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Synthesis and structure of new composite hydrogels based on poly(*N*-vinyl caprolactam) with nanosized anatase

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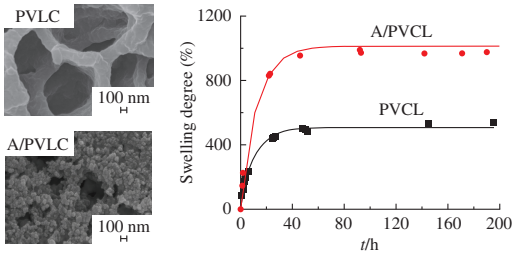
Hydrogels based on poly(*N*-vinyl caprolactam) (PVCL) with nanosized anatase (A particles) were synthesized by a sol–gel method and explored by powder X-ray diffraction and scanning electron microscopy. The internal structure of A/PVCL has pores smaller than those in a PVCL hydrogel. The water swelling capacity of A/PVCL is higher than that of the initial PVCL.



Hydrogels are the systems of high-molecular-weight compounds, which form an infinite three-dimensional macromolecular network with water in the network cavities.[1] The presence of another component in composite hydrogels imparts additional functional properties to the hydrogels. Composite hydrogels based on poly(*N*-vinyl caprolactam) [$(C_8H_{13}NO)_n$, PVCL] hold promise. This polymer is nontoxic to cells at short exposure times.[2] Composite hydrogels based on PVCL are used for medical purposes.[3–6] Here, we report the sol–gel synthesis and characterization of composite hydrogels based on PVCL with nanosized anatase particles, which have bactericidal properties[7] and can be used for the design of new materials for medical applications.

PVCL-based hydrogels (Figure S1, see Online Supplementary Materials) were synthesized from PVCL,[8] tetraethoxysilane and nanosized anatase particles (A).† We studied the native (as-prepared) hydrogels (**1**), hydrogels air-dried to constant weight at 20 °C (**2**) and then finely ground to powder (**3**), and freeze-dried native hydrogels (**4**).

The PVCL hydrogel (**4**) had a surface with irregular pores of sizes 140(5) nm (~30% pores) and a three-dimensional structure with an average pore size of ~1400(100) nm and a pore wall thickness of 250(5) nm [Figure 1(*a*)] (SEM and EDX).‡ The surface of the A/PVCL (**4**) hydrogel possessed 500–600 nm pores and the aggregates of nanosized anatase particles of ~250 nm in these pores, and its internal structure contained smaller pores of size ~300 nm compared to PVCL [Figure 1(*b*)]. Anatase nanoparticles formed associates of size 20–60 nm, which were deposited on the pore walls during gel formation.

The X-ray diffraction pattern of native PVCL hydrogel (**1**) [Figure 2(*a*)] has three peaks (Table S1, see Online Supplementary Materials). The first peak is related to the intermolecular interactions of C–C polymer chains [based on an interpretation for poly(*N*-vinyl pyrrolidone),[9] which has a similar structure]. The second peak is attributed to both inter- and intramolecular correlations. Two relevant length scales related to two XRD peaks emerge as a consequence of intermolecular interactions between vinyl groups and between side groups. The third peak is assigned to a network of bonds between PVCL and TEOS hydrolysis products. The X-ray diffraction pattern of powdered PVCL hydrogel (**3**) has two reflections unlike the native PVCL (**1**) [Figure 2(*b*), Table S1] and an amorphous halo at 2θ~21° shifted towards smaller angles due to a decrease in water molecules content. The shift of the second peak to larger angles is indicative of a higher water content of A/PVCL (**3**), as compared with that of PVCL (**3**) [Figure 2(*c*)]. The changes caused by drying are reflected not only in the positions of the shifted peaks, but also in a substantial decrease in the intensity of the second peak responsible for the water content [Figure 2(*d*)]. The peak at 2θ of ~25° belongs to nanosized anatase-phase TiO_2 (JCPDS 89-4921) with an average crystallite size of 54(3) Å, which is smaller compared with initial Hombifine N [82(4) Å].[10] The XRD data provide evidence for the amorphiza-

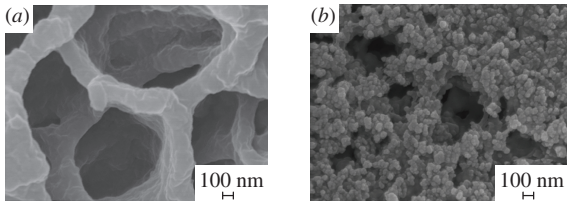


Figure 1 SEM images of cross-sections of freeze-dried native (*a*) PVCL and (*b*) A/PVCL hydrogels.

† Hydrogels were prepared as follows. 2-Dimethylaminoethanol catalyst (DMAE, $C_4H_{11}NO$, ⩾99.5%, Sigma-Aldrich), surface-active substance macadamia oil Glycereth-8 esters (ResPharma, Italy), and reagent-grade tetraethoxysilane (TEOS, $SiC_8H_{20}O_4$, Sigma-Aldrich) were added at concentrations of 0.05, 0.1, and 7 wt%, respectively, to an aqueous solution of PVCL ($M_w = 1 \times 10^6$ Da) at a concentration of 10 wt%. The mixture was stirred (1500 rpm) at room temperature (22 °C) for 30 min and then poured into a mold covered with a lid. The thickness of the mixtures in the mold was 4–6 mm. To prepare A/PVCL composite hydrogels, commercial Hombifine N (Sachtleben Chemie GmbH, Germany) with nanosized anatase particles was added at a concentration of 0.25 wt% before the addition of TEOS. For characteristics of the hydrogeles synthesized, see Online Supplementary Materials.

‡ For SEM, EDX and XRD data and swelling degree characterization, see Online Supplementary Materials.

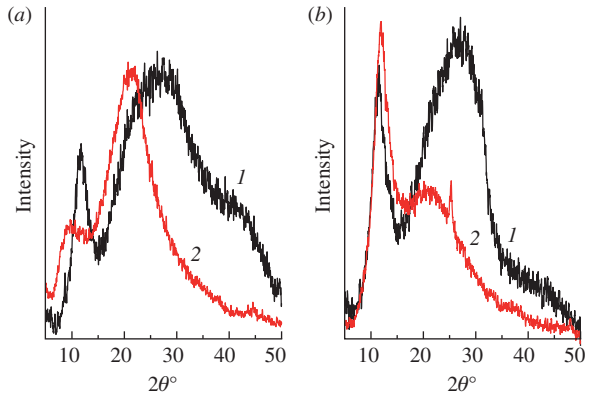


Figure 2 Powder X-ray diffraction patterns of (*a*) native (*1*) PVCL and (*2*) A/PVCL hydrogels and (*b*) powdered (*1*) PVCL and (*2*) A/PVCL hydrogels.

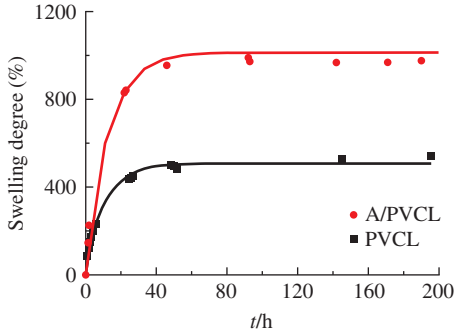


Figure 3 Swelling curves for air-dried PVCL and A/PVCL hydrogels.

tion of nanosized anatase particles. The peaks of SiO_2 were not observed due to either a low concentration or an X-ray amorphous state.

The A/PVCL hydrogel (**2**) has a swelling capacity in water higher by a factor of 2 than that of PVCL (**2**) (Figure 3), which is expected based on their X-ray diffraction patterns: the water content of PVCL [see Figure 2(*b*)] is much higher than that of A/PVCL [see Figure 2(*d*)], based on the synthesis conditions. The swelling process of PVCL and A/PVCL obeys the second-order kinetics. The composition of air-dried samples (**2**) and powdered A/PVCL (**3**) depends on that of the initial composite hydrogel A/PVCL (**1**) (the water content). Hence, the shape and the ratio of the curves in Figure 3 and the degree of swelling (Table S2) will be different. TiO_2 was not released from A/PVCL composite hydrogel throughout the swelling process (200 h). All dried PVCL and A/PVCL hydrogels are characterized by high rigidity, and they are stable during swelling. The calculated diffusion constant *n* was 0.53, which suggests that the diffusion of water is not described by Fick's law.[11]

In conclusion, we synthesized PVCL and A/PVCL hydrogels by a sol–gel method and characterized them in different states. The nanosized anatase particles exert a significant effect on the water content of the hydrogels and on the microstructure of A/PVCL. The surface of the A/PVCL composite hydrogel is more developed, and its internal structure comprises pores of smaller sizes compared with PVCL hydrogel, which can be attributed to higher water concentrations in the pores. The A/PVCL hydrogel exhibits a twice as high swelling capacity in water as that of PVCL.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.013.

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