



Self-assembly of oil microdroplets at the interface in co-continuous polymer blends



Corinne Jegat^{a,*}, Nick Virgilio^b, Basil D. Favis^b

^a Université de Lyon, Université de Saint-Etienne, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, F-42023 Saint-Etienne, France

^b CREPEC, Department of Chemical Engineering, École Polytechnique de Montréal, Montréal, Québec H3C3A7, Canada

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ABSTRACT

The distribution of hazelnut oil (HNO) in a melt-processed co-continuous blend of poly(ϵ -caprolactone) (PCL) and polyethylene oxide (PEO) shows the formation of a dense array of self-assembled HNO microdroplets at the PCL/PEO interface, as revealed by electron and Fourier transform infrared (FTIR) microscopy. The microstructure formation is dominated by thermodynamics and corresponds to a partial wetting type of morphology, as predicted by a set of three spreading coefficients, where all three phases meet along a common line of contact. The effects of oil concentration (2.5–10%) on the microdroplets size is investigated at two mixing temperatures, 100 and 150 °C. Interestingly, the interfacial microdroplets do not perturb the co-continuous morphology, are particularly stable, and demonstrate almost no size dependence on oil concentration. This work opens up new perspectives for material design comprising active agent transfers at interfaces.

1. Introduction

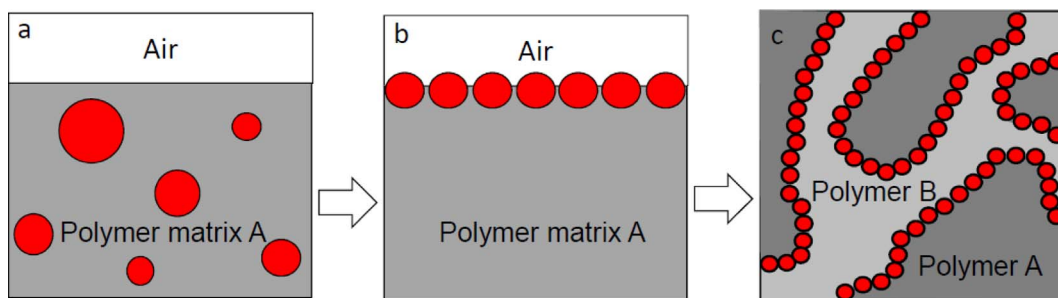
The scientific interest for vegetable oils in the field of polymeric materials is growing because these oils constitute polymer precursors widely available in nature [1] and can also provide, in a rough state and without chemical modification, excellent blending partners for renewable composite polymers prepared in the melt state as plasticizers [2,5], toughening agents [3,4] or coupling agents between filler and polymer [6].

Besides these interesting properties, vegetable oils can be used for their biological properties (*anti*-mite, anti-fungal, insect repellent, protective, moisturizing, anti-oxidant, anti-septic, etc.), as essential oils possess the advantages of being much more easily available and less volatile. When the oil is not bioactive, it can instead be used as the excipient of a lipophilic active ingredient [7–9]. The microencapsulation of a lipophilic active ingredient is a very common formulation for controlled release systems in the pharmaceutical and food industries [10,11].

Hot melt extrusion is one of several microencapsulation technologies rapidly growing in importance because it allows a one-step manufacturing process, from the design to the shaping of controlled release materials, within a few minutes and without the use of solvents. The classical encapsulation techniques comprising successive steps such as emulsification, consolidation, separation, drying and then dispersion of microcapsules in a polymer matrix are shunted or avoided with extrusion processing. Other factors make this encapsulation technology attractive, such as effective mixing and the possibility to combine it with other production technologies such as injection molding or co-extrusion. The manufactured products are solids, can be shaped in various forms and sizes, and provide a high added value when used as scaffolds for biomedical applications (implants, patches). A wide range of polymers and

* Corresponding author.

E-mail address: corinne.jegat@univ-st-etienne.fr (C. Jegat).



Scheme 1. New design of a controlled release polymer system by self-assembly of droplets in melted matrix (a) Dispersed oil droplets in polymer matrix (b) Self-assembled oil droplets at the surface of a polymer matrix, (c) Self-assembled oily microreservoirs at the interface of a co-continuous polymer blend.

lipids, whether natural or synthetic, can be melt-processed because they exhibit thermoplastic characteristics and thermal stability in the required extrusion temperature range and become solids again at the extrusion processing outlet.

The incorporation of a vegetable oil at concentrations below 10% in a polymer matrix by extrusion processing often results in an immiscible binary blend with a typical matrix/dispersed droplets morphology. Beyond this concentration, a phase inversion is observed with lubrication of the polymer matrix [3,4,12,13]. This range of oil concentrations is suitable for controlled release systems, but the formulation of materials with a random dispersion of droplets (Scheme 1a) may be a downside because the release kinetics depends essentially on the nature of the polymer matrix, and entrapped droplets might be difficult or impossible to release. An interesting alternative would be to selectively locate the droplets near or at the surface of the polymer material (Scheme 1b). The controlled release of an active agent in the environment could be improved with such a structure because the release kinetics of the active agent could essentially depend on the microreservoirs' properties, and on its partition coefficient between the oily microreservoirs and the environment.

Co-continuous polymer blends prepared by melt processing are an interesting class of materials for such an application, since the selective extraction of one component following processing yields porous polymer monoliths with high specific surfaces [14,15]. Furthermore, Favis et al. have demonstrated in a series of articles that a third minor polymer phase can be selectively located at the interface by carefully tuning the viscoelastic and interfacial properties, and processing parameters [16]. Finally, this third phase can either form a uniform thin film at the interface [17] or an array of very dense droplets [18]. Some porous devices derived from co-continuous polymer blends were used for controlled drug release [19].

The main objective of this work is to selectively locate droplets of an immiscible oil phase at the interface of two polymers forming a co-continuous microstructure, by a 1-step melt-processing approach. The auto-assembly of oil droplets at the interface of co-continuous polymer blend could provide pathways of vectorization (Scheme 1c). To the best of our knowledge, controlling the selective localization of an oil phase in a co-continuous polymer blend prepared by melt processing has not been reported so far.

A ternary blend composed of hazelnut oil (HNO), poly(ϵ -caprolactone) (PCL) and polyethylene oxide (PEO) has been selected as a model system: HNO has a high thermal stability with a smoke point = 221 °C [20], while PEO and PCL are two commercially available thermoplastics with many biological and medical applications [21,22]. They are semi-crystalline polymers (crystallinity degree between 40 and 60%) with relatively close glass transitions (ca. -60 °C) and melting temperatures (c.a. 60 °C, among the lowest in common thermoplastics) [23,24]. As a consequence, processing can be performed at a low temperature. On the other hand, they have opposite affinities for water. PEO of high molar mass is one of the few water-soluble thermoplastics [25], while PCL is known as a lipophilic thermoplastic with very low water uptake [26].

2. Materials and methods

2.1. Materials

A commercial-grade poly(ϵ -caprolactone) (PCL, CAPA6800, $M_w \sim 80,000$ g·mol $^{-1}$) was provided by Perstorp (UK). Poly(ethylene oxide) (PEO) (POLYOX™ WSR-N10, $M_w \sim 100,000$ g·mol $^{-1}$) was supplied by Dow (USA). Hazelnut oil (HNO) was a food grade product supplied by Cauvin (France). Propan-2-ol used for selective extraction of oil, toluene used for extractions of PCL and oil, were purchased from Thermo Fischer Scientific.

2.2. Thermal analyses

Thermal stability analyses of the neat materials were carried out using a TGA Q500 instrument (TA Instruments) at a heating rate of 10 °C·min $^{-1}$ from 20 to 600 °C, under a nitrogen atmosphere, with a platinum pan filled with 15–20 mg of sample.

The glass transition, crystallization and melting temperatures were determined using a DSC Q1000 instrument (TA Instruments) equipped with a LNCS apparatus for cooling down to -150 °C. Two cycles of heating and cooling were performed at a rate of 10 °C·min $^{-1}$ from -90 to 150 °C, under helium flow (25 mL·min $^{-1}$) with 8–10 mg samples sealed in hermetic alumina pans. The thermal properties of the neat materials are reported in Table 1.

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