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Preparation and characteristics of pH-sensitive Poly(acrylic acid) and Poly(vinyl alcohol) Interpenetrating Polymer Networks Hydrogels

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Hydrogels can respond to external stimuli such as pH, ionic strength, temperature, and electric current. Such polymeric systems are useful as stimulus responsive drug carriers and are often called 'intelligent' or 'smart' materials because of their quick response to the external stimuli. The pH-sensitivity of the hydrogels is due to the presence of weakly acidic and/or basic functional groups on the backbone. Their water uptake properties are attributed to the ionization of functional groups, which depend upon the pH and ionic strength of the external medium thereby making them useful as pH-sensitive drug delivery systems.

Hydrogels based on poly(vinyl alcohol) (PVA) has been applied successfully as controlled release system for drug delivery because of their biocompatibility with the human body. Poly(acrylic acid) (PAA) is ionizable hydrophilic polymers. Cross-linked PVA and PAA are able to swell in water. Its swelling behavior is greatly pH-dependent due to the ionization/detionization of the carboxylic acid group. At low pH values the -COOH groups are not ionized and keep the network at its collapsed state. At high pH values, the -COO-groups repel each other, leading to PAA swelling.

The interpenetrating polymer network (IPN) of PVA and PAA were synthesized by free radical copolymerization. GA was used as the crosslinking agent for PVA and EGDMA was used as a crosslinking agent for AAc and KPS was used as the initiator. Nitrogen was bubbled through the monomer/solvent mixture for 20 min to remove oxygen dissolved in the reaction mixture. The reactants solution was heated at 70°C for 6 hr. Hydrogel was cut into thin disk of 10mm diameter and washed with water. Swollen gel disks were initially dried under a mild air stream in the venting hood and transferred into vacuum oven for complete drying.

The dynamic swelling behavior was determined by soaking the dried drug loaded hydrogel disks in a buffer solution at several different pH's of 2, 4, 6, 7, and 10 at room temperature. This buffer solution range was selected because it bracketed the typical pH range of the eye and ophthalmologic solutions.

Swelling ratio of a sample was calculated as follows:

$$\text{Swelling ratio (\%)} = (W_s - W_d) / W_d$$

W_d and W_s are the weights of dry and swollen samples, respectively.

A pH-responsive hydrogel with IPN structure for controlled nano-sized drug release was proposed. The hydrogel, which consisted of copolymers of poly(vinyl alcohol) and poly(acrylic acid), showed dynamic swelling behavior and pH sensitivities in the range of pH7 to pH10.

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Properties of hybrid nanocomposites cross-linked with methacryloxy propyl trimethoxy silane and TEOS using sol-gel reaction

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Copolymers were synthesized by free radical chain polymerization by using 3-trimethoxysilyl propyl methacrylate(MPS), benzyl methacrylate(BzMA) and methyl methacrylate (MMA) monomers.

The conversion of produced copolymers was confirmed by using H-NMR analysis and was more than 99%. Organic/inorganic hybrid composites were prepared by sol-gel reaction for the mixture of tetraethylorthosilicate(TEOS) and organic copolymers. Both copolymer hybrid composites and copolymer/TEOS hybrid composites had good properties of transparency. The methoxysilyl group of copolymer can be used for the reaction between inorganic materials and organic materials in molecular level by forming the covalent bonding. These characteristics played a role in improving the compatibility between organic and inorganic materials and could make fine dispersion state between two materials. The hybrid nanocomposites had good thermal characteristics in comparison with the organic copolymer. Large extent of weight loss was found between 200-400°C in the organic copolymer, but the hybrid composite had residual more than 25% of weight above 600°C. Coupling agents in copolymer made it possible to form crosslinked network with inorganic materials and organic materials through hydrolysis and condensation. Also, the hybrid composite had a good chemical resistance. The thin film, which was prepared by sol-gel reaction for the mixture of TEOS and organic polymers, was dipped in NMP solvent for 1 minute. Hybrid composite thin film was not swollen in the dipping test but organic film was swollen. Normally, organic materials have inferior mechanical property than inorganic materials. So they were limited to various applications. But this hybrid composite was proved to have an abrasion resistance and hardness in comparison with organic copolymer by abrasion test and nano-indentation test. With increasing MPS content in copolymer, mechanical strength of the hybrid composite increased.

The improved thermal stability, chemical resistance and mechanical strength of hybrid composite, which was prepared by sol-gel reaction for the mixture of TEOS and organic copolymers having functional groups to bond inorganic materials, enabled these hybrid composites to be applied in the various applications such as coating materials in TFT LCD industry.

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