



Transient materials from thermally-sensitive polycarbonates and polycarbonate nanocomposites



Katherine L. Camera ^a, Brandon Wenning ^a, Amit Lal ^b, Christopher K. Ober ^{c,*}

^a Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

^b Department of Electrical and Computer Engineering, Cornell University, Ithaca, NY 14853, USA

^c Department of Materials Science and Engineering, Cornell University, 310 Bard Hall, Ithaca, NY 14853, USA

ARTICLE INFO

Article history:

Received 12 June 2016

Received in revised form

10 August 2016

Accepted 12 August 2016

Available online 15 August 2016

Keywords:

Polycarbonates

Thermal degradation

Acid catalysis

Young's modulus

OMMT

ABSTRACT

Transient materials, or materials with designed short lifetimes, are of great interest in many fields of research. This work describes the development of polycarbonates as a thermally-triggered vaporizable substrate platform. Good mechanical properties over operational temperature ranges in combination with fast and clean decomposition at slightly higher temperatures create an effective transient substrate. Therefore, characterization of the thermal and mechanical properties of vaporizable polycarbonates (VPC) and their composites are indispensable for creating such materials systems. A tailor-made VPC and its blends with a commercially available poly(propylene carbonate) were investigated. Both polycarbonates have acid sensitive backbones; therefore, when combined with an acid source, catalyzed decomposition was observed within minutes, achieving a range of decomposition temperatures between 160 °C and 250 °C. Polymer with organo-modified montmorillonite nanocomposites were investigated to provide structural support. These nanocomposites resulted in Young's moduli ranging from 4 MPa to ~2 GPa. Their tunable nature allows for designer control over the substrate's properties based on application needs.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Transient polymeric materials are designed with a short or temporary lifetime and are attracting much interest in various fields of research. A controlled or triggerable loss of the physical and/or functional properties of these materials has found use in applications including fabrication of nano- or microchannels in fluidics devices [1–5], controlled drug release [6–10], and transient electronics [11–17]. In particular, the concept of a fully transient electronic device has gained momentum for technological advancement and potential applications where collection, recovery, or disposal of the material may be difficult. To create an effective transient electronic device, it must be accompanied by transient substrates for support, and different applications will require specifically tailored properties (e.g. chemical, mechanical, and physical) from these transient materials. Recent work has shown that use of biodegradable polymers and electronic components can be combined to achieve a fully degradable implant for biomedical

devices. Transient electronic components have been developed and circuits were tested on multiple biodegradable substrates including poly(lactic-co-glycolic acid), poly(lactic acid), poly(caprolactone), rice paper, and silk, where water and phosphate buffer solution are used to dissolve the substrate and electronic components [11,13,14,16]. Another study by Acar et al. showed that poly(vinyl alcohol) composites with glucose and sucrose could be fabricated into transient substrates with a triggered degradation occurring in the presence of water [15]. However, solution triggered degradation of these polymers limits their applications. Moore and co-workers have used metastable cyclic poly(phthalaldehyde) (cPPA) as a UV-sensitive substrate material for printed electronics [12]. When cPPA is combined with a photoacid generator (PAG) and cast into a substrate, UV light can be used to activate the PAG, which releases acid, which in turn causes chain unzipping (degradation) of cPPA. Upon continuous exposure to UV light there was destruction of a free standing transistor array on cPPA, leaving behind a slight residue. Park et al. also showed that cPPA can be thermally triggered to degrade in the presence of acid, where heat is used to release encapsulated acid that degrades both the cPPA and the electronic components [17]. However, in both cases some material remains.

* Corresponding author.

E-mail address: cko3@cornell.edu (C.K. Ober).

In this paper, we report a thermally-sensitive polycarbonate system as a vaporizable transient substrate with tunable thermal and mechanical properties. Polycarbonates, like the polyphthalaldehydes, are acid sensitive, allowing for catalyzed decomposition in the presence of acid and heat. Polycarbonates can be designed to degrade into volatile compounds, leaving no substantial residue behind upon disintegration, allowing for effective substrate transience. Previous work in the field of lithography has shown effective vaporization of polycarbonates when subject to acid and heat [18–20]. Applying these techniques, thin and thick film substrates containing acid can be heated leading to clean and fast decomposition. Two polycarbonates, poly(propylene carbonate) and a synthesized vaporizable polycarbonate (VPC) were investigated separately, and in a blend of the two as thermally-sensitive substrate materials. Studies of the thermal degradation of PPC indicate that the decomposition of PPC occurs via chain unzipping and chain scission, producing volatile products of cyclic propylene carbonate and 1,2-propanediol, and that the addition of certain PAGs can significantly reduce the degradation temperature [21,22]. The thermal degradation products of polycarbonates, similar to the VPC synthesized in this report, were studied and found to also be volatile [23]. In this study we confirm the use of PAGs for acid catalyzed degradation and introduce a new acid source, a thermal acid generator (TAG), which also effectively catalyzes degradation of these polycarbonates and their combination. The use of multiple acid sources allows for tunable degradation temperatures. Lowering the degradation temperature, for example, lowers the amount of energy needed to vaporize a polymer, making transience more facile.

Thermally-triggered transience is not the only important property needed in a substrate. To be an effective substrate or packaging for transient electronics, the material must have sufficient mechanical strength in order to allow the device to function during its operational lifetime. Different applications require various mechanical properties in substrates. Therefore, the modulus, toughness, and tensile strength of the polycarbonates were assessed and nanocomposites with an organo-modified montmorillonite (OMMT) (clay) were investigated as a reinforcing phase to give a range of mechanical properties. The ability to behave as a stable substrate during process and operating conditions, possessing tunable thermal and mechanical properties, and employ of a thermal trigger for substrate degradation allow this polycarbonate system to achieve criteria necessary to be an effective transient substrate.

2. Experimental

2.1. Materials

Reagents for the synthesis of VPC were purchased from Sigma Aldrich and used without purification, except for tetrahydrofuran, which was dried over calcium hydride before use. Triphenylsulfonium triflate was used as photoacid generator 1 (PAG1) and was purchased from Sigma Aldrich and used without further purification, and P-cumenyl(p-tolyl)iodonium tetrakis(pentafluorophenyl) borate was used as PAG2 and was purchased from Boc Sciences and used without further purification. 2,4,5-trichlorobenzenesulfonic acid was used as a thermal acid generator (TAG) and was purchased from Sigma Aldrich and used without further purification. Organo-modified montmorillonite (OMMT) 20A was purchased from Southern Clay Products. Poly(propylene carbonate) (PPC) at 130 kDa was supplied by Novomer.

2.2. Characterization

Molecular weight of VPC was determined using gel permeation

chromatography (GPC) using a Waters Ambient Temperature GPC with THF as the solvent and measured against a polystyrene standard. The decomposition temperature (T_d) was measured on a TA Instruments Q500 Thermogravimetric Analyzer (TGA) with a 10 °C/min ramp rate. The thermal decomposition products from the polymers were analyzed using gas chromatography mass spectrometry (GC-MS) with an Agilent 6890 GC equipped with an autosampler and a JEOL double-focusing sector MS. High resolution images were taken using a Tescan-Mira3 scanning electron microscope (SEM). Young's modulus for samples was measured on TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) using a constant force ramp of 1 N/min at room temperature. Film thickness was measured using a P10 profilometer.

2.3. Synthesis of VPC

The custom-made vaporizable polycarbonate (VPC) was synthesized according to previous procedures [19,23], and the final structure is depicted in Fig. 1 (along with structures of PPC, PAG1, PAG2, and TAG). VPC had a molecular weight of 3.5 kDa.

2.4. Film formation

Solutions of VPC, VPC + PAG, and VPC + TAG were made by dissolving 5 wt% of VPC in dichloromethane (DCM) and adding in 5 wt%, with respect to solid content, of either PAG1 or TAG (or neither in the case of the native VPC solution). The solution was stirred vigorously to ensure complete dissolution and dispersion in DCM. The stirred solution was then dropped casted onto a silicon wafer and spun at a rate of 2000 rpms for 60 s with a ramp rate of 1000 rpms/s. The spin coated film was then subjected to a post apply bake for 60 s at 120 °C.

Solutions of PPC, PPC + PAG2, and PPC + TAG were made by dissolving 10 wt% of PPC in DCM and adding in 5 wt%, with respect to solid content, of either PAG2 or TAG (or neither in the case of the

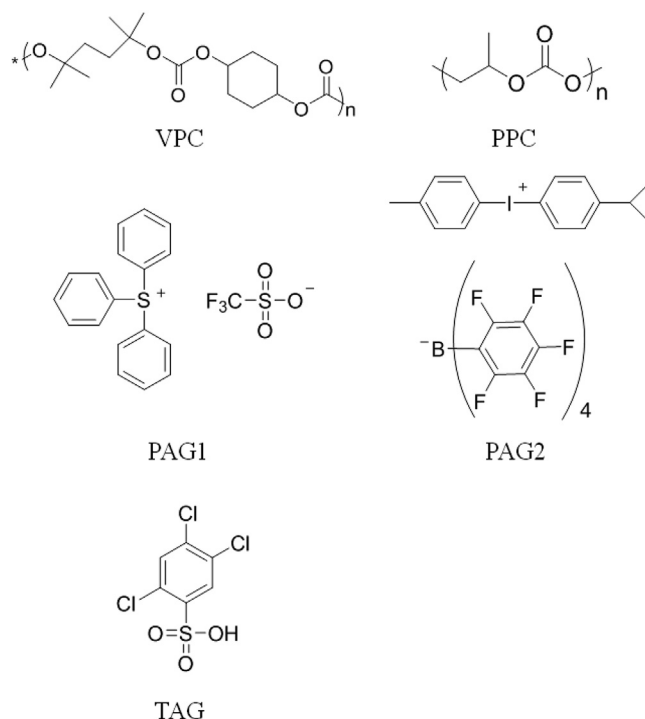


Fig. 1. Chemical Structures of compounds used in this study.

Download English Version:

<https://daneshyari.com/en/article/5178889>

Download Persian Version:

<https://daneshyari.com/article/5178889>

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