

Summary

In the present work a computer simulation of homopolymer 2-hydroxyethyl methacrylate (HEMA) and its copolymers with vinylpyrrolidone (VP) [P(VP-*co*-HEMA)] and 2-methacryloyloxyethyl phosphorylcholine (PC) [P(MPC-*co*-HEMA)] with different sequences and number of individual mers were performed. The simulations were done for bulk and polymeric thin films with different water content (0, 10, 20, 40 and 60 wt %).

It was found that all systems have an amorphous structure. P(VP-*co*-HEMA) copolymers are characterized by higher glass transition temperature T_g than pure PHEMA homopolymer, while P(MPC-*co*-HEMA) copolymers exhibit lower values of T_g . Moreover T_g depends on the number of mers in polymeric chain as well as their sequence.

Analysis of the radial distribution function $g(r)$ allowed determining the microscopic structure of the simulated polymeric systems. It was determined that the regardless of chemical composition the spatial distribution of the HEMA and VP side groups does not change. Changing the sequence and number of individual mers in polymeric chains as well as water content does not affect the short-range order and length of the mers. PHEMA and P(VP-*co*-HEMA) polymers are stable and not very flexible systems. MPC mers exhibit clear changes of the geometry depending on the water content and polymeric sequence. P(MPC-*co*-HEMA) polymers are more flexible than HEMA and P(VP-*co*-HEMA) and have better water absorption capability.

The mobility of the side groups of polymers increases with the increase of polymer hydration and it is the subject to sub-diffusion processes. The highest mobility is observed for P(MPC-*co*-HEMA) copolymers, especially for water content equal to 40 and 60 wt %, which confirm the fact, that water acts as plasticizer increasing the polymer chain mobility. Preferred sites for hydrogen bond formation with water molecules are oxygen atoms of hydroxyl and carbonyl groups of HEMA mers and carbonyl groups of VP mers. The phosphate and choline groups in the case of bulk materials are mainly responsible for the

high hydrophilicity of MPC mers, while the carbonyl group also shows high affinity in the case of thin films.

In low hydrated systems, water is well dispersed and forms mainly hydrogen bonds with the polymer chains. At higher concentrations of water molecules, water–water hydrogen bonds are also formed. In addition, it was observed that with the increase of the hydration, water comes to the surface of the polymer, creating free water with high diffusion capacity. For low hydration materials water molecules are subjected to sub-diffusion, tending to normal diffusion for high hydration systems. The water diffusion coefficient increases with increasing of the hydration. It can be attributed to the increase of weight percentage of intermediate and free water. The highest values of D_w were obtained for P(MPC-co-HEMA) copolymers, while the lowest ones were observed for P(VP-co-HEMA). Water diffusion in low hydrated polymers is based on the „hopping” process involving free volumes present in the polymer. It was found that copolymerization of PHEMA with MCP mers influences the increase, while with VP mers – the decrease of the free volume fraction, which reflects in the diffusion of water molecules. The „hopping” process in the case of more hydrated systems is not as clear as in systems with lower water content because it is dominated by free water diffusion.

Based on the conducted investigations it can be concluded that the MPC may be added to contact lens as a lubricant, it is also a good oxygen carrier and a UV filter. The combination of HEMA and MPC produces a hydrogel material with suitable properties for ophthalmic applications.

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