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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Eksik, Osman , Erciyas, A. Tuncer and Yagci, Yusuf(2008) '*In situ* Synthesis of Oil Based Polymer Composites Containing Silver Nanoparticles', Journal of Macromolecular Science, Part A, 45: 9, 698 — 704

To link to this Article: DOI: 10.1080/10601320802218887

URL: <http://dx.doi.org/10.1080/10601320802218887>

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In situ Synthesis of Oil Based Polymer Composites Containing Silver Nanoparticles

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Received and accepted February, 2008

Using electron transfer reaction and free radical polymerization processes a series of triglyceride oil based polymer-silver nanocomposites were successfully prepared. The whole process was divided into two simultaneous stages; (i) copolymerization of macromonomers obtained from partial glycerides with styrene and (ii) the reduction of silver nitrate to metallic silver nano particles with radicals stemming from the thermolysis of 2,2'-azoisobutyronitrile (AIBN). Nanocomposites were characterized by TEM and TGA. The obtained polymer nanocomposite was also examined in view of antibacterial effect against Gram-positive, Gram-negative, and Spore forming bacteria. It was demonstrated that nanocomposite samples exhibited an antibacterial effect against these bacteria. Film properties of the samples as potential coating material were also studied. Nanocomposite samples showed better film properties than that of the polymer without silver nanoparticles.

Keywords: oil based polymers; macromonomer; styrene; composite; silver nanoparticle

1. Introduction

Polymer/inorganic nanoparticle composites have attracted much interest during the past decade due to their unique size dependent chemical and physical properties (1–6). Dispersion of very small metal particles in polymeric matrixes has proved to be an effective and low-cost method to improve the performance of the already existing polymer material properties such as mechanical properties, elasticity, transparency or specific absorption of light, optical properties, electrical conductivity, and, antimicrobial effects (7–13).

Several approaches have been used to prepare polymer/metal nanocomposites. As a conventional method, polymerization of monomers and formation of metal nanoparticles were separately performed, and then they were mechanically mixed to form composites (14). However, it is extremely difficult to disperse nanoparticles homogeneously into the polymer matrix by *ex situ* methods because of the easy agglomeration of nanoparticles (15). A disturbing factor in such a filled polymer system is non-uniformity of composite properties owing to poor dispersion of the particles in the

polymer. Surface modification of the filler with a suitable coupling agent is often recommended to enhance filler dispersion, as well as to prevent filler agglomeration (16). Therefore, the convenient and effective ways of preparing nanoparticles in polymer materials are still in strong demand. For this purpose, various methods were used to produce metal nanoparticles within a polymeric matrix. Most of them are based on *in situ* reactions, that is, the particles are generated from the respective metal precursors in the presence of the matrix polymer. The options for *in situ* formation of nanoparticles range from chemical reductions, photoreductions and thermal decompositions, to vapor deposition (17–20). A commonly employed method is the dispersion process, in which the solutions of the metal precursor and the protective polymer are combined, and the reduction is subsequently performed in solution. Another method concerns immersion process where the solid polymeric material is placed into a solution containing the metal precursor. Uptake of the metal precursor proceeds by diffusion into the swollen polymeric matrix. After drying, the reduction is performed within the solid sample. Alternatively, the combined solutions containing the metal precursor and the polymer are deposited onto a substrate, and the reduction to the metal colloids is performed within the thin solid film after removal of the solvent (21, 22). Additionally, a number of polymers, containing nanoparticles, prepared by reducing the polymer–metal chelates were reported. Typical examples include polyaniline (PANI)/Au, poly(vinyl

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alcohol) (PVA)/Ag, polyimide (PI)/Ag, and poly(acrylic acid) (PAA)/Cu-composites (23–25). However, both polymer and metal nanoparticle simultaneous formation in the same reaction media has not been often employed. Kim et al. reported simultaneous synthesis of silver nanoparticles and the polymer film constituting the nanocomposite film through an *in situ* electron transfer reaction and the copolymerization of styrene with amphiphilic urethane acrylate non-ionomer (UAN), which contains hydrophobic poly(propylene oxide) segments and hydrophilic poly(ethylene oxide) segments along the same backbone (26).

The selection of the polymeric matrix for the polymer/inorganic hybrid materials is crucial for the optimization of the systems. Frequently, the polymers are not only employed as protective polymers, but also used as a dispersing and stabilizing media for the metal nanoparticles. Amphiphilic block copolymers seemed to be remarkably suitable materials for this purpose. In addition to the good dispersion effect, the size of the nanoparticles dispersed within this matrix can be controlled by changing the block lengths of the hydrophobic and hydrophilic chains in the amphiphilic block copolymers (7).

Triglyceride oils have been widely used in the preparation of polymers, not only because of the environmental and energetic issues, but also for improving the end-product properties. We have previously reported a macromonomer method to combine triglyceride structures with synthetic polymers (27–32). As part of our ongoing research efforts in the design and development of new methods for the preparation of complex macromolecular architectures based on triglyceride oils, we, herein, report an efficient synthetic methodology for *in situ* synthesis of oil based polymer-silver nanocomposites. As will be shown below, first a macromonomer carrying vinyl groups was prepared by using partial glycerides, toluene diisocyanate and 2-hydroxyethyl methacrylate (HEMA). This obtained macromonomer was copolymerized with styrene in the presence of silver precursor to eventually yield polymer nanocomposites possessing nano sized silver particles. The structures of polymer nanocomposite were characterized by using transmission electron microscopy (TEM), thermogravimetric analysis (TGA). It is well known that silver displays good antibacterial properties (33–40). Due to this fact, the film of composite material obtained by our methodology was examined in view of its antibacterial properties. Additionally, the film properties of the nanocomposites were also determined and compared with those of the classical styrenated oil samples.

2. Experimental

2.1 Materials

Refined sunflower oil purchased from the market was used as received. Sunflower oil is a semi-drying oil and contains mainly oleic and linoleic acids bearing one and two double bonds on their chains, respectively. The average molecular weight of the sunflower oil, based on the ester value, was

found to be $895 \text{ g} \cdot \text{mol}^{-1}$. Toluene diisocyanate and silver nitrate (AgNO_3), were obtained from Aldrich Chemicals. Monomers, styrene (St) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich and purified by conventional drying and distillation procedures. 2,2'-Azobisisobutyronitrile (AIBN, Fluka) was recrystallized from ethanol.

2.2 Preparation of Partial Glyceride

Partial glyceride was prepared by glycerolysis reaction between triglyceride oil and glycerol. For the urethane oil preparation, the reactant ratio given by Stanton (41) was applied. Thus, 120 g of oil and 10.4 g of glycerol, (oil/glycerol, mol/mol:1.19), were placed into the reaction flask and heated. When the temperature reached 218°C , calcium hydroxide (0.1 wt% of the oil) was added as catalyst. The temperature was then set at 232°C and kept constant. At predetermined time intervals, samples were taken and poured into three-fold ethanol. Transesterification reaction was ended when the alcohol solution became clear. The reaction was continued for 1 h. The flask content was taken into diethyl ether and washed first with dilute sulphuric acid and then with distilled water to remove the catalyst and free glycerol. In order to understand that the glycerol was removed completely, the spot test based on selective oxidation of glycerol with periodic acid was applied to the washings (42). The ethereal solution was dried over Na_2SO_4 and the solvent was removed. The hydroxyl value of the dry and glycerol free sample was determined. The hydroxyl value is the number of mg of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylation with 1 g of sample. For this determination, an acetic anhydride solution in pyridine was used as an acetylation agent (43).

2.3 Preparation of Oil Based Macromonomer from Partial Glycerides

Preparation of oil based macromonomer, partial glyceride and HEMA were combined through urethane linkage by the reaction with TDI. The reactants (TDI, HEMA, and [OH] contributed by partial glyceride) were used in equimolar amounts and heated in dry xylene to $40\text{--}50^\circ\text{C}$, and TDI was added slowly over a 30 min period. Lead naphthenate as a 24 wt% solution in white spirit was added in the amount of 0.02 wt% of the oil portion. The temperature was set at $90\text{--}95^\circ\text{C}$ and the reaction was continued for 4 h.

2.4 Synthesis of Polymer Silver Nanocomposite by Using Oil Based Macromonomer

The conditions for the synthesis of the nanocomposite films are summarized in Table 1.

An oil based macromonomer was first dissolved in styrene at a various macromonomer/styrene weight ratio to form a homogeneous solution. An appropriate amount of silver

Table 1. Synthesis^a recipe for oil based polymer composite (OBPC) containing silver nanoparticles

Sample	Macromonomer (g)	Styrene (g)	AIBN (g)	AgNO ₃ (g)
OBPC-1	1	2	0.03	0.03
OBPC-2	1	2	0.01	0.03
OBPC-3	1	3	0.01	0.03

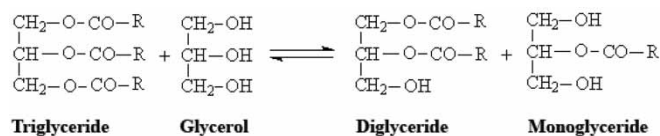
^aPolymerization was performed at 65°C for 4 h.

nitrate was then added to this solution and mixed at room temperature until silver nitrate crystals vanished. This directly indicates the uptake of silver nitrate by the macromonomer in the solution. After all the silver nitrate crystals disappeared, the radical initiator, AIBN was added and the content was stirred until it became clear (Stage A) in a manner similar to that described by Kim et al. (44). Then, the film samples were prepared on a glass plate by using a Bird film applicator and subsequently placed in an oven maintained at 65°C for 4 h (Stage B) to complete polymerization. At the end of the polymerization, cross-linked samples were further kept in an oven under vacuum. The remaining monomer, if any, was removed by treatment with methanol. In order to prevent the oxidization of silver nitrate by light, all processes were carried out in the dark.

2.5 Characterization

Molecular weights were determined using a Gel Permeation Chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL min⁻¹ and a Waters 410 Differential Refractometer detector. The structure of macromonomer was characterized by using fourier-transform infrared spectroscopy (recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer).

The structures of the film samples were characterized by Transmission Electron Microscopy (TEM) JEOL JEM 1011 and Thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyser (TA Instrument, TGA 2050). For the TEM measurements, thin film samples were prepared by cutting the crosslinked composite by using a microtome apparatus. The film properties such as flexibility (according to the DIN 53 152) adhesion (according to the ASTM D 3359-90 Test method B.), Rocker hardness, water resistance (according to the ASTM D 1647-89), alkali resistance (according to the ASTM D 1647-89), and acid resistance (according to the ASTM D 1647-89) were determined (45–47). Film samples on the related substrates were prepared with the reaction content of Stage A. Then, the film samples were placed in an oven to complete polymerization. For the flexibility and water resistance tests, tin plate panels were used as a substrate, while glass tubes were used for the alkaline and acid resistance tests, as explained in the related standard methods. In adhesion and hardness

**Sch. 1.** Synthesis of partial glycerides.

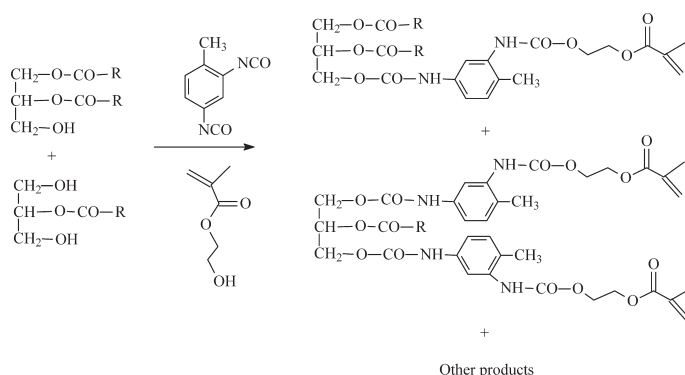
determinations, a Bird film applicator with 40 μm aperture was used for film application on a glass plate. For other tests, films are performed by dipping method.

For the examination of the antibacterial activity of the composites, a inhibition zone test was applied to film samples with and without silver nanoparticles. The film samples were immersed into the water for 48 h at 20°C prior to the test. The antibacterial properties were evaluated against Gram-positive (*Staphylococcus aureus*, ATCC 6538), Gram-negative bacteria (*Pseudomonas aeruginosa*, NCTC 6749), and spore forming (*Bacillus subtilis*, ATCC 9372) bacteria. All bacterial suspensions which previously adjusted to 0.5 McFarland turbidity (10⁸ CFU/mL.) were inoculated onto Mueller-Hinton agar and tests were performed according to described method (34, 38). The films were placed on inoculated agar plates, and incubation was performed at 37°C for 24 h.

3. Results and Discussion

As stated previously, the first step of the process is the conversion of triglyceride oils into partial glycerides. The glycerolysis reaction and structure of the resulting partial glycerides are shown in Scheme 1. The hydroxyl and acid values (acid value, number of mg of potassium hydroxide to neutralize the acids present in 1 g of sample) of the partial glyceride were found to be 113 and 2.45, respectively.

For the preparation of vinyl macromonomer, partial glycerides were combined with HEMA through urethane linkage by using TDI (Scheme 2) in an equivalent amount to total hydroxyl groups. The reaction between isocyanates and hydroxyl groups forming urethane linkage was monitored by FTIR. As can be seen from Figure 1, the free isocyanate

**Sch. 2.** Synthesis of partial glyceride macromonomers.

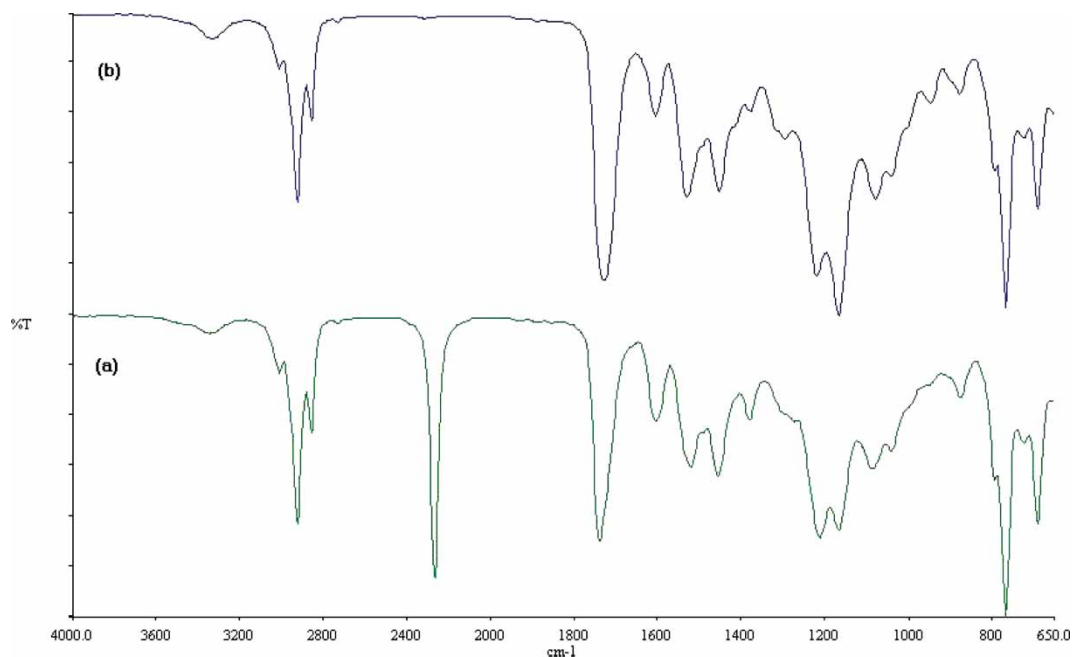
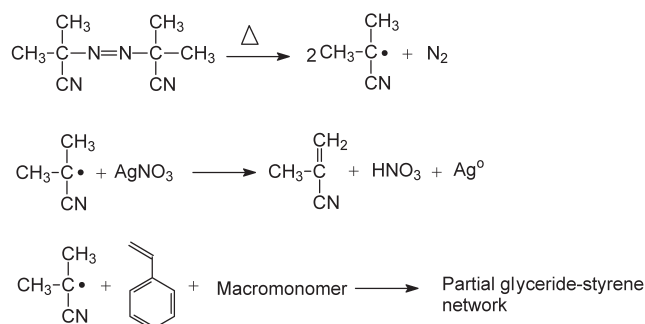


Fig. 1. FTIR spectra of TDI based reaction mixture (a) at the beginning, (b) after 4 h, final product.

(-NCO) stretching band appearing at 2265 cm^{-1} disappeared after 4 h indicating completion of the reaction. As illustrated in Scheme 2, through the hydroxyl groups of mono- and diglycerides, polymerizable methacrylate double bonds were inserted into the structure. The unsaturated terminal groups are expected to act as a crosslinker in the subsequent polymerization step. The number average molecular weight of the macromonomer synthesized was determined to be 3280 with a polydispersity of 2.21 as determined by G.P.C. The observed relatively high polydispersity is expected since the obtained macromonomer is a mixture of various products formed from mono and diglycerides.

Experimentally, St monomer was copolymerized with the macromonomer by using AIBN as free radical initiator in the presence of silver nitrate. The radicals stemming from the thermal decomposition of AIBN initiate the polymerization, and at the same time, partly undergo electron transfer reaction with the silver salt present in the system. Thus,



Sch. 3. *In situ* synthesis of triglyceride oil based polymer silver nanocomposite.

reduction to metallic silver and cross-linking polymerization occur simultaneously. The overall process for the *in situ* synthesis of oil based polymer-silver nanocomposite is represented in Scheme 3.

All the composites prepared were transparent indicating the formation of silver particles in nanometer range size, which was also confirmed by TEM analysis. In Figure 2, bright field TEM micrographs for the composites prepared by using 1 wt% AIBN (based on macromer) and macromer/styrene weight ratio of 1:2 is reported. It can be seen that

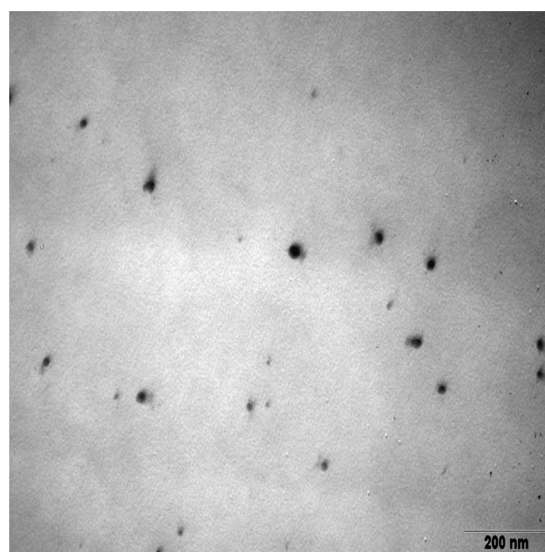


Fig. 2. TEM images of oil based polymer composite containing silver nanoparticles synthesized by using 1 wt% of AIBN (based on macromer) and weight ratio of macromer/styrene 1:2.

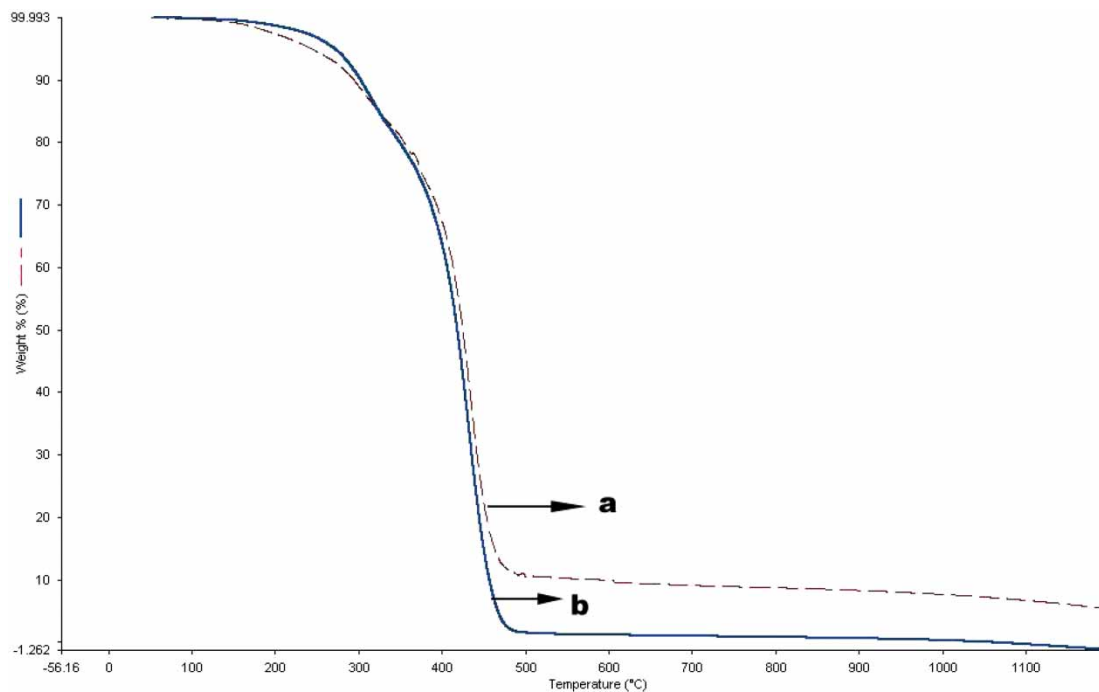


Fig. 3. TGA curves of (a) styrenated oil by macromonomer method and (b) oil based polymer nanocomposite.

metallic particles are well dispersed with no significant macroscopic agglomerations. The particle size distribution is within the range of 13–26 nm. It should be noted that when the AIBN concentration was increased threefold, particle size increased, the range being 20–40 nm. This indicates that the size of silver nanoparticles formed within the polymer matrix strongly depends on the concentration of radical initiator. At a higher AIBN concentration, a higher number of radicals are formed and consequently causes the formation of a greater number of silver nanoparticles which increases probability of their interaction resulting in aggregation. It is also interesting to note that, when the styrene content in the feed is increased, the hydrophobic domain increases which results in the formation silver nanoparticles with smaller size being in the range of 8–20 nm.

Thermogravimetric analysis (TGA) of the polymer composite was also carried out and compared with that of the network formed under identical experimental conditions in the absence of silver nitrate (Figure 3). Interestingly, the sample prepared without silver lost 98% of its original weight at 480°C whereas nanosized silver containing sample lost 88%. This implies that even a very little amount of silver (1%) nanoparticles gives considerable resistance to thermal degradation.

For their potential use as coating materials, film properties of the nanocomposite and polymer samples without metal particles were determined. The results obtained were collected in Table 2. As shown, composite and polymer samples showed good adhesion, flexibility, water, acid, and alkali resistances. Compared to classical styrenated

Table 2. Film properties of polymer films prepared at different conditions containing silver nanoparticles

Sample	Applied test					
	Flexibility ^a	Adhesion ^b	Hardness	Acid resistance ^c	Alkali resistance ^d	Water resistance
OBPC-1 ^e	2 mm	5B	14	No change	75 min pp	No change
SO-M ^f	2 mm	5B	6	No change	53 min pp	No change
SO-C ^g	2 mm	5B	—	No change	31 min pp	5 min

^aThe diameter of cylinder which caused no crack on the film.

^bTest method B was applied.

^cTest was carried out at 25°C with 9% H₂SO₄ solution.

^dTest was carried out at 25°C with 3% NaOH solution, pp = partial peeling.

^eOil based polymer composite with silver nanoparticles (see Table 1 for the details).

^fStyrenated oil prepared by macromonomer method (32).

^gStyrenated oil prepared by classical method (27).

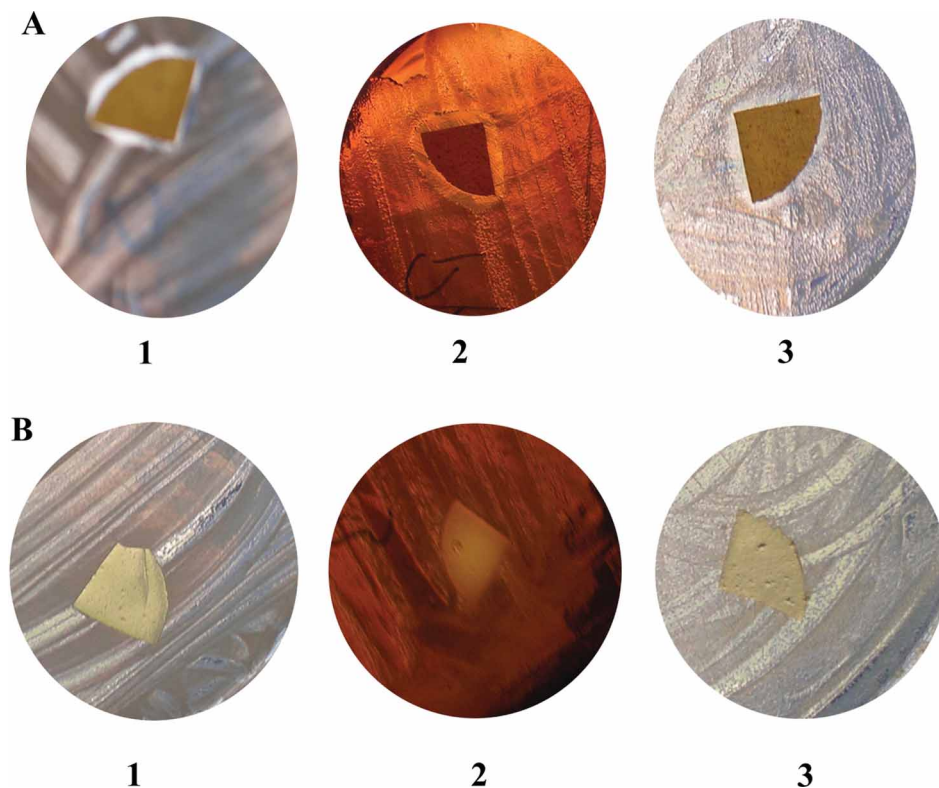


Fig. 4. Photographs showing zone of inhibition of the films prepared with 1 wt% of AgNO₃ (A) and without AgNO₃ (B): (1) *B. subtilis*, (2) *S. aureus*, (3) *P. aeruginosa*.

oil, the samples with and without nano-sized silver showed better film properties. For further extension of their use as antimicrobial coatings, antibacterial properties were also studied. The composite film sample had good antibacterial effect against Gram-positive (*S. aureus*), Gram-negative (*P. aeruginosa*), and spore forming (*B. subtilis*) bacteria as shown in Figure 4. All kinds of bacteria were killed and an inhibition zones were formed due to the antibacterial effect of the silver in the surrounding of the film samples. On the other hand, without silver no inhibition zone was detected. Additionally, after removing the silver composite films, incubation was continued for 24 h at 37°C. At the end of this period, there was no bacterial growth indicating that the composite film has killing effect rather than growth inhibition.

4. Conclusions

In situ synthesis of triglyceride oil based polymer-silver nanocomposite was achieved by simultaneous reduction of silver salt and free radical polymerization processes. The hydrophilic and hydrophobic domains of the polymer are provided by the presence of oil portion (partial glyceride) and styrene segments in the structure, respectively. While some of the radicals formed from the free radical initiator, AIBN,

induce copolymerization of the macromonomer with styrene, the other portion of the radicals undergoes electron transfer reaction to produce metallic silver nanoparticles. The composites obtained in this way contain silver nanoparticles homogeneously distributed in the network without macroscopic agglomeration and exhibit good film and antibacterial properties. It should also be emphasized that the importance of this study is closely related to the components of the network structure. The precursor triglyceride oil is obtained from renewable agricultural sources. Recently, the use of renewable sources in the preparation of various industrial materials has been revitalized because of the environmental concerns. Natural oils consisting predominantly of triglycerides are considered to be the most important class of renewable sources. Previously, we reported various conceptually different strategies to synthesize polymers from triglyceride oils (27–32) and compared with the conventional methods (48). Previously, amphiphilic block copolymers were used as templates for the preparation of inorganic nanoparticles (49–51). In the present study, a novel strategy was applied to synthesize nanocomposites from triglyceride oil based polymer exhibiting an amphiphilic characteristics to facilitate the formation of nanoparticles. This way, shortcomings associated with the high cost and complicated experimental procedures for the preparation of block copolymers were overcome. The applicability of the approach described

here was recently extended to epoxy systems which polymerize via cationic mechanism (52).

Further studies on the preparation of similar nanocomposites by photochemical means are now in progress. It is well known (53) that certain photoinitiators generate free radicals with better electron donating properties and it is expected that these radicals may reduce silver salt more readily than those generated from AIBN.

5. Acknowledgments

The authors thank Istanbul Technical University, Research Funds for financial support, and also thank Istanbul University Histology and Embriology Departments for TEM measurements.

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