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Influence of gold nanoparticles on the photo-polymerization processes and structure in acrylate nanocomposites

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ABSTRACT

Parameters of photo-polymerization process (induction time, rate and degree of conversion) as well as the change of the refractive index, micro hardness and so of the resulting structure were investigated in urethane–acrylate based nanocomposites. Monomers were functionalized by adding SiO_2 and Au nanoparticles by means of direct incorporation. The structural changes due to addition of nanoparticles and photo-polymerization were investigated by micro-Raman spectroscopy and X-ray diffraction (XRD). The real time changes in the refractive index due to irradiation were monitored by Surface Plasmon Resonance imaging (SPRi), which is a novel application of this platform. It is established that these nanoparticles have an influence on the polymer structure and on the transformation of selected bonds during the photo-polymerization process. The plasmon field of gold nanoparticles has a specific additional influence on these changes. These effects can be used to enhance surface relief recording in such nanocomposites due to the photo-stimulated mass transport of the nanoparticles embedded to the polymer matrix.

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1. Introduction

Nowadays the research of nanocomposites, which can essentially differ from composites with larger particles, is in the focus of basic and applied research related to electronics, optics, information technologies and many other applications [1]. In particular, distribution of nanoparticles within the polymer matrix under light treatment is a basis for efficient holographic recording [2,3].

Recently it was shown, that gold nanoparticles (GNP) influence the holographic recording in acrylate-based nanocomposites, resulting in increased diffraction efficiency of the fabricated gratings [4,5]. The influence of the plasmon fields of nanoparticles, for example gold or silver ones, on optical processes, luminescence in organics and other materials was also demonstrated and published in a number of papers [6,7]. The possible influence of GNP, plasmons on the polymerization processes and the resulting structure of different polymers is not completely investigated and clear up to now, in spite of the numerous studies, see for example works [8–11]. It was shown, that rather high (up to 5%) concentration of specific gold nanoparticles introduced chemically together with co-initiators have influence on the polymerization of the selected acrylates due to the charge-transfer processes and can be used for creating conductive polymers with GNP [8–11]. Besides the pure chemistry-associated problems the optical properties, first of all the transparency and the changes of the

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refractive index are extremely important for photonic applications. A separate problem consists in the fabrication of polymer nanocomposites with low scattering for optical purposes, especially with metallic nanoparticles, which influence not only the polymerization but the refractive index as well. Here the influence of resonant plasmon excitation at small concentration of separated, not aggregated gold or silver particles can be essential. The direct introduction of the pre-formed nanoparticles with distinct parameters (for example maximum of plasmon resonance) to the polymer is preferable for these purposes.

The aim of our work was to investigate the processes of photo-polymerization and structure formation by detecting the refractive index (by means of Surface Plasmon Resonance imaging) and structural transformations (by micro-Raman spectroscopy) as well as micro hardness changes in urethane–acrylate based nanocomposites with different degree of cross-linking in the presence of SiO_2 and Au nanoparticles. Combinations of compositions and illumination conditions were used to establish the possible influence of plasmon fields on the investigated processes and resulting structure of the selected nanocomposites, which may be applied for optical recording of amplitude-phase reliefs in polymer-based photonic structures.

2. Experimental details

2.1. Initial materials

The next materials and chemicals were used in this work:

- Diurethane dimethacrylate, mixture of isomers (436909 ALDRICH, UDMA).
- Isodecyl acrylate (408956 ALDRICH, IDA).
- Initiator – 2,2-dimethoxy-2-phenylacetophenone (19611-8 Aldrich, In2).
- Dodecanethiol functionalized gold nanoparticles with size 5 nm (Nanoprobes, No. 3014, GNP).
- SiO_2 nanoparticles with size 14 nm (Aldrich No. 066K0110, SiO_2NP).
- The structure formulas of the investigated monomers used are shown in Fig. 1.

2.2. Preparation of Au-monomer system

Compositions of Au–SiO_2-monomer composites are presented in Table 1. The preparation of the composites was the following. Silicon oxide nanoparticles were added to the above mentioned monomers and the homogeneous mixture was prepared by UHF – dispergation. Solution of GNP in toluene and initiator (0.5 wt% In2) was added to this mixture. Nanocomposite layers with thicknesses 20–300 μm were formed on a glass substrate in the gap between the glass and covered with polyester film.

2.3. Experimental measurements

The photo-polymerization process was investigated by measuring the change of the refractive index during

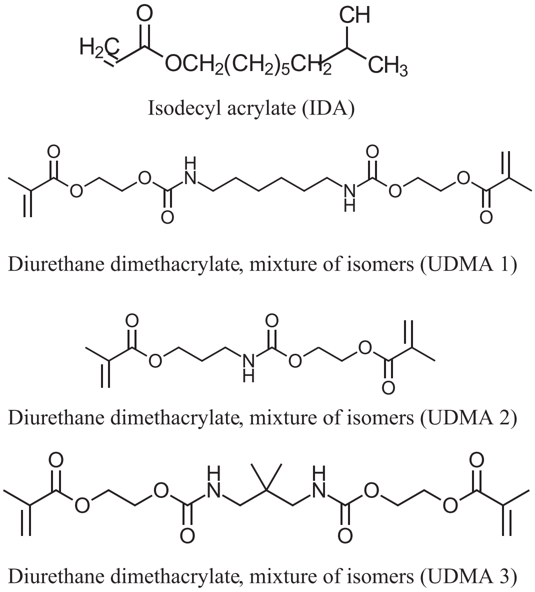

Fig. 1. The structure formulas of the investigated monomers: Isodecyl acrylate (IDA) and Diurethane dimethacrylate, mixture of isomers (UDMA).

Table 1
Vickers hardness of the nanocomposites. UDMA/IDA = 3/7 denotes the ratio of components in a mixture. gated samples.

Sample type	Monomers + 10 wt%SiO_2NP	GNP (wt%)	Vickers hardness
Sample 12a	UDMA	–	8.1
Sample 12Au	UDMA	0.15	9.5
Sample 14a	UDMA/IDA = 3/7	–	4.9
Sample 14Au	UDMA/IDA = 3/7	0.15	6.1
Sample 19Au	UDMA/IDA = 3/7	0.08	5.0

irradiation. The refractive index change caused by UV source (output $P = 1$ W, operating wavelength 325 nm) and green laser diode (output $P = 14$ mW, operating wavelength 533 nm) illumination was measured by Surface Plasmon Resonance imaging (SPRi). The light beam of the sources was defocused, so the intensity of illumination on the sample was 4 mW/cm^2 for the green laser diode and 5 mW/cm^2 for the UV source. For the measurements a custom-built SPRi instrument [12] was used which utilizes Kretschmann optical configuration with a 680 nm superluminescent light source and a 1 MP CCD camera with 25° range of incident angle. In this configuration, the positions of the light source and the camera are fixed and only the prism holder platform can be rotated to scan and find the inflexion point of the SPR peak in order to maximize the sensitivity. There are no moving parts during the measurements. Although the SPRi instrument was designed to measure primarily in aqueous environments, we re-calibrated the device to be able to measure polymers with much higher refractive indexes, such as the investigated nanocomposites.

For SPRi measurements the investigated nanocomposites were dispersed onto a SPRi chip (50 nm gold deposited on a glass substrate, purchased from Mivitec, Germany), then a thin layer was formed by pressing an UV