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New type of gel polyelectrolytes based on selected methacrylates and their characteristics. Part I. Copolymers with (3-(trimethoxysilyl) propyl methacrylate)

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ABSTRACT

An extensive study of various properties of gel electrolyte systems based on 2-ethoxyethyl methacrylate (EOEMA) was conducted with several experimental techniques in order to clarify the influence of varying composition of the samples. The addition of 3-(trimethoxysilyl) propyl methacrylate (SPMA), used here with the aim of decreasing flammability of the ether-oxygen rich system, was investigated in terms of resulting mechanical, thermal and electrochemical properties. Furthermore, changes in these properties based on the use of different cross-linker monomers, salt and its solvent were studied.

1. Introduction

On-going search for new types of lithium battery systems is triggered by the ever increasing demands on their electrochemical performance combined with many practical aspects such as low weight, high efficiency, fast recharge or high capacity [1]. At the same time, operational safety of the batteries is of paramount importance including high requirements on a stable charge–discharge process with no danger of overheating, prevention of electrolyte leakage and fire safety. Decreased flammability of electrolyte materials has been approached by choice of fire-retarding additives and components such as fluorinated, phosphazene- or sulphone-based monomers, fillers or ionic-liquids [2–14], while electrolyte leakage has been solved by replacing liquid electrolytes by polymer-based materials [15,16]. Wide variety of polymer materials have been used and tested with addition of many salts and additives, as well as various preparation techniques. Several reviews as well as useful classifications of existing electrolyte systems have been published [17–24].

Evolved from the classical polymer electrolytes based on lithium salt dissolved in polyethylene oxide (PEO), are the so called gel polymer electrolytes, incorporating a salt-containing liquid solvent in a polymer matrix [25]. Besides the renowned PEO, many other polymer systems have been investigated such as poly (acrylonitrile) (PAN), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF) or poly(methyl methacrylate) (PMMA), both by themselves, in combination as blended systems or polymerized into copolymers [15].

Our approach, already described in an earlier publication [26] represents one possibility toward functional systems, where gels based on 2-ethoxyethyl methacrylate (EOEMA) are prepared in combination with various crosslinking ethylene glycol-based dimethacrylates. These are basically the well-studied “glymes or PEGs” [27,28] with methacrylate group attached to each end of the short chains to enable two-sided chemical attachment to the main polymer thus creating a cross-linked network structure. Additionally, trimethoxysilyl groups are introduced in the form of 3-(trimethoxysilyl) propyl methacrylate (SPMA) and added as side-groups to the main chains, in an effort to decrease flammability of the system. Addition of SPMA was made based on the fact that introduction of ether bonded oxygens in the ethylene glycol groups although electrochemically suitable,

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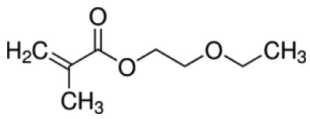
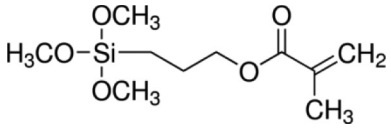
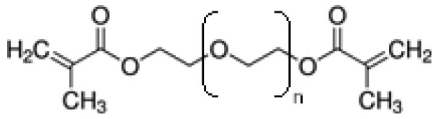
Table 1
Overview of components used in the samples.

Monomers	EOEMA (100–60 mol%)	
	SPMA (0–40 mol%)	
Cross-linkers (0.5 mol%)	EDMA (n = 0) DEGDMA (n = 1) TEGDMA (n = 2) TTEGDMA (n = 3)	
Solvents (30 wt.%)	PC EC/DMC (1:1 vol.)	
Salts (1 M)	$LiClO_4$ $NaClO_4$ $LiBF_4$	

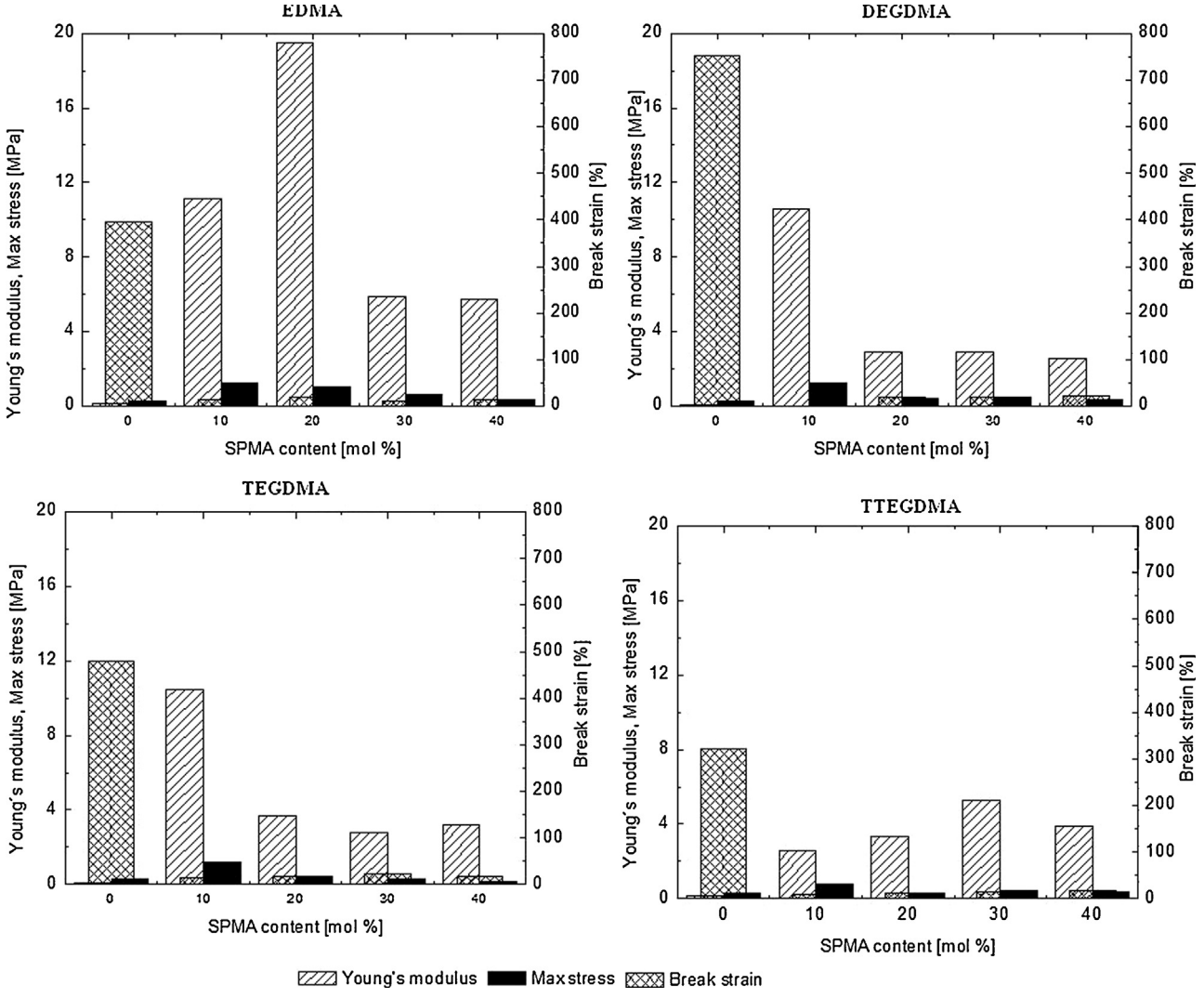


Fig. 1. Dependence of mechanical properties on the use of cross-linker shown for the five measured SPMA concentrations.