

Thermal switching between solid- and liquid-like behavior of dispersed semi-crystalline telechelics and nanohybrids tailored for temperature-induced healing of polyethylene cracks



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HIGHLIGHTS

- Temperature-induced healing of cracks in polyethylene surface.
- Thermal switching of dispersed oligo(cyclooctenes) to liquid-like behavior.
- Crack sealing by migration of healing agent.

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ABSTRACT

Thermal switching between solid- and liquid-like behavior of polyethylene additives such as semi-crystalline telechelics and their corresponding nanohybrids, both of which are uniformly dispersed as nanophases within the high density polyethylene (HDPE) matrix, enables temperature-induced crack healing of polyethylene by interfacial self-assembly. Key intermediate is oligo(cyclooctene) with different end groups having molar mass of 2000 g mol⁻¹ and melting at 60 °C prepared by ring-opening metathesis polymerization of cyclooctene in the presence of olefinic chain transfer agents (CTA). Whereas 1-octene as CTA leads to non-functionalized oligo (cyclooctene) (POC) the use of 1-undecylenic acid leads to monocarboxylic-acid-terminated oligo(cyclooctene) (cPOC). Neutralization of cPOC with diethyl zinc yields nanohybrids (iPOC) having a semi-crystalline POC shell and a zinc carboxylate core. Opposite to high molar mass POC, owing to their much lower melt viscosity and excellent compatibility with polyethylene, all oligo(cyclooctenes) are uniformly dispersed in polyethylene melts during extrusion forming crystalline nanophases which strongly adhere to the HDPE matrix. Upon annealing at temperatures above 60 °C but well below the HDPE melting temperature, they are rendered liquid and mobile within the solid HDPE matrix. As verified by microscopy, driven by pressure build-up due to their volume expansion resulting from POC melting they migrate to polyethylene cracks and heal them by means of interfacial self-assembly and cocrystallization upon cooling.

1. Introduction

Inspired by living bio systems and their autonomous self-healing response to injuries, it is an important challenge in polymer development to equip plastics with either autonomous or stimulus-triggered self-healing capabilities. This is particularly beneficial with respect to improving their damage tolerance, reliability, safety and extending their product life time while simultaneously reducing the maintenance efforts. In addition to restoring structural integrity in the case of

mechanical failure and scratching, self-healing can prevent premature failure by healing of microcracks which are a prerequisite for fatal crack propagation. Several strategies, among them many exploiting nanostructure formation, have emerged targeting self-healing of polymers [1–11]. Prominent approaches toward chemical self-healing polymers entail release of healing agents such as monomers or adhesives either by crack-induced rupture of micro and nano capsules and tubes [12–15] or by autonomous release from three-dimensional microvascular systems, respectively [16]. In 2012 microencapsulated dicyclopentadiene

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monomer together with a solid phase Grubbs's catalyst was incorporated into a polyethylene matrix in order to achieve self-healing [17]. In view of the long life span of HDPE pipes this self-healing method would require excellent barrier properties of the capsule shells which should resist high shear forces during pipe extrusion and must prevent highly undesirable emission of dicyclopentadiene for a prolonged period of time. No healing agent addition is required when exploiting self-healing by stimulus-responsive reversible polymer cross-linking and supramolecular assembly [18–21], shape memory effect [19,22] or nanoparticle migration deposition at interfaces [1,23,24]. By means of a microencapsulation and nanoparticle deposition technique, termed “repair-and-go”, the mechanical properties of damaged polymer films are restored by interfacial self-assembly of surface functionalized silica nanoparticles. They are released from polymer-stabilized emulsion droplets, migrate through the polymer matrix and are deposited at the interface of damaged regions [25]. Pioneered by Giannelis, surface-modified nanoparticles can be tailored to exhibit liquid-like behavior enabling facile nanoparticle dispersion and assembly of a wide variety of functional nanostructures and nanostructured organic/inorganic hybrid materials [26–30]. Among polymeric materials nanostructured copolymers of ethylene with methacrylic acid and their corresponding ionomers, prepared by partially neutralizing the pendant carboxyl groups, are unique with respect to their efficient autonomous self-repair upon ballistic impact [31–37]. Immediately after a bullet punctures the polymer, the resulting bullet hole is thermomechanically sealed as the impact energy is sufficient to locally melt down the polymer which flows and entangles while the ionomer crosslinks rearrange and assure dimensional stability and mechanical recovery. Most attempts to expand this intriguing concept to other ionomers have failed. Moreover, such materials and their blends are not suited as healing agents of polyethylene pipes. Albeit remarkable progress has been made in self-healing of polar thermoplastics and thermosets, much less is known with respect to self-healing of non-polar polyolefin thermoplastics like polyethylene and polypropylene. As high molar mass semi-crystalline hydrocarbons they are incompatible with most conventional healing agents and poorly adhere to polar compounds. Moreover, advanced catalyst systems for olefin polymerization are exceptionally active but readily poisoned by trace amounts of polar compounds. Hence the functionalization of polyolefins requires separate post-polymerization steps. For instance, grafting of polypropylene with maleic anhydride followed by neutralizing carboxyl groups with zinc oxide afforded nanostructured polypropylene ionomers as self-healing shape memory materials [38]. Coumarin-functionalized polyolefins with light induced reversible crosslinking were claimed as self-healing semiconductor packaging materials [39]. In view of polyolefin applications it is highly desirable to develop polyolefin healing agents as additives which are added during processing and do not require polyolefin modification. Particularly, healing agents are in demand which heal cracks and prevent slow crack growth which is considered to be one of the most common failure modes in HDPE pressure pipe applications [40]. Crack formation can account for premature failure resulting from poor stress crack resistance and also enables intrusion of contaminants such as micro-organisms and moisture which further shorten the product life time of HDPE pipes. Hence the research focus is placed upon crack healing as preventive method rather than on healing damaged pipes after complete mechanical failure has occurred. Herein we report on tailoring thermoresponsive semi-crystalline oligo(cyclooctenes) with different end groups as healing agents and new polyethylene additives which are solid at room temperature and are rendered liquid by annealing above their melting temperature but well below the melting temperature of the HDPE matrix. Inspired by self-healing of plants driven by turgor pressure, we exploit volume and pressure changes associated with thermal switching from crystalline to liquid state to enable migration of semi-crystalline oligo(cyclooctene)-based healing agents to polyethylene crack interfaces resulting in crack sealing by means of interfacial self-assembly and cocrystallization with

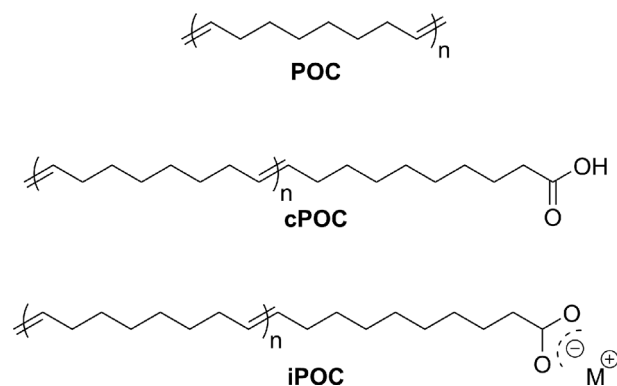


Fig. 1. Semi-crystalline poly(cyclooctene) (POC) and the corresponding carboxylic-acid-terminated oligo(cyclooctene) telechelic (cPOC) and nanohybrid (iPOC), both of which serve as healing agents and additives for HDPE.

polyethylene. The influences of telechelics' molecular architectures, functionalities, and nanohybrid formation on morphology development, healing agent migration, HDPE mechanical properties, and crack healing are examined.

2. Results and discussion

Non-functionalized oligo(cyclooctene) (POC, Fig. 1) as well as semi-crystalline carboxylic-acid-terminated oligo(cyclooctene) (cPOC, Fig. 1), both of which having molar mass around 2000 g mol^{-1} , were the key intermediates for tailoring healing agents as new polyethylene additives. They enable thermal switching between liquid- and solid-like behavior by annealing their blends with high density polyethylene (HDPE) above their melting temperature of $60 \text{ }^\circ\text{C}$ but well below the polyethylene melting temperature of $135 \text{ }^\circ\text{C}$. It is well known that carboxyl-terminated telechelics dimerize via hydrogen bridging of carboxyl end groups [41,42]. The corresponding nanohybrids containing an inorganic nanometer-scaled core and semi-crystalline oligo(cyclooctene) shell (iPOC, Fig. 1) are readily available via ionomer formation of cPOC. High molar mass non-functionalized POC was reported to form compatibilized blends with high density polyethylene (HDPE), owing to excellent interfacial adhesion via POC cocrystallization with HDPE [43–45]. However, blending HDPE with high molar mass POC yields micron-sized POC phases dispersed within the HDPE matrix and does not markedly improve crack healing of HDPE. Moreover, saturated oligoethylene wax is not suited as additives for two reasons. Firstly, their melting temperatures are higher and close that of the HDPE matrix which would melt before the additive is rendered liquid. Secondly, the addition of extremely low molar mass oligoethylene wax or even stearic acid would cause emission and odor problems intolerable in polyethylene processing.

Typically, following procedures reported by Hillmyer and coworkers for the preparation of dicarboxylic-acid-terminated POC [46,47], cPOC was readily tailored by catalytic ring-opening metathesis polymerization (ROMP) of cyclooctene (CO) in the presence of the 2nd generation Grubbs catalysts (G2) and olefinic carboxylic acids as chain transfer agent (CTA). Herein cross-metathesis with 1-undecylenic acid as CTA enabled both molar mass and end group control (see Scheme 1). The cyclooctene/undecylenic acid (CO/CTA) molar ratio (5–35) governed both molar mass ($2300\text{--}11400 \text{ g mol}^{-1}$) and melting temperature ($57\text{--}60 \text{ }^\circ\text{C}$) which primarily depended upon the cis/trans ratio unaffected by the CO/CTA molar ratio. The corresponding ^1H NMR spectrum (Figure S1) is displayed in supplementary information.

As displayed in Scheme 2 cyclooctene ROMP in the presence of 1-undecylenic acid can afford different end groups including monofunctional cPOC as well as difunctional di-cPOC together with different olefin end groups resulting from isomerization of the vinyl end groups. It is also known that POC macrocycles are formed as by-products

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