EWA ANDRZEJEWSKA*), AGNIESZKA MARCINKOWSKA, KATARZYNA WEGNER
Poznan University of Technology
Institute of Chemical Technology and Engineering
Pl. Sklodowskiej-Curie 2, 60-965 Poznań, Poland

Nanocomposites obtained by photopolymerization of (methacrylate monomer)/(methacrylate functionalized polyhedral oligomeric silsesquioxane) system

RAPID COMMUNICATION

Summary — Nanocomposites based on a mixture of poly(ethylene glycol) dimethacrylate (PEGDM) with poly(ethylene glycol) monomethacrylate (PEGMM) (mass ratio 1:1) and propyl methacrylate functionalized polyhedral oligomeric silsesquioxane (M-POSS) were obtained by photopolymerization. Both the polymerization kinetics of compositions (with M-POSS contents loadings between 0 and 100 wt. %) and mechanical properties (with M-POSS contents between 0 and 35 wt. %) were investigated. It was found that M-POSS addition accelerates or retards the polymerization, depending on its concentration and reduces double bond conversion, however significantly increases modulus (*E*), tensile stress (σ_M) and hardness (*H*) of the resulting nanocomposite.

Keywords: nanocomposites, polyhedral oligomeric silsesquioxanes, methacrylates, photopolymerization, kinetics, mechanical properties.

NANOKOMPOZYTY OTRZYMYWANE METODĄ FOTOPOLIMERYZACJI UKŁADU MONOMER METAKRYLOWY/FUNKCJONALIZOWANY POLIEDRYCZNY SILSESKWIOKSAN

Streszczenie — Otrzymano nanokompozyty na bazie równowagowej mieszaniny mono- i dimetakrylanu glikolu poli(oksy)etylenowego oraz poliedrycznego silseskwioksanu funkcjonalizowanego grupami metakryloksypropylowymi (M-POSS). Zbadano kinetykę fotopolimeryzacji kompozycji zawierających 0—100 % mas. M-POSS oraz właściwości mechaniczne [wytrzymałość na rozciąganie (σ_M), moduł (*E*), wydłużenie przy zerwaniu (ε_B), twardość wg Shore'a A (*H*)] produktów zawierających 0—35 % mas. M-POSS (rys. 3). Stwierdzono, że dodatek M-POSS zwiększa szybkość fotopolimeryzacji (R_p) próbek o średnich stężeniach M-POSS (do 15 % mas.), a zmniejsza w przypadku próbek o stężeniach wyższych (rys. 2). Stopień konwersji wiązań podwójnych (p^f) maleje ze wzrostem zawartości M-POSS (rys. 2b). Pomimo tego, zaobserwowano wzrost sztywności materiału przejawiający się gwałtownym wzrostem wartości modułu *E* (w próbce o zawartości POSS wynoszącej 35 % mas. aż 30-krotnym), wzrostem σ_M (nawet 4-krotnym), spadkiem ε_B oraz znaczącym wzrostem *H* (ok. 3-krotnym w próbce o zawartości M-POSS 35 % mas.).

Słowa kluczowe: nanokompozyty, poliedryczne silseskwioksany, metakrylany, fotopolimeryzacja, kinetyka, właściwości mechaniczne.

Polyhedral oligomeric silsesquioxanes (POSS) are compounds with the generic formula $(RSiO_{1.5})_n$, where R denotes various substituents, and n = 6, 8, 10 or a higher number. This class of materials has recently attracted a considerable attention because of the increased commercial availability and its feature to be simultaneously highly compatible with a wide range of polymers and directly reacting in the polymerization reactions by the tailoring of different organic groups R. The resulting materials are often referred to as organic-inorganic hybrid nanocomposites, and "nano" refers to the nanoscale dimensions of the POSS core. Generally, their mechanical properties are improved, flammability is reduced, glass transition temperature (T_g) increases, and thermal stabi-

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*) Author for correspondence; e-mail: ewa.andrzejewska@put.poznan.pl

lity increases as a crosslinked POSS core acts as an anchor point within a polymer matrix [1, 2].

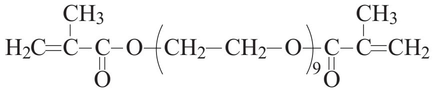
One of the methods of hybrid nanocomposite preparation is copolymerization of a vinyl or methacrylate monomer with POSS molecules bearing the same or similar functional group in one or all of their pendant arms. Covalent bonds are thereby formed between the polymer matrix and the POSS derivative. Although a lot of papers have been devoted to *in situ* preparation, polymerization and properties of polymer/POSS nanocomposites, only few of them mentioned photochemical initiation [3—7] and described photopolymerization kinetics [8]. Photopolymerization is a convenient method, enabling preparation of nanocomposites in minutes or even seconds at ambient temperature.

This paper presents preliminary results of our ongoing investigations on preparation by means of photopolymerization of polymer/POSS nanocomposites and investigation of their properties. As a model system, a mixture of poly(ethylene glycol) dimethacrylate (PEGDM) and poly(ethylene glycol) monomethacrylate (PEGMM) (with 1:1 mass ratio) has been selected and combined with various amounts of propyl methacrylate functionalized POSS (M-POSS).

EXPERIMENTAL

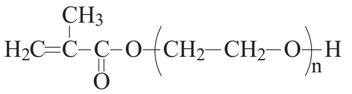
Materials

Poly(ethylene glycol) dimethacrylate [PEGDM, formula (I)], poly(oxyethylene) monomethacrylate [PEGMM, formula (II), n ≈ 6] and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator), were purchased from Aldrich.



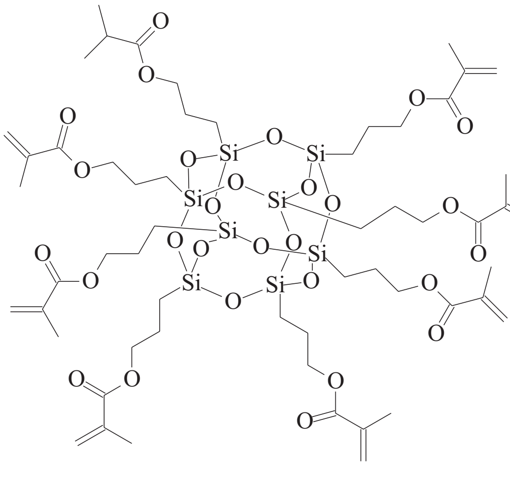
$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-O\left(CH_2-CH_2-O\right)_9\underset{\underset{\displaystyle O}{\|}}{C}-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

(I)



$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-O\left(CH_2-CH_2-O\right)_n H$$

(II)



(III)

Propyl methacrylate functionalized polyhedral oligomeric silsesquioxane [M-POSS, formula (III)] was a product of Hybrid Plastics [trade name methacrylPOSS®, cage mixture (8, 10, 12)].

Methods of testing

The photopolymerization kinetics were monitored by isothermal differential scanning calorimetry (DSC) method (366 nm light, intensity 2.75 mW/cm^2, argon atmosphere, 40 °C) using Pyris 6 DSC instrument from Perkin-Elmer. Other details of measurements and determinations of polymerization rate (R_p) and conversion of double bonds (p^f) are described in ref. [9]. For kinetic measurements the M-POSS contents in the photocurable compositions were 0, 5, 10, 15, 20, 25, 30, 35, 50 and 100 wt. %.

For mechanical testing the samples were cured in a steel mold with polyethylene terephthalate (PET) cover and the whole spectrum of a Dymax lamp has been applied. The mechanical properties were investigated according to standards PN-ISO 868:2004 and PN-EN ISO 527-1:1998 with the use of an universal testing machine (Z020 Zwick Roell) and a Shore hardness testing machine (Zwick Roell). For mechanical measurements the M-POSS contents in the photocurable compositions were 0, 5, 10, 20, 25, 30 and 35 wt. %.

Viscosity of the investigated compositions before the polymerization was measured with DV-II+ PRO Brookfield Rheometer. Theoretical values of viscosity (η) and excess logarithm viscosities $(\ln \eta)^E$ were calculated as described elsewhere [10].

RESULTS AND DISCUSSION

Viscosity values (η, experimental and theoretical) of compositions before the polymerization as a function of M-POSS content are given in Figure 1. A curve describing $(\ln \eta)^E$, also presented in this figure, illustrates negative deviations from the theoretical values in the whole range of compositions. Those deviations indicate that intermolecular interactions between molecules of monomer or between molecules of M-POSS are stronger than those between monomer and M-POSS molecules. This in turn may influence the compatibility of the system.

Figure 2a presents kinetic curves of monomer/M-POSS mixtures. The maximum polymerization rate (R_p^{max}) values increase with M-POSS concentration up to 15 wt. % (see also Fig. 2b). Addition of higher amounts of M-POSS reduces the R_p^{max} value. The acceleration of the polymerization results from the reduction of the macroradical mobility, which limits termination. It is caused both by the increasing initial viscosity of the formulations (M-POSS is 48 times more viscous than the monomer mixture at the polymerization temperature) as well as by the increasing crosslink density due to addition of multi-

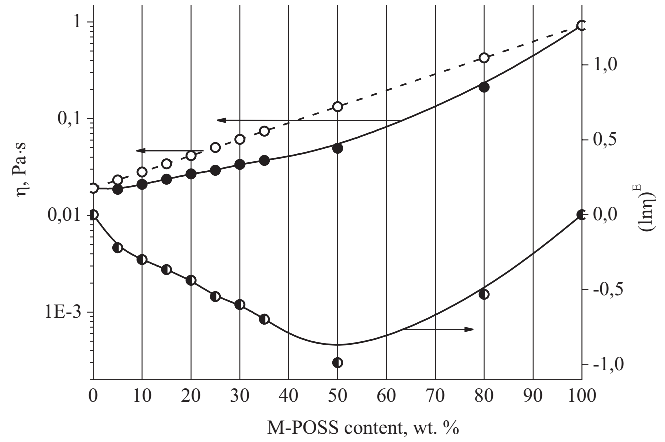


Fig. 1. Viscosity (η) of the monomer/M-POSS mixtures at 40 °C, measured (filled symbols) and calculated (open symbols) along with excess logarithm viscosity ($\ln \eta)^E$ as a function of M-POSS concentration

functional M-POSS molecules. However, too high crosslink density leads to diffusional limitations of propagation at earlier polymerization stages and is the reason of the R_p^{max} decrease at M-POSS content higher than 15 wt. %. On the other hand, the final conversion of double bonds (p^f) decreases monotonically with the increasing M-POSS content due to reduction of the polymer network mobility (Fig. 2b). It is worthy to note that the final conversion of the neat M-POSS does not exceed 30 %.

The addition of M-POSS to PEGDM and PEGMM mixture dramatically influences mechanical properties of the polymerization product as it is shown in Figure 3. The

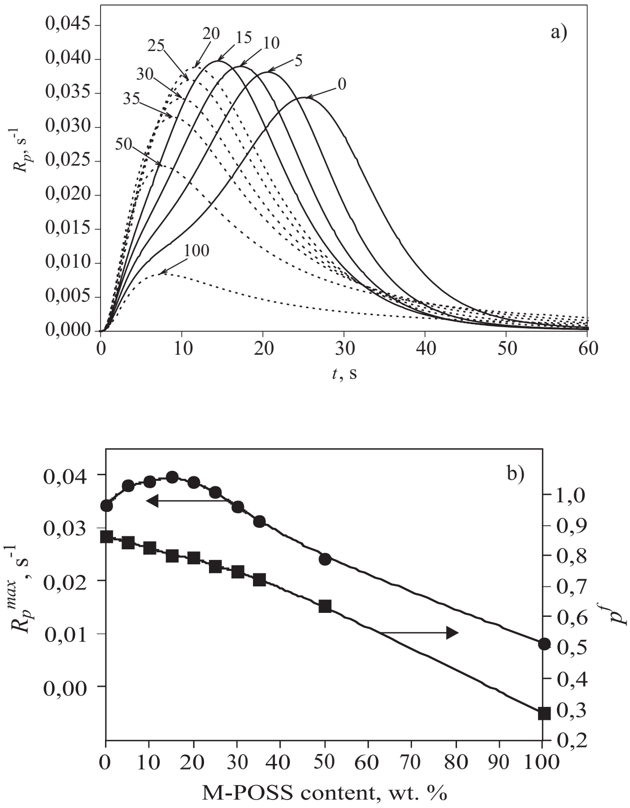


Fig. 2. Polymerization kinetics for (PEGDM + PEGMM)/M-POSS mixtures at 40 °C: a) polymerization rate (R_p) as a function of time (t), numbers labelling the curves indicate M-POSS content (wt. %) in the feed; b) maximum polymerization rate (R_p^{max}) and final double bond conversion (p^f) as a function of M-POSS content

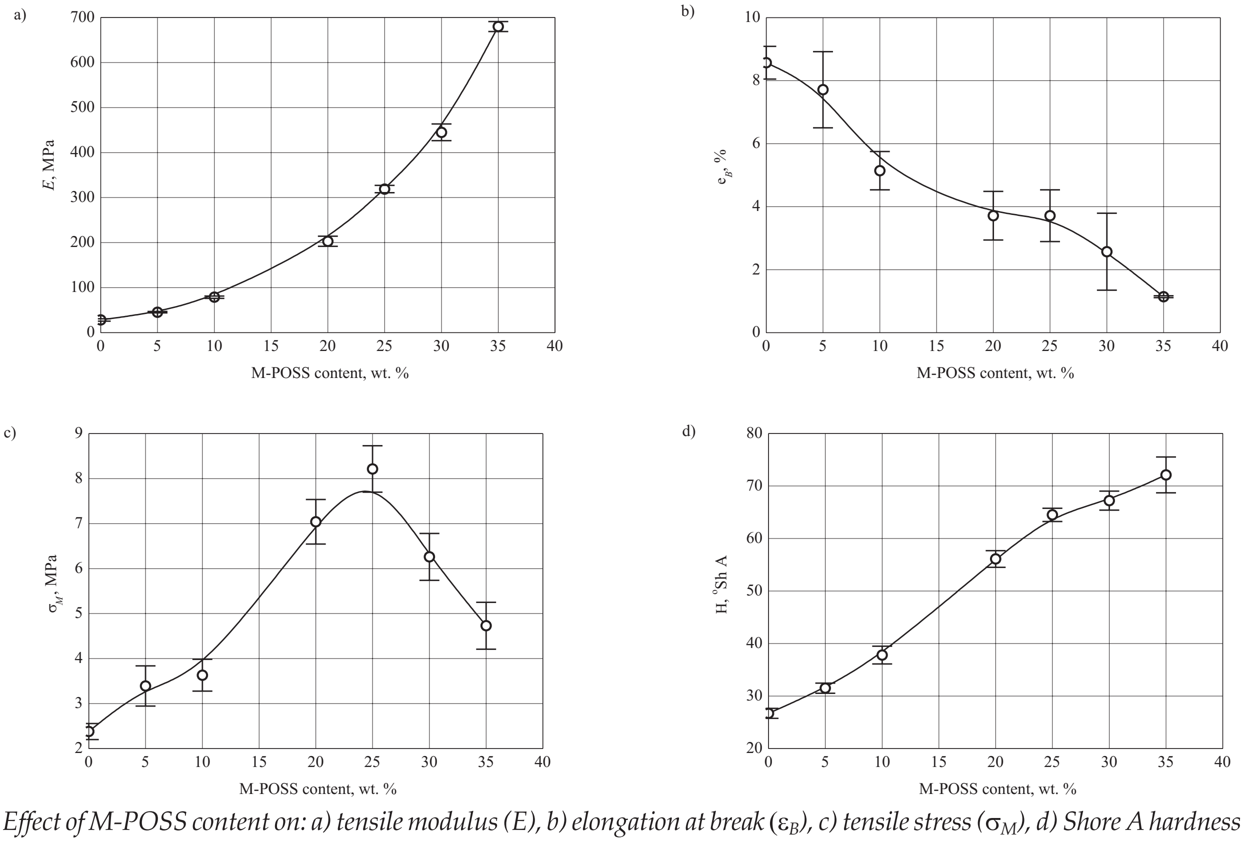


Fig. 3. Effect of M-POSS content on: a) tensile modulus (E), b) elongation at break (ε_B), c) tensile stress (σ_M), d) Shore A hardness (H)

modulus *E* increases rapidly with M-POSS content (a 30-fold increase at 35 wt. %), elongation at break (ε_B) decreases, whereas Shore A hardness (*H*) increases substantially (about 3 times for sample with 35 wt. % of M-POSS). The tensile stress (σ_M) reaches a maximum value at 25 % of M-POSS addition (a 4-fold increase).

In conclusion we can say that despite the substantial reduction of the double bond conversion in the methacrylate/M-POSS nanocomposites, the stiffness of the material increases with increase M-POSS content. For the system investigated, the best balance of the mechanical properties and the kinetic behavior seems to occur at 25 wt. % of M-POSS content.

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