



## Review

## Mechanical properties of PNIPAM based hydrogels: A review

Muhammad Abdul Haq<sup>a,b</sup>, Yunlan Su<sup>a,\*</sup>, Dujin Wang<sup>a</sup><sup>a</sup> Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China<sup>b</sup> Laboratory of Food Engineering, Department of Food Science & Technology, University of Karachi, Karachi, Pakistan

## ARTICLE INFO

## Article history:

Received 8 June 2016

Received in revised form 13 September 2016

Accepted 29 September 2016

Available online 30 September 2016

## Keywords:

Poly(*N*-isopropylacrylamide)

Hydrogel

Smart material

Mechanical properties

## ABSTRACT

Materials which adjust their properties in response to environmental factors such as temperature, pH and ionic strength are rapidly evolving and known as smart materials. Hydrogels formed by smart polymers have various applications. Among the smart polymers, thermoresponsive polymer poly(*N*-isopropylacrylamide) (PNIPAM) is very important because of its well defined structure and property specially its temperature response is closed to human body and can be finetuned as well. Mechanical properties are critical for the performance of stimuli responsive hydrogels in diverse applications. However, native PNIPAM hydrogels are very fragile and hardly useful for any practical purpose. Intense researches have been done in recent decade to enhance the mechanical features of PNIPAM hydrogel. In this review, several strategies including interpenetrating polymer network (IPN), double network (DN), nanocomposite (NC) and slide ring (SR) hydrogels are discussed in the context of PNIPAM hydrogel.

© 2016 Elsevier B.V. All rights reserved.

## Contents

1. Introduction . . . . .	842
2. Mechanical features of native PNIPAM hydrogel . . . . .	843
3. Strategies to improve the mechanical strength of PNIPAM hydrogel . . . . .	844
3.1. Interpenetrating polymer network . . . . .	844
3.2. Double network hydrogel . . . . .	845
3.3. Slide ring hydrogel . . . . .	846
3.4. Nanocomposite PNIPAM hydrogel . . . . .	847
3.5. Copolymerized PNIPAM based hydrogel . . . . .	850
4. Applications of PNIPAM hydrogels with improved mechanical strength. . . . .	851
4.1. Soft robotics . . . . .	851
4.2. Injectable hydrogel . . . . .	851
4.3. Shape memory hydrogel . . . . .	851
5. Conclusion & future perspective . . . . .	852
Acknowledgements . . . . .	852
References. . . . .	852

## 1. Introduction

Material science and technology has grown tremendously in last few decades. Smart materials which reversibly respond to the change in their environment are examples of these developments [1–4]. Although few low molecular weight compounds have been reported to possess smart properties [5–8], the majority of them are polymers. Polymers

are attractive candidates for smart materials because they may contain different domains or moieties. The affinity of these domains towards environment is altered under different conditions. This results in conformational change, e.g. from globule-to-coil or helix-to-random coil, which is associated with phase transition [9].

Many potential applications of smart materials are in aqueous medium. Polymers can form extended three dimensional structures which hold the solvent. Water insoluble crosslinked three dimensional network of polymer which hold water is known as hydrogel. Hydrogel microstructure resembles to natural tissue [10–12], therefore they can be

\* Corresponding author.

E-mail address: [ylsu@iccas.ac.cn](mailto:ylsu@iccas.ac.cn) (Y. Su).

applied for various biomedical purposes e.g. drug delivery, tissue engineering and imaging [13–17]. Further applications of smart hydrogels include analytical separation and detection [4,18,19], antifouling coatings [20–22], flow controlling devices [23–25], soft mechanics [26–29] and water desalination using forward osmosis [30].

Smart hydrogels are capable of responding to the changes in temperature, pH, humidity, light, specific ions or molecules, electrical fields, solvent and ionic strength etc. Temperature and pH sensitive materials are most commonly studied because these parameters change naturally and can be easily controlled. Among them, thermoresponsive hydrogels prepared from thermosensitive polymers are widely studied. These polymers might be negatively or positively thermosensitive. The former possess a lower critical solution temperature (LCST) while the latter exhibit upper critical solution temperature (UCST). The LCST polymers contract upon increase in temperature beyond their critical temperature while UCST polymers show the similar behavior upon decrease in temperature [31,32]. More precisely, around critical temperature the polymer in solution exhibits a phase transition from a soluble state (i.e. random coil) to an insoluble state (i.e. collapsed or globule form). A well-known example of UCST polymer is gelatin which forms gel upon cooling. However, LCST polymers are more favorable for biomedical purposes because they can release the substance at human body temperature. Thermoresponsive phenomenon originates from the delicate balance between the hydrophobic and hydrophilic moieties in the monomer of the polymer. The interaction between polymer segments and water is altered by the small change in temperature due to shift in hydrophilic and hydrophobic forces [33]. Although copolymers such as poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) block copolymer and poly(ethylene oxide)-*b*-poly(D,L-lactic acid-*co*-glycolic acid)-*b*-poly(ethylene oxide) (PEO-*b*-PLGA-*b*-PEO) triblock copolymers have been reported as thermosensitive polymers, they are not extensively studied due to their difficulty in preparation, [34]. In thermoresponsive homopolymers, the monomer structure is generally hydrophilic which possesses some hydrophobic groups such as methyl, ethyl and propyl groups. Examples are *N* substituted poly(acrylamide) such as poly(*N*-isopropylacrylamide)(PNIPAM), poly(*N,N*-diethylacrylamide)(PDEAM), poly(*N*-ethylmethacrylamide)(PNEMAM) and others poly(methylvinylether)(PMVE), poly(2-ethoxyethylvinylether)(PEOVE), poly(*N*-vinylisobutyramide)(PNVIBAM) and poly(*N*-vinylcaprolactam) (PNVCa) [13]. Among the known thermosensitive polymers, PNIPAM is most promising because of its well defined structure and property specially its LCST is closed to human body and can be finetuned as well. There are numerous references referring to PNIPAM hydrogel.

PNIPAM is characterized by amide (—CONH—) and propyl (—CH(CH<sub>3</sub>)<sub>2</sub>) moieties in the monomer structure. When temperature is low, the hydrophilic amide group is solvated by the water molecules thus the polymer is soluble. This hydrogen bonding results in the highly structured hydration shell. When the temperature is elevated, the hydrogen bonding is weakened and subsequently, interactions among the hydrophobic groups (—CH(CH<sub>3</sub>)<sub>2</sub>) become strong. This ultimately results in the release of water from the structure. Simultaneously the abrupt collapse of polymer chains happens, thus a volume phase transition (VPT) also occurs [12]. PNIPAM hydrogel exhibits VPT temperature at about 34 °C, which is somewhat higher than the LCST (≈32 °C) of the polymer in aqueous solution. In general, hydrogels exhibit low mechanical properties and PNIPAM hydrogel is not the exception. The situation is even more complex because thermoresponsive properties of the PNIPAM hydrogel are not good as well. The response of native PNIPAM hydrogels is very slow with respect to external temperature alterations. This is mainly because of the creation of an impenetrable surface structure, which slows down the outward flow of water throughout the hydrogel crumpling phenomenon. The response rate can be increased by the incorporation of pore forming additives e.g. sucrose-modified starches [35], silica particles [36] and poly(ethylene glycol) (PEG) [37] during the gel formation. Other strategies include the use of special

solvents, high molecular weight crosslinker and control of polymerization temperature [31]. These methods generally do not improve the mechanical strength of the hydrogel [38].

Many applications of PNIPAM hydrogels are in aqueous medium in which they swell to a very high degree. This results in low density of the polymer chains which makes the gels extremely poor in physical strength. This is a great hurdle in their applications. For example in soft robotics applications, the robotic arm must be able to securely grip the objects [39]. In other applications such as filtration where permeate flux is directly proportional to applied pressure, the thermoresponsive antifouling coatings must be robust [40]. Similarly, in water purification by forward osmosis, thermoresponsive draw solutes must be capable of withstanding the high pressure (several MPa) of squeezing [41–43]. The mechanical profiles required in biological applications are even more diverse and difficult to achieve. For example, the mechanical properties of the scaffold for cell growth should match that of the host tissue [44]. Different tissues have very dissimilar mechanical strength, e.g. Young's modulus of brain tissues is reported to be in the range of 1 kPa [45] whereas bones exhibit Young's modulus in the range of GPa [46]. Thermally activated artificial muscles are another potential application of PNIPAM based hydrogels which are not explored yet due to low mechanical strength [47]. Moreover, in drug delivery application, the hydrogel has to be removed surgically because PNIPAM is non-biodegradable and it is very difficult to completely remove the fragile hydrogel by present surgical procedures. Therefore a number of techniques have been reported to enhance the mechanical properties of the PNIPAM hydrogel.

## 2. Mechanical features of native PNIPAM hydrogel

PNIPAM hydrogels prepared by free radical redox polymerization technique are too weak and fragile to be accurately characterized using standard mechanical testing devices [48]. A number of parameters affect the mechanical properties e.g. initial monomer concentration, crosslinker ratio, polymerization and measurement temperature, degree of swelling at the time of measurement and the technique of measurement. This makes the precise comparison of any mechanical parameter very difficult. Nevertheless, different mechanical properties of PNIPAM hydrogel from various studies are presented in Table 1. The Young's modulus ( $E_0$ ) of PNIPAM hydrogel was first reported in 1997 by Takigawa et al. [48]. In a typical tensile test, they observed a linear stress-strain curve of the swollen as well as collapsed gel with the  $E_0$  about hundred times higher in collapsed state. The fracture strain was reported to be 35% in swollen state and 75% in collapsed state. The linearity of stress-strain curve beyond 35% strain was not observed in a later comprehensive study of mechanical and rheological properties of PNIPAM hydrogel by Puleo et al. [49] in 2013. They proposed the neoHookean model to explain the non-linear stress-strain curve (Fig. 1). The fracture strain was reported to be 79% in case of compression while it was only 30% in tensile (Fig. 2). They articulate that the difference in compressive and tensile testing is due to dissimilar water behavior in hydrogel matrix during two types of tests. In compression mode, water is redistributed in the matrix thus allows larger strain, which does not happen in tensile testing thus lower fracture strain is achieved. The Young's modulus calculated by complex modulus from rheological experiment was found to be 1.2 kPa under the assumptions of incompressibility, homogeneity and isotropy for the hydrogel, which is about one magnitude lower than those measured by tensile test. This shows that the technique of measurement greatly affects the magnitude of the mechanical parameter. The polymerization temperature also affects the mechanical strength. At low temperature the kinetics is slow and the material is formed via few polymer chains of high molecular weight, which results in high strength. In all the studies of Table 1, the polymerization temperature was room temperature (20–25 °C) except the report of Gundogan et al., who prepared the gel at 5 °C [50]. Unusually high compressive strength (81 kPa) is reported by Fei et al. in two

Download English Version:

<https://daneshyari.com/en/article/6481352>

Download Persian Version:

<https://daneshyari.com/article/6481352>

[Daneshyari.com](https://daneshyari.com)