni rozmiar (*Z-average diameter*) i indeks polidyspersyjności (*PDI*) cząstek napełniacza, jak również przez potencjał Zeta oraz lepkość (η) kompozycji (tabela 1). Stwierdzono, że maksymalna szybkość polimeryzacji (R_p^{max}) i konwersja wiązań podwójnych (p) wzrastają po dodaniu krzemionki oraz rosną ze wzrostem jej zawartości osiągając maksymalną wartość przy stężeniu 5 lub 4 % mas., w zależności od rodzaju krzemionki. Dalszy wzrost zawartości napełniacza obniża zarówno R_p^{max} jak i p (rys. 1). Wynik ten dobrze koreluje ze stabilnością kompozycji określoną przez potencjał Zeta. Kompozycje o najwyższych wartościach R_p^{max} wykazywały najmniejsze wartości potencjału Zeta (rys. 2).
Słowa kluczowe: nanokrzemionka, metakrylan, kompozyty, fotopolimeryzacja, potencjał Zeta.

Polymer nanocomposites have attracted growing attention in the past few years [1—7]. Silica (SiO_2) is one of the most commonly used nanofillers. However, it is very difficult to manufacture nanocomposites with the nanoparticles dispersed uniformly because nanoparticles have very high surface energies and are prone to agglomerate into larger particles during the preparations of materials [8—11].

A new and very convenient technique of preparation of nanocomposite materials is an "*in situ*" method — the photoinitiated polymerization of a composition containing a nanoscale filler. A number of papers have been devoted to UV-curable silica-containing nanocomposites, but only few of them focused on the kinetics of the curing process. It was observed, for instance, that an addition of small amounts (several percent) of an unmodified fumed silica to 1,6-hexanediol acrylate generally accelerates the polymerization and increases the conversion [4] although an adverse effect of silica addition was also reported [8]. The accelerating effect was attributed mainly to the light scattering by aggregates of silica particles, which lengthen the path length of the UV light enhancing light absorption by the photoinitiator and thereby accelerating the initiation [4]. On the other hand, it was speculated that too high silica content (beyond 15 %) retards the polymerization due to aggregation of silica nanoparticles [4, 12].

In our work we took into account another factor — stability of the silica dispersion in the monomer. This paper presents preliminary results of our investigations and focuses on the photopolymerization kinetics of systems consisting of triethylene glycol dimethacrylate and various amounts (3—15 wt. %) of two Aerosil type silicas.

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EXPERIMENTAL

Materials

Triethylene glycol dimethacrylate (TEGDM) and 2,2-dimethoxy-2-phenylacetophenone, used as photoinitiator, were purchased from Aldrich.

Nanosilicas: Aerosil R7200 (12 nm) and R9200 from Degussa, are structure modified fumed silicas after-treated with methacrylsilane.

Sample preparation

The investigated mixtures were prepared by direct dispersion of silica particles in TEGDM with photoinitiator (in concentration 0.2 wt. %) using an ultrasonic bath. The polymerization was initiated by the light of a medium pressure Hg lamp (glass filter 366 nm, light intensity 2.75 mW/cm^2). The reaction was carried out at temp. 40 °C.

Method of testing

The reaction course was monitored by differential scanning calorimetry method using Pyris 6 from Perkin-Elmer. The particle size, polydispersity index (*PDI*) and Zeta potential were measured using Zetasizer ZS laser light-scattering instrument (Malvern).

RESULTS AND DISCUSSION

The investigated monomer/silica mixtures contained 3, 4, 5, 10 or 15 wt. % of Aerosil R7200 or Aerosil R9200. The properties of the photocurable composites involving mean particle diameter of silica filler (z-average diameter) and its *PDI* values along with the formulation viscosity η are given in Table 1.

T a b l e 1. Some properties of the investigated monomer/silica dispersion systems

Silica content wt. %	Aerosil R7200			Aerosil R9200		
	z-average diameter of silica filler, nm	*PDI*	η, cP	z-average diameter of silica filler, nm	*PDI*	η, cP
0	—	—	4.9	—	—	4.9
3	324	0.402	5.58	348	0.462	5.92
5	326	0.603	6.98	362	0.627	6.59
10	469	0.608	9.63	658	0.640	9.43
15	478	0.443	13.8	730	0.384	13.4

The data presented in Table 1 suggest that the silica dispersions in the monomer are both nano- and microsized, which corresponds with high polydispersity indices. The viscosities of the formulations are low and increase only slightly with silica content, even after addi-
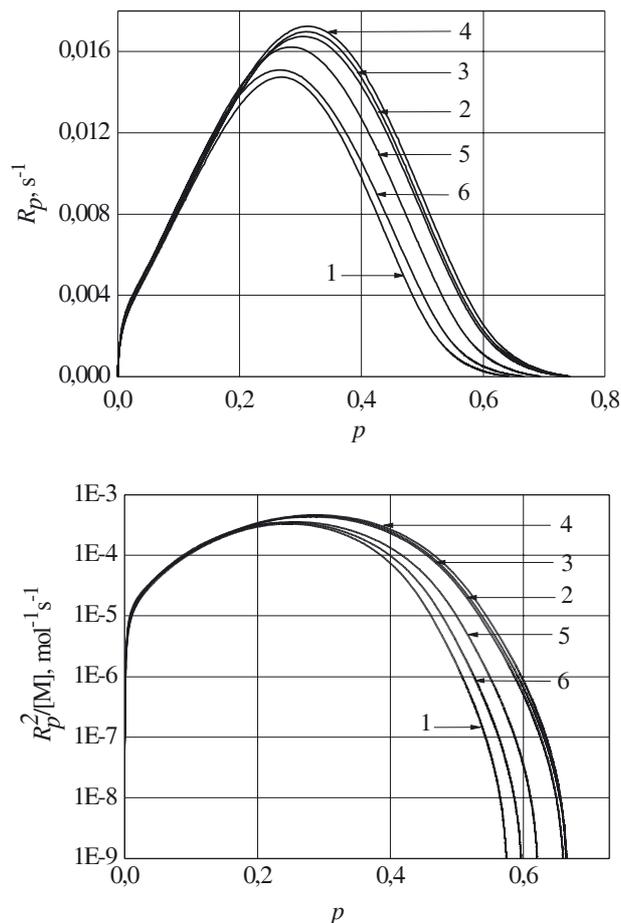
Fig. 1. The effect of double bond fractional conversions p of TEGDM/Aerosil R9200 system on rate of polymerization (R_p) (a) and rate of polymerization squared (R_p^2) divided by the methacrylate double bond concentration [M] (b) at various silica content: 1 — no additive, 2 — 3 wt. %, 3 — 4 wt. %, 4 — 5 wt. %, 5 — 10 wt. %, 6 — 15 wt. %

tion of 10 wt. % of silica (the lack of substantial increase in viscosity is associated with structural modification of the Aerosils used [13]).

The dependence of polymerization rate (R_p) on double bond conversion (*p*) for different TEGDM/Aerosil R9200 composites is shown in Fig. 1a. The maximum polymerization rate R_p^{max} increases with silica concentration and reaches the highest value at 5 wt. % of the filler; further increase in silica content decreases R_p^{max}. One can speculate that such a behavior is a result of two opposite tendencies:

— increase in viscosity, which suppresses the termination and, in consequence, accelerates the polymerization,

— dilution effect, which decreases the polymerization rate due to a decrease in the concentration of double bonds.

However, the final degree of conversion shows the same tendency like R_p^{max}, which suggests that the system viscosity is not the main cause of the effect observed, because viscosity increase usually reduces the final con-
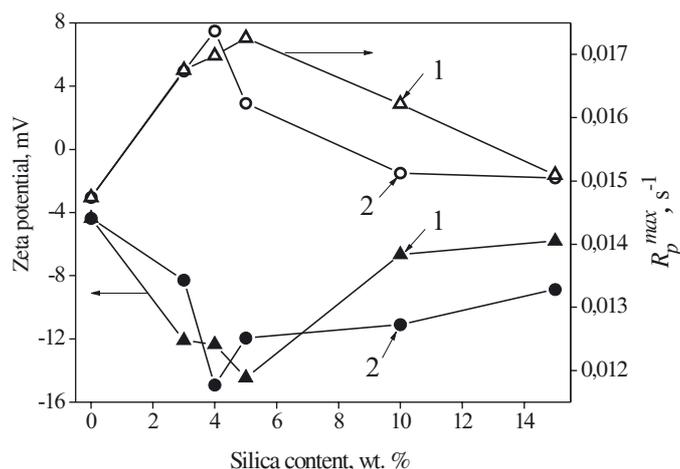
Fig. 2. The dependence of the maximum polymerization rate R_p^{max} and Zeta potential values on silica content in the system. 1 — Aerosil 9200, 2 — Aerosil 7200

version. The analysis of the kinetic curves shows that silica begins to influence the polymerization kinetics not before about 15—20 % of double bond conversion (in our conditions after about 30 s of the reaction). This suggests in turn that the light scattering and reflection by particles is not significant, at least at the beginning of the reaction.

More detailed analysis based on $R_p^2/[M]$ = f(p) dependence, where $[M]$ is the concentration of double bonds [14] (Fig. 1b) shows that the silica addition shifts both reaction diffusion controlled termination and diffusion controlled propagation to higher conversions when silica content increases up to 5 wt. %. An adverse effect occurs at higher silica contents.

Qualitatively the same results were obtained for TEGDM/Aerosil R7200 system, but the highest R_p^{max} value was obtained at 4 wt. % silica content.

The stability of a colloid system is described by Zeta potential. Stability is higher, if greater is the absolute value of Zeta potential [15]. When the absolute value exceeds 40 mV, the system is stable [16]. The dependence of the maximum polymerization rates on the filler content along with the values of Zeta potential for two TEGDM/Aerosil systems is shown in Figure 2. Graph shows an excellent correlation between changes in R_p^{max} and changes in Zeta potential when the silica content increases: the highest R_p^{max} values are reached by the most stable monomer/silica dispersions (here with lowest Zeta potential values). This clearly indicates that the

tendency to aggregation of nanofiller particles has a significant impact on the polymerization kinetics. Further work to explain this phenomenon is in progress.

In conclusion we can say that photocuring of silica-containing composites is a complex process with kinetics influenced by many factors. The results presented in this work clearly indicate that a very important factor is the stability of the nanofiller dispersion, associated with the surface state of silica particles (which in turn can be influenced by monomer adsorption).

REFERENCES

1. Górnicka B., Czołowska B., Mazurek B., Zawadzka J., Górecki L.: *Polimery* 2007, **52**, 367.
2. Garcés J. M., Moll D. J., Bicerano J., Fibiger R., McLeod D. G.: *Adv. Mater*. 2000, **12**, 1835.
3. Burris D. L., Boesl B., Bourne G. R., Sawyer W. G.: *Macromol. Mater. Eng*. 2007, **292**, 387.
4. Cho J. D., Ju H. T., Hong J. W.: *J. Polym. Sci. Part A* 2005, **43**, 658.
5. Obłój-Muzaj M., Zielecka M., Kozakiewicz J., Abramowicz A., Szulc A., Domanowski W.: *Polimery* 2006, **51**, 133.
6. Brzeziński S., Jasiorski M., Maruszewski K., Ornat M., Borak B., Malinowska G., Karbownik I.: *Polimery* 2007, **52**, 362.
7. Galeski A., Piotrowska E.: *Polimery* 2007, **52**, 323.
8. Xu G. C., Li A. Y.; Zhang L. D., Wu G. S., Yuan X. Y., Xie T.: *J. Appl. Polym. Sci*. 2003, **90**, 837.
9. Aso O., Eguizábal J. I., Nazabal J.: *Composites Sci. Technol*. 2007, **67**, 2854.
10. Raghavan S. R., Hou J., Baker G. L., Khan S. S.: *Langmuir* 2000, **16**, 1066.
11. Peng Z., Kong L. X.: *Polym. Bull*. 2007, **59**, 2007.
12. Li F., Zhou S., You B., Wu L.: *J. Appl. Polym. Sci*. 2006, **99**, 1429.
13. "Aerosil R9200 to improve the scratch resistance of paint and coating system", Technical information of Degussa, No 1284.
14. Anseth K. S., Kline L. M., Walker T. A., Anderson K. J., Bowman C. N.: *Macromolecules* 1995, **28**, 2491.
15. Jesionowski T.: *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2003, **222**, 87.
16. Kosmulski M.: "Chemical properties of material surfaces", Marcel Dekker, New York, 2001.