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Author(s)	Karobi, Sadia Nazneen
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学 位 論 文 内 容 の 要 旨

Abstract of Doctoral Dissertation

博士の専攻分野の名称　博士 **(生命科学)**　氏 名 サディア ナズニン カロビ

Degree requested **Doctor of Life Science** Applicant name **Sadia Nazneen Karobi**

学 位 論 文 題 名

Title of Doctoral Dissertation

Time Dependent Deformation of Tough Polyampholyte Hydrogels

(強靭なポリアンフォライトハイドロゲルの時間依存変形)

Load-bearing soft materials are necessary not only for tissue engineering but also for different bio-medical applications, drug delivery systems etc. Hydrogels are three-dimensional networks composed of cross-linked macromolecules and abundant water, belonged to soft & wet material. Based on some similarities to biological tissues, for example their soft and hydrated form, hydrogels have drawn great attention as synthetic equivalents for use in biological systems. However, the scope of hydrogel applications is often severely limited by their mechanical weakness and brittleness. The recently developed tough polyampholyte (PA) hydrogels, synthesized from random copolymerization of oppositely charged ionic monomers, have a great potentiality as a smart structural material for their multifarious unique properties like toughness, fatigue resistance, shape-memory effect, shock absorption capability, self-healing and self-recovery. But, for the realistic application of these tough hydrogels as a potential replacement of load-bearing soft materials, it is very essential to characterize the time-dependent deformation behavior of this material.

The aim of dissertation is to reveal the time dependent deformation behavior of PA hydrogels. The tough PA hydrogels P(NaSS-*co*-MPTC), synthesized by radical copolymerization from their monomers; sodium 4-vinyl-benzenesulfonate (NaSS) and (3-acryloyloxy)-trimethylammonium chloride (MPTC) in charge balanced composition, are chosen as model polyampholyte system. Different experimental techniques; tensile test, creep test, stress relaxation test, and dynamic oscillation frequency sweep test, have been used to study the time dependent deformation behavior. The structure factors in relating to the time dependent deformation behavior of PA hydrogels have been identified. Finally, a novel strategy for developing hydrogels with excellent rheological performance has been provided to implement hydrogel-based load-bearing soft materials practically in different branches of material science. This dissertation contains 7 chapters.

In **Chapter 1**, outline of the dissertation was discussed.

In **Chapter 2**, a general background study of PA macromolecular systems has been discussed. Although, PAs are charged polymeric system but there is a huge difference in their solution properties from common positively or negatively charged polyelectrolyte systems. They can form globule like conformations in aqueous solution due to fluctuation induced attractive intra-chain interaction. The globule conformations can be polarized by the surface electric field of substrates which can initiate adsorption process in wet environment.

In **Chapter 3**, creep deformation behavior of P(NaSS-*co*-MPTC) hydrogel has been investigated for its use as a load bearing soft material. It was observed that a neutral charge-balanced physical PA hydrogel can sustain <0.1 MPa stress for 36 hours. To improve creep deformation behavior, a lightly chemically cross-linked hydrogel was used. It was found that, this lightly cross-linked hydrogel can sustain 0.2 MPa stress for a long time. It suggests that, creep deformation behavior can be significantly improved by increasing chemical cross-linker density of PA hydrogel. A highly chemically cross-linked PA hydrogel showed complete resistance to creep flow. Furthermore, it has been revealed that the creep is due to the thermally activated rupture of the ionic bonds, having a bond life time of ~10^5s. These ionic bonds can be ascribed to the strong bonds of the system.

In **Chapter 4**, the effect of the ionic strength of the medium on the time dependent deformation behavior of PA hydrogels has been studied. For this purpose, rheological measurement, i.e., dynamic oscillation frequency sweep has been carried out in presence of different salt concentration. Strong frequency dependence was observed over a wide frequency range. The comparison of time-salt superposition was made with temperature perturbed rheological behavior of PA hydrogel. Weak ion bond and strong ion bond activation energy was calculated from this experiment. Studying rheological behavior reveals very slow relaxation mode, which was the most significant behavior in comparison with other hydrogels.

In **Chapter 5**, entanglements controlled toughening of a PA hydrogel has been discussed in terms of studying their time dependent deformation by changing molecular weight of the materials. For this purpose, radical polymerization has been done in presence of different initiator concentration. Then creep deformation and dynamic relaxation modulus has been measured in presence of different initiator concentration. It has been revealed that, with the decrease in chain length, terminal relaxation time of the PA hydrogel decreases. From this behavior, it has been concluded that, topological entanglements control terminal relaxation of PA hydrogels.

In **Chapter 6**, the effect of chemical structure of the ionic moiety on the time dependent deformation behavior has been investigated. For this purpose, the behaviors of P(NaSS-*co*-MPTC) hydrogel has been compared with another PA hydrogel P(NaSS-*co*-DMAEA-Q) synthesized from NaSS and acryloyloxethyltrimethylammonium chloride DMAEA-Q) by studying dynamic relaxation modulus with time at different temperature . It was found that, softening temperature is the main controlling parameter for their difference in the time dependent deformation behavior. P (NaSS-*co*-DMAEA-Q) has lower softening temperature (17^0C) in comparison with P(NaSS-*co*-MPTC) (48^0C). Due to this low softening temperature, P(NaSS-*co*-DMAEA-Q) hydrogel shows higher mobility in room temperature than P(NaSS-co-MPTC) hydrogel.

Finally in **Chapter 7**, a strategy to develop sticky and tough supramolecular hydrogels has been proposed. The idea is to use polymer that form abundant of dynamic bonds, such as ionic bond, hydrogen bond, etc. The dynamic bonds have several effects on the mechanical properties of the gel. They will serve as sacrificial bonds and enhance the toughness of the gel by dissipating energy at deformation. As a result, such kind of hydrogels will exhibit excellent time dependent deformation behavior with a high toughness.