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MODELLING THE INFLUENCE OF GOLD NANOPARTICLES ON THE POLYMERIZATION KINETICS DURING THE DIFFRACTION GRATING FORMATION IN PHOTOPOLYMER MATERIALS

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Mutual diffusion dynamic model is modified to consider the additional influence of the gold nanoparticles (AuNPs) on the photophysical process during holographic exposure. The presence of AuNPs when decreasing the polymerization rate results in a higher modulation of all the components and a narrower distribution profile of the nanoparticles in the dark regions.

Introduction. The diffraction grating formation as a periodic distribution of the additional neutral component in the bulk of polymer film during optical exposure is explained by the photopolymerization driven counter diffusion of the components due to the imbalance in the concentration of the components in the regions of the sample corresponding to the bright and dark regions of the interference pattern. When metal nanoparticles are dispersed into the polymeric matrix, the simple mutual diffusion mechanism is not enough to describe the kinetics of the diffraction grating formation. Consequently, it is necessary to build a theoretical model that considers the additional influence of the metal NPs. Therefore, to obtain an insight into the influence of AuNPs to the photophysical process during holographic exposure, a mutual diffusion dynamic model modified to include the effect of AuNPs is suggested.

Main part. In general, AuNPs influence the photophysical and photochemical process during holographic exposure, which include the photo-polymerization process (induction time, rate and degree of conversion) and the diffusion process of the components, and also influence the physical properties of the resulting structure such as the hardness. It was found that AuNPs may interact with some photo-initiator, through the formation of a donor-acceptor bond between the initiator and the positively charged surface of the AuNPs. Moreover, the AuNPs effect on the polymerization kinetics and the polymer structure depends on the radiation wavelength - if within or out of the spectral region of the AuNPs plasmon resonance, and on the type of the photo-initiator and its region of sensitivity.

The presence of AuNPs in acrylate nanocomposites with photo-initiator Irg784 results in the formation of a stable complex between AuNP and Irg784, and this increases the decomposition rate of the initiator when irradiated with 532nm laser (within the spectral region of the AuNPs plasmon resonance), and increasing the concentration of AuNPs in the composition leads to significantly enhanced Irg784 decomposition rate in acrylate nanocomposites. In result, the surface relief modulation of the recorded diffraction grating decreased. On the other hand, the same composite when irradiated with 442 nm laser light which is out of the spectral region of the AuNPs plasmon resonance was shown to slow down the decomposition rate of the photo-initiator and enhanced the surface relief modulation structure.

Mutual diffusion dynamic model was modified to considers the additional influence on the diffusion process during holographic recording in photopolymer materials. Three different cases of AuNPs effect were studied and compared. The first case is when there is no effect, so the polymerization dependence on the AuNPs was omitted when solving the coupled diffusion equations of the mutual diffusion dynamic model. The second case it was assumed that AuNPs increase the polymerization rate, so the later was considered to be directly proportional to the AuNPs concentration. The third case assumed that AuNPs decrease the polymerization rate, which considered to be inversely proportional to the AuNPs concentration.

We noticed that the presence of AuNPs when increasing the polymerization rate results in a lower modulation of all the components and a lower diffusion flux. On the other hand, when decreasing the polymerization rate results not just in a higher modulation of the polymers but also in the nanoparticles distribution. This can be explained as following. In the bright areas with the decreasing density of AuNPs, the polymerization process becomes faster and in the dark areas where the AuNPs density increases it terminates the polymerization process. Therefore, during the exposure, the increasing gradual concentration of AuNPs between the bright and the dark areas enhances the gradient in the polymerization rate between them, and results in a higher mutual diffusion of both monomers and nanoparticles. The obtained higher diffusion flux of both monomers and nanoparticles supports this result. Another interesting result is that the effect of AuNPs also leads to a narrower distribution profile of the nanoparticles in the dark regions. This narrower distribution of the AuNPs may explain the higher surface relief structure of the diffraction gratings in composites with AuNPs.

Conclusion. The influence of AuNPs to the photophysical process during holographic exposure was studied theoretically using a modified version of the mutual diffusion dynamic model. Three different cases of AuNPs effect were studied and compared. The first case is when there is no effect. The second case AuNPs increase the polymerization rate. The third case assumed that AuNPs decrease the polymerization rate. We noticed that the presence of AuNPs when decreasing the polymerization rate results in a higher modulation of all the components and a narrower distribution profile of the nanoparticles in the dark regions.

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