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NOVEL NANOCOLLOIDAL INKS FOR 3D-PRINTING BASED ON POSITIVELY AND NEGATIVELY CHARGED LATEX NANOPARTICLES

E.O. Ryabchenko, T.G. Statsenko, E.F. Krivoshapkina
Scientific advisor – Dr. S.M. Morozova
(ITMO University, Saint Petersburg,
Russia)

Abstract. This paper describes a novel method of counterfeit prevention based on 3D printing of optical-active structures with gelated shear-thinning inks based on latex nanoparticles with different charge. Modified with dyes, they could be implemented as optical-active elements available to be imprinted due to their shear-thinning properties. According to these properties, described optical-active structures could be imprinted not only on surfaces with simple geometry, but also on more complicated (e.g. angles, coarse surfaces) which is very useful in increasing of protection power of this method.

Introduction. Counterfeit of goods seems as serious economic disaster for present day. Manufacturers around the world losses 10-15% of their income due to counterfeit and fraud. According to this fact, novel methods of counterfeit prevention extremely needed for present day. Development of new materials for the protection of identification documents, credit cards, and authentication labels against counterfeiting has been an active area of research.

One of the perspective methods – printing of optical-active structures. These structures such as holographical labels, quantum dots and others was previously developed for inkjet printing and at now has application at various spheres of industry. Photoactive materials such as liquid crystalline polymers, photopolymers for digital holographic recording, and photonic crystal based holograms has successfully used as the recording media. Nevertheless, they has few disadvantages – impossibility for imprinting on surfaces with complicated geometry, commercial unavailability, bad adhesion on various substrates and other. However, these materials are suitable for creating 2D objects, while the transition to 3D objects will expand the scope of application.

Our work is devoted to the topic of design, obtaining and 3D-printing of optical-active structures with novel inks based on latex nanoparticles with different charge. Modified with dyes, these structures could emit light under irradiation (e.g. UV-light, 380 nm). These inks more commercial available and has shear-thinning properties with fidelity. Last one advantage provide sustainability of printed structures and lead to the printing on complicated geometry that could increase power of protection from counterfeit. Novelty of our work also consist in printing of these structures under ambient conditions, which is useful as solution for protection of wide range of goods.

Materials and methods. As for monomer, ethyl-methacrylate (EtMa) chosen due to their good compability with dyes and commercial availability. As dyes, which have to emit light under irradiation, we select fluorescinacrylate (FA, as a green-labeled dye) and 9-vinylantrcene (VA, as blue-labeled dye). For synthesis positively charged latex nanoparticles we chosen cetyl trimethylammonium bromide (CTAB) as surface active substance (SAS), and 2, 2'- Azobis(2-methylpropionamidine)dihydrochloride (V-50) as initiator of polymerization. For synthesis negatively charged latex nanoparticles, we chosen sodium dodecyl sulfate (SDS) as SAS, and potassium persulfate (KPS) as initiator of polymerization.

Based on them, we have synthesed 4 types of charged nanoparticles: positively charged EtMa (non-labelled), FA-EtMa (green), VA-EtMa (blue); negatively charged EtMa (non-labelled). From these charged latex nanoparticles, mixing them in optimal ratio for gelation we obtained 3 types of

gelated inks – non-labelled, labeled green and labeled blue. Analysis of excitation-emission showed that FA-EtMa+, exhibit a strong emission peak at 526 nm under excitation at 450 nm, while VA-labeled NPs emit at 428 nm at excitation at 257 nm. To examine the formation of a nanocolloidal gel, due to electrostatic attraction of charged NPs, a dispersion of negatively charged latex NPs was added dropwise to 1 mL of the dispersion of positively charged latex NPs at room temperature with a step of 100 μL, with vigorous mixing after each step. Gelation at a particular ratio of concentrations of the NPs identified using a flip test. Using this method, sol-gel equilibration successfully investigated. As for rheology, we studied the self-healing properties of ink. Variation in complex viscosity with varying shear-rate proved their shear-thinning properties. Step-wise oscillation test showed us that the inks has full-time recovery after cycle of loading.

Obtained inks successfully printed with 3D-pneumoprinter Cellink Bio X. For 3D-printing we chose many types of models – simple lines, text, ing-yang, pattern «Bird Fish» created by painter M.C. Escher and barcode. After optimization of printing parameters, all of these structures successfully printed on a glass substrate.

Conclusion. In this study, the concept of security printing with inks consists of charged nanoparticles was developed. This research demonstrated that described novel nanocolloidal inks seems as perspective material for security 3D-printing due to their propierties. Our plans with this work associated with further researches of coding/decoding information processes and printing on various substrates including surfaces with complicated geometry.

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E.O. Ryabchenko

S.M. Morozova