A novel elastomer/liquid crystal polymer nanocomposite created in situ from controlled radical graft-polymerization†

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We present the original design and properties of a novel, all-polymer hierarchical composite comprising an elastomer and a fluorinated liquid crystal polymer. The material follows from the phase separation between the two highly incompatible components, occurring in situ during the controlled radical graft-polymerization of the liquid crystal monomer onto functionalized elastomeric chains. We demonstrate that the composite remarkably combines the mechanical properties, static and dynamic, of both an elastomer and a semi-crystalline polymer. We thereby illustrate how the careful choice of a graft can provide a simple rubbery material with original and antonymic functionalities. Here, the temperature-sensitive liquid crystal polymeric domains act as hard particulate fillers under their fusion temperature and liquid softening inclusions above, with fast reversible transitions from one state to another. A variety of composites combining physico-chemical features difficult to marry otherwise may be designed following this simple method.

Introduction

Microphase separation of highly incompatible fluorinated liquid crystal polymer (LCP) hard inclusions occurs upon their in situ graft-polymerization onto functionalized elastomeric poly(butadiene) (PBD) chains.1,2 The process leads to a novel composite comprising an elastomer and a liquid crystal polymer, organized at several length scales, from nano- to microscopic, as sketched in Fig. 1. The reaction is carried out via a nitroxyl-mediated controlled radical polymerization (NM-CRP).3,4 The technique allows control of the grafting-from polymerization of the functional monomer, as well as the quality of phase separation in terms of domain size, homogeneity, etc, advantages that conventional free radical polymerization processes have never offered so far. High-impact poly(styrene) may be one of the most famous (if not, the unique) example in day-to-day life, of the use at an industrial level of a conventional free radical polymerization process effectively producing graft copolymers. However, the extent of control achieved over the microphase separation occurring upon polymerization, remains poor. In practise, conventional radical processes offer little control over the grafting reaction in terms of chain growth, molecular weight, polydispersity or overall grafted content. As a result, phase separation upon reaction is not well controlled and occurs over a wide range of domain sizes, from nano- to macroscopic, which often impacts the materials’ performance. Reactive coextrusion (which effectively produces graft-copolymers as well) recently showed a remarkable potential for designing complex phases with antonymic or complementary mechanical properties. The challenge of creating from the start and in situ at the synthesis step, a composite using graft copolymerization, was then renewed.

The NM-CRP process is applied on a pure bulky material, in the present case, an elastomeric film simply immersed directly into the reactive monomer. In the end, a grafted composite film is recovered. In practise, as will be shown, the technique provides an apparent linearity between the reaction time and the amount of liquid crystal polymer grafted. The extent of modification achieved inside the film is thus very easy to tune. This reliable grafting process constitutes a convenient way to gain easy access to complex composites with remarkable properties, which we will focus on. We detail the hierarchical structure from nano- to microscopic scales, of this novel smectic-B LCP/elastomer composite. The mechanical properties of both an elastomer and a semi-crystalline

**Fig. 1 Schematics of an elastomer-graft-LCP in situ composite at different length scales. (a) 1 μm: continuous PBD matrix filled with 10–100 nm sized strongly phase separated LCP domains. (b) 0.2 μm: a LCP inclusion chemically bound to PBD chains, with chemical/topological crosslinks in the elastomer. (c) 50 nm: a crystalline domain with lamellar order between neighbouring chains, separated by 32.8 Å, and a 5.7 Å distance between consecutive fluorine pendant groups on a LCP chain.**