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Feature article

Role of mechanical factors in applications of stimuli-responsive polymer gels – Status and prospects

Alexander V. Goponenko, Yuris A. Dzenis*

Department of Mechanical and Materials Engineering, Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, NE 68588-0526, USA

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ABSTRACT

Due to their unique characteristics such as multifold change of volume in response to minute change in the environment, resemblance of soft biological tissues, ability to operate in wet environments, and chemical tailorability, stimuli-responsive gels represent a versatile and very promising class of materials for sensors, muscle-type actuators, biomedical applications, and autonomous intelligent structures. Success of these materials in practical applications largely depends on their ability to fulfill application-specific mechanical requirements. This article provides an overview of recent application-driven development of covalent polymer gels with special emphasis on the relevant mechanical factors and properties. A short account of mechanisms of gel swelling and mechanical characteristics of importance to stimuli-responsive gels is presented. The review highlights major barriers for wider application of these materials and discusses latest advances and potential future directions toward overcoming these barriers, including interpenetrating networks, homogeneous networks, nanocomposites, and nano-filamentary gels.

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* Corresponding author.
E-mail address: ydzenis@unl.edu (Y.A. Dzenis).

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Abbreviations

4VP	4-vinylpyridine
AAc	acrylic acid
AAm	acrylamide
AFP	α-fetoprotein (tumor-specific marker glycoprotein)
AMERAH	arm-wrestling match between an EAP actuated robotic arm and a human
AMP	adenosine 5′-monophosphate
AMPS	2-acrylamido-2′-methylpropanesulfonic acid
APTAC	(3-acrylamidopropyl)trimethylammonium chloride
ATP	adenosine triphosphate
BZ	Belousov–Zhabotinsky (reaction)
CMP	cytidine 5′-monophosphate
ConA	concanavalin A
DETA	diethylene triamide
DMAEM	2-dimethylamino ethyl methacrylate
DMAPAAm	*N*-(3-dimethylamino propyl) acrylamide
EAP	electroactive polymer
GMP	guanosine 5′-monophosphate
GOx	glucose oxidase
HEMA	2-hydroxyethyl methacrylate
iOA	iso-octyl acrylate
LCST	low critical solution temperature
MAAc	methacrylic acid
NEAAm	*N*-ethylacrylamide
NIPAM	*N*-isopropylacrylamide
P4VP	poly(4-vinylpyridine)
PAAc	poly(acrylic acid)
PAAm	poly(acrylamide)
PAMPS	poly(2-Acrylamido-2-methylpropanesulfonic acid)
PAN	poly(acrylonitrile)
PCCA	polymerized colloidal crystalline arrays
PDGI	poly(dodecyl glyceryl itaconate)
PEDOT	poly(3,4-ethylenedioxythiophene)
PEG	poly(ethylene glycol)
PMAAc	poly(methacrylic acid)
PMMA	poly(methyl methacrylate)
PNIPAM	poly(*N*-isopropylacrylamide)
PSS	poly(styrenesulfonate)
PVA	poly(vinyl alcohol)
QCM	quartz crystal microbalance
$Ru(bpy)_3$	ruthenium tris(2,2′-bipyridine)
SRG	stimuli-responsive gel
TE	tissue engineering
TFMPA	trifluoromethyl propenoic acid
UCST	upper critical solution temperature
UMP	uridine 5′-monophosphate
VI	vinyl imidazole
α-CD	α-cyclodextrin

1. Introduction

Covalent polymer gels are crosslinked polymer networks swollen by a solvent. They consist mostly of liquid, but behave like a solid due to three-dimensional crosslinked macromolecular network. Their properties can be varied in a broad range because a wide variety of polymers can form 3D gel networks, while density and structure of the cross-links allow additional degree of control. Large inner volume of gels, accessible for storage, is used in many applications such as superabsorbents, drug delivery carriers, and batteries. The gels are particularly attractive for biomedical applications, such as tissue engineering, owing to their resemblance of soft biological tissues and their operation in wet environments. In fundamental research, gels proved to be useful for understanding polymer thermodynamics and rubber elasticity.

Gels are known to change their volume in response to alteration of the environmental parameters. The change in volume results from the absorption or release of the fluid and may reach hundreds and even thousands percent. Often it is accompanied by considerable swelling force. Gels that demonstrate substantial (and often abrupt) volume change in response to small environmental change and gels that are selective to a specific stimulus are called stimuli-responsive or responsive gels (SRGs).

One of the first experimental observations of reversible and profound volume change in gels was reported by Kuhn and Katchalsky who also noted the resemblance of such gels to muscles [1–3]. Almost at the same time, Flory and Rehner developed a theory of swelling of polymer networks [4–6] that was found to be capable of explaining gel response to stimuli.

The development of responsive gels accelerated in the last quarter of the twentieth century. Tanaka demonstrated abrupt gel volume change caused by small change of environmental conditions, which was named volume phase transition [7]. He created gels responsive to different stimuli, such as solvent composition [7], temperature [7], metal ions [8], electric field [9], and light [10]. Tanaka also advanced the theory of equilibrium swelling of responsive gels and developed a theory of gel swelling kinetics [11–14]. By the end of the twentieth century, responsive gels became an important class of functional materials. The number of applications of SRGs, as well as the amount of research in this field, is continually increasing. Several applications have already been commercialized.

To ensure further success of SRGs in a broad range of practical application, it is becoming critical to better understand and control their mechanical properties. This report describes the current state in the assessment and control of properties of gels relevant to their mechanical behavior, discusses challenges and their proposed or potential solutions, and identifies and reviews new directions.

The scope of this report is limited to covalent stimuli-responsive polymer gels. Other relevant materials, including self-assembled gels and stimuli-responsive and shape-memory materials that are not gel-based are not covered. Nevertheless, it still would be