THE GELLING KINETICS OF SELFDEVELOPING DICHROMATED GELATIN LAYERS SYNTHESIZED FOR HOLOGRAPHIC APPLICATIONS

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Abstract

The gelling kinetics of the selfdeveloping dichromated gelatin layers sensitized by the methylene blue dye is investigated. It is shown that glycerol in this system is not only a plasticizer but it also increases the number of intermolecular links with macromolecules of gelatin. On the basis of polarographic and holographic studies, an optimal proportion between the glycerol and gelatin in the system is chosen. Adding the glycerol in the gelatin decreases the rate of attaining the maximum diffraction efficiency.

KEY WORDS: dichromated gelatin, glycerol, selfdeveloping, volume holograms, red sensitivity, methylene blue

Introduction

Dichromated gelatin holographic material has been known since 60-th as a highly efficient holographic medium with ultralow noise level and high resolution [1]. Recent investigations have demonstrated the possibility to create a new version of the material with self-developing properties [2,3,4]. The goal of our research is to improve the efficiency, resolution, sensitivity and other properties of this material.

We analyzed the interferometric pattern formation inside the material via investigation of the photosensitive properties of dichromated gelatin (DG) layers. Earlier, the mechanism of the gelatin photosensitivity was shown [5] to consist in a sequence of hierarchical interrelated phase transitions at various levels of gelatin structure, including intermolecular, molecular, and supramolecular levels. There are several basic levels in the structure organization of gelatin. The primary structure is determined by the composition and the sequence of amino acid radicals in a macromolecule of the polypeptide chain. The secondary structure is determined by the configuration and relative spatial arrangement of protein macromolecules elements, which have the shape of helixes, folds, or glomerules. The hypersecondary structure is determined by the aggregation of secondary-structure elements into a single macromolecule, which is manifested, in particular, as the phase state of the globular nucleus. The domain structure is determined by the external parameters (the layer thickness, the degree of layer-to-substrate adhesion, etc.) responsible for the formation of separate and relatively weakly bonded globular segments of a macromolecule. The ternary structure is determined by the conformation of protein helixes in the form of fibrils or globules. The quaternary structure is determined by the aggregation of protein fibrils and globules and, similar to the domain structure, is highly sensitive to the external conditions (the conformation of a collagen-like triple hyperhelix is the limiting case of the quaternary structure for gelatin macromolecules).

Our aim was to study how the glycerol partially replacing the water in the gelatin gel affects the kinetics of gelatinization of self-developing DG (SDDG) layers and the holographic properties of the photosensitive layers sensitized by the methylene blue (MB) dye.

1. Technique for layers synthesis and research methods

The emulsion composition for the layers synthesis was the following:

Gelatin	3, 7, 10 % water solution (w.s.)
Glycerol	4, 7, 10,13, 17 % w.s. (for each gelatin concentration).
Dichromated ammonium	5 % w.s.
Methylene blue dye	0.001 % w.s.

The gelatin was allowed to swell for 2 hours in water at the temperature 25°C, then the glycerol was added and the solution was maintained at the temperature 40°C for 2 hours. Then, the dichromated ammonium of the desired concentration was added to the resulting homogeneous solution. The ammonia was being added in portions until pH=9 was achieved, and then the required quantity of the dye methylene blue was added. For polarization experiments, the prepared emulsion solution was poured in a transparent glass cell, with the distance between the walls of 20 mm.

For holographic experiments, the prepared emulsion solution was poured in a transparent glass cell with the distance between the walls of 2 mm and then was allowed to gelatinize for 24 hours at the temperature 20°C.

2. Polarization studies of the SDDG gelling kinetics

It was shown that the glycerol in the SDDG system is a plasticizer playing a double role: on the one hand, as the plasticizer, the glycerol weakens the intermolecular bonds of gelatin macromolecules, and, on the other hand, it acts as an electron donor for the holographic information recording [6, 7]. In the present research, the processes of spatial structures' rise and manifestation, as well as the nature and mechanisms of gelling are studied. The SDDG structure control was carried out by introduction of various glycerol amounts into the emulsion.

Changes in the spatial structure of gelatin conformation transitions can easily be observed by changing the angle of optical rotation of the polarization plane. So, an ordered state (the macromolecules are in helix conformation) corresponds to the greatest value of the optical rotation angle. The disordered state (gelatin macromolecules are in coil conformation) is characterized by smaller values of the optical rotation angle. The experimental setup consists of the light source (He-Ne laser, λ=632,8 nm) and a pair of perpendicularly crossed linear polarizers. Between the polarizers, the temperature-controlled glass cell under study was located. Behind the second polarizer, a radiation detector was located. Rotating the second polarizer the minimum radiation intensity is achieved, it is possible to determine the polarization plane rotation angle for a given gelatin concentration. The normalized polarization plane rotation angle is equal to:

$$[\alpha] = \frac{\alpha \cdot 100}{lc}$$

Where α is the measured polarization plane rotation angle at a given wavelength and temperature; *l* is the glass cell length, in decimeters, and *c* is the concentration of the investigated emulsion in 100 ml of solution. The error of measuring of the rotation angle was 0.05°. The necessary requirement for obtaining the reliable and reproducible results is the investigated sample's thermostability. In our experiment the temperature variation did not exceed 0.1C. The power of the light source did not exceed 0.1 mW to prevent nonreversible photochemical emulsion transmutations. The results of the experiments for the photosensitive systems with gelatin concentration of 3%, 7%, and 10% are showed in Fig 1.

From the diagrams it is possible to make the following conclusions:

The increase of gelatin concentration increases the specific rotation angle in the initial diagram's fragment.

The spiral sections accumulation rate essentially depends on the gelatin concentration. The rate of achieving the saturation α is seen to increase with increasing gelatin concentration. This is because this process is mainly determined by intermolecular interactions. Also, the formation of individual spirals is stabilized by intramolecular bonds.

Adding the glycerol in the amounts not exceeding the total gelatin mass in the solution does not cause a specific rotation decrease [α], but only reduces the rate of helix formation at gelatin macromolecules sections. Further adding of glycerol not only decreases the change [α] rate, but also limits the possible range of values of the rotation angle. It is explained by the fact that the glycerol molecules form padding links between the gelatin macromolecules already at initial stages of gel formation when the molecules are in a coil conformation. Thus, a portion of gelatin macromolecules are interlinked in coil conformation, thus preventing the development of helix segments.

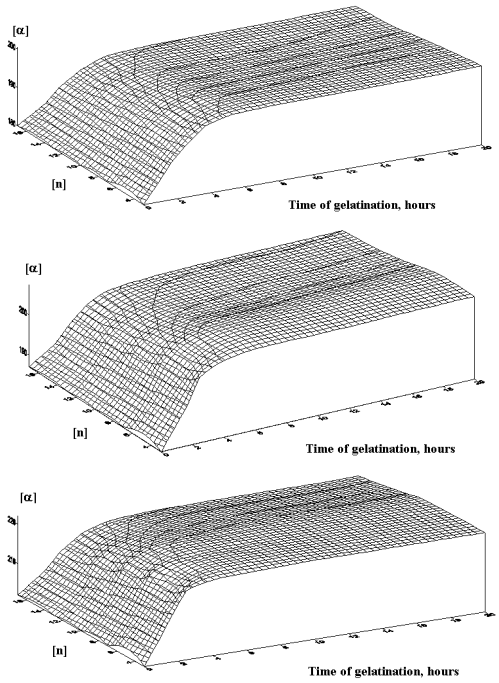

Fig. 1. The change of kinetics of the normalized optical rotation angle at 20C for SD DG layers with the gelatin concentration: a) 3 %, b) 7 %, c) 10 %. [n] = glycerol concentration.

3. Investigation of holographic properties of the SDDG layers

The main advantage of the SD DG layers is real-time recording of phase optical information. As the recording occurs in a closed glass cell, the optical path-length difference between the exposed and non-exposed areas is caused only by photo-induced changes. There are two key characteristics of any photosensitive material – the maximum achievable diffraction efficiency (DE) and the light sensitivity. Apparently, for the maximal DE to be attained it is necessary to ensure the maximal difference of the refractive index between the exposed and non-exposed areas. In the meantime, to increase the light sensitivity it is necessary to decrease the energy required to ensure that maximal refractive index difference.

The experimental setup has a standard configuration. The experiments were carried out in real time. For recording and reading-off the holographic information the He-Ne laser was used. The beam was expanded by a collimator and was divided into two equal-intensity

beams by a 50%-mirror. The convergence angle of the two beams corresponded to a spatial frequency of 500 mm^{-1}. One of the beams traveled through a rotating chopper disk placed before the sample. The diameter of the area in which the holographic information was recorded was equal to 1 cm^2.

The results of the holographic experiments for photosensitive systems with the gelatin concentration of 3 %, 7 %, and 10 % are shown in Fig 2. As can be seen from the diagrams, the increasing glycerol concentration leads to a decreasing rate of achievement of maximal DE, which is clearly seen in the diagram in Fig. 2c. It can also be seen that the maximum achievable DE is observed for the glycerol-gelatin proportion of 1:1. The gelatin concentrations increasing from 3% to 10% essentially increase the sensitivity and maximum achievable DE. Maximal DE is observed for the gelatin concentration equal to 10%. So, to ensure high DE it is necessary to have high gelatin concentrations in the system. This leads to the increased degree of order of the gelatin matrix, as well as ensuring the approach of the photochemical reagents.

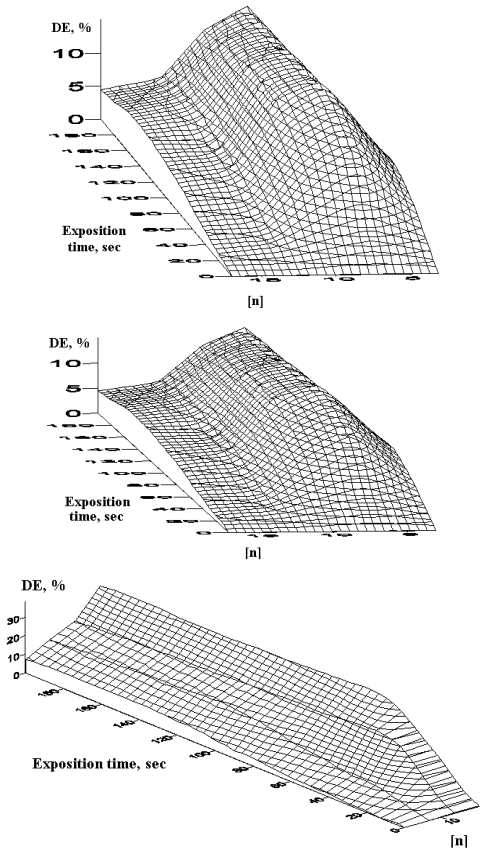

Fig. 2. The diffraction efficiency vs the time of exposure by the light of 10 mW/cm^2 for the SD DG layers with the gelatin concentrations:
a - 3 %, b- 7 %, c- 10 %. [n] = glycerol concentration

Conclusion

Based on the studies conducted, we can conclude that the glycerol in the SD DG system is not only a plasticizer, but it mostly acts as an elasticizer by increasing the number of intermolecular bonds in the polymeric matrix. If the increased glycerol concentration starts to exceed the gelatin concentration this leads to the deteriorated conditions of helix conformation formation due to the interlinking of gelatin macromolecules by the glycerol, thus stabilizing the coil conformation in the gelatin matrix. This also decreases the rate of attaining the maximum DE in the holographic experiment. It should be noted that glycerol, apparently, plays the role of an electronic donor that ensures the dark reduction of MB and, thus, takes part in the dark reduction of chrome ions, thus reducing the life-time of unexposed layers.

The designed material sensitive in red region of spectrum allows real-time recording of images. It can be used for studying the holographic recording features. The material is simple in preparation, well reproducible and cheap. In future, it is proposed to increase the life-time of the recorded holograms. The results of the experiments have formed a basis for developing inexpensive, high-performance and super-thick phase selfdeveloping media, capable of working in red range of spectrum. Designed by the polarization method of optimization of the holographic characteristics, the SD DG layers sensitized by MB may be used for recording super-deep holograms and selectograms, and for development of new systems of holographic data storage.

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