Polymer Degradation and Stability 134 (2016) 194–201

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Pluronic nanoparticles as anti-oxidant carriers for polymers

Nadka Tzankova Dintcheva [a, *], Giuliana Catalano [a], Rossella Arrigo [a], Elisabetta Morici [a], Giuseppe Cavallaro [b], Giuseppe Lazzara [b], Maurizio Bruno [c]

[a] Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128, Palermo, Italy
[b] Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, Parco d'Orleans II, 90128 Palermo, Italy
[c] Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Viale delle Scienze, Parco d'Orleans II, 90128, Palermo, Italy

ARTICLE INFO

Article history:
Received 28 July 2016
Accepted 13 October 2016
Available online 14 October 2016

Keywords:
PEO-PPO-PEO nanoparticles
Anti-oxidant carrier
Photo-oxidation

ABSTRACT

The immobilization of anti-oxidant stabilizers for polymers, particularly naturally occurring systems, can be considered a valuable route for preventing their migration, volatilization, thermo-degradation and decomposition at typical high processing temperatures, as well as for enhance their solubility in polymers. In this work, an innovative approach for the immobilization of naturally occurring stabilizer, through the encapsulation in copolymer nanoparticles, is proposed. Pluronic nanoparticles (PNPs), based on PEO-PPO-PEO, (PEO: poly (ethylene oxide); PPO: poly(propylene oxide)), without and with quercetin, Q, have been successfully formulated and the critical micellar conditions have been established through accurate analyses performed by micro-calorimetry, dynamic light scattering and fluorescence spectroscopy. PNPs have been introduced in poly(ethylene glycol), PEG, and the so formulated films have been subjected to artificial weathering, with the aim to probe the effectiveness of the use of PNPs as anti-oxidant carriers. The obtained results highlight that the proposed innovative route, consisting in the encapsulation of Q molecules in PNPs, allows to enhance the Q solubility in the polymer matrix, leading to the formulation of advanced materials with prolonged durability.

1. Introduction

Currently, water-soluble nonionic triblock copolymers such as PEO-PPO-PEO, (Pluronic, PEO: poly (ethylene oxide); PPO: poly(-propylene oxide)) are extensively used as a potential agent for drug delivery and gene therapy [1–3]. The formation of Pluronic spherical micelles through self-arrangement in water (PEO becomes hydrophilic, while, PPO is hydrophobic) depends on the solution temperature and pH, copolymer concentration and molecular architecture [4,5]. Besides, the micelles sizes and the phase behaviour of PEO-PPO-PEO solutions can be appropriately modified through the introduction of additives, for example an anionic surfactant such as sodium dodecyl sulfate [6]. Interestingly, considering PEO-PPO-PEO copolymer as excellent candidate for drugs encapsulation, among other naproxen, indomethacin, anesthetics and ibuprofen), its aggregation behaviour has been accurately investigated in order to establish the critical micellar temperature (CMT) and gelation temperature when drugs were added to Pluronic solution [7–9]. Furthermore, all studies agree that the micelles dimensions and the self-assembling process mainly depend on the copolymer solution concentration and environmental conditions [10]. If the concentration of PEO-PPO-PEO is high, the micelles can arrange themselves in micrometric cubic crystalline order and this results in a transition from liquid to solid phase [11,12].

The degradation of polymers and bio-polymers can be accurately prevented and/or slow downed through the introduction of appropriate stabilizing systems during polymer processing, as well known [13]. Unfortunately, the stabilizing systems, particularly the naturally occurring stabilizers, can migrate and volatilize at typical high temperatures during polymer processing [14,15]. The use of suitable carriers for thermo-sensible moieties can overcome the drawbacks related to their migration, volatilization, thermal-degradation and/or decomposition. For instance, the immobilization of stabilizing systems onto the surface of nanoparticles can be considered a suitable route to prevent the stabilizing migration and volatilization. Besides, in this way, the stabilizing systems are able to act preferentially at the interface between the host polymer matrix and the nanoparticles, i.e. in a critical zone for the beginning

* Corresponding author.
E-mail address: nadka.dintcheva@unipa.it (N.T. Dintcheva).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.10.008
0141-3910/

Table 1
Weight compositions of the aqueous solutions used for the preparation of formulated films.

Film	Weight composition of the solution (F127: PEG: H_2O)	Concentration of quercitin (mol L^{-1})
F127	5:0:95	–
F127/Q	5:0:95	$1.2 \cdot 10^{-4}$
PEG	0:12:88	–
PEG/Q	0:12:88	$8{,}06 \cdot 10^{-6}$
F127/PEG	5:50:45	–
F127/PEG/Q	5:50:45	$3{,}68 \cdot 10^{-4}$

of the polymer degradation [16]. The beneficial effect of the use of carbon nanotubes and clay minerals as anti-oxidant carriers, has been accurately investigated and the immobilization of different stabilizing systems such as hindered phenols [17,18], hindered amine light stabilizers [19] and naturally occurring stabilizing moieties [20–23] has been probed. The polymer based systems containing the immobilized stabilizers showed extended thermo- and photo-oxidation resistance with respect to the systems containing free added stabilizers.

In this work, an innovative approach for the immobilization of naturally occurring stabilizer is proposed. Particularly, PEO-PPO-PEO micelles have been exploited to encapsulate a suitable anti-oxidant for biopolymers, such as quercetin (Q). Besides, the micelles without and with Q have been introduced in PEG and the critical solution conditions for polymer nanoparticles (PNPs) formation have been accurately investigated. As well known, Q shows limited solubility in polymers and bio-polymers [24], and this drawback can be overcome through its encapsulation in PNPs, as proposed in this work. Accurate experimental analyses, through micro-calorimetry, dynamic light scattering and fluorescence spectroscopy, confirm that the PNPs formation and sizes are not influenced by the Q presence. Moreover, the PEG-based films containing PNPs have been formulated and subjected to accelerated weathering in order to verify the beneficial effect of Q encapsulation on the photo-oxidation behaviour.

2. Experimental part

2.1. Materials

The materials used in this work were:

- Poly(ethylene glycol), PEG, with average molecular weight Mn = 20.000, melting point Tm = 63–66 °C has been supplied by Sigma-Aldrich and used as received.
- Pluronic® F127, F127, is a triblock copolymer PEO-PPO-PEO, where PEO is a poly (ethylene oxide); and PPO is a poly(-propylene oxide), supplied by Sigma-Aldrich.
- Quercetin, Q, has been supplied by Sigma-Aldrich and used as received. The Q has molecular weight 302.24 g/mol.

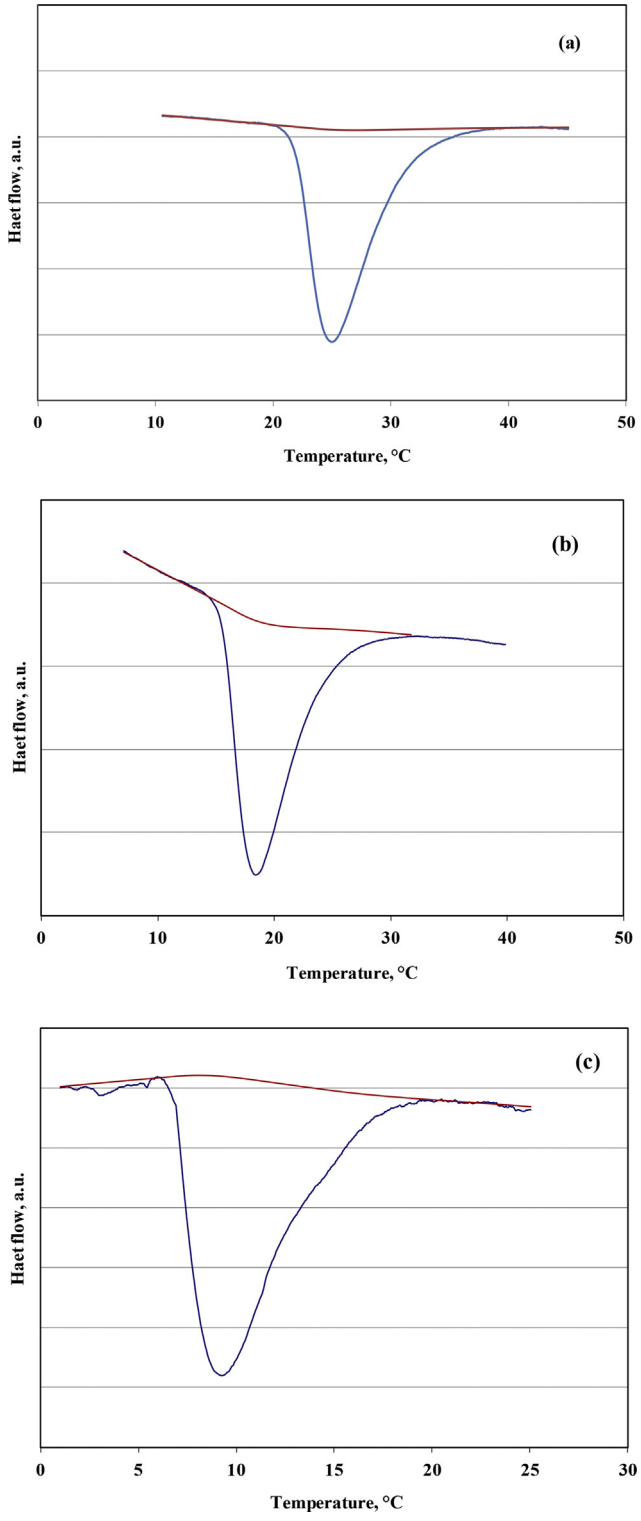

Fig. 1. DSC trace of PEG:F127 mixtures at different mass ratio: (a) 0, (b) 0.33 and (c) 1.

2.2. Pluronic nanoparticles (PNPs) preparation

Aqueous solution of Pluronic F127 was prepared adding the copolymer, in form of powder, to water and keeping the mixture under magnetic stirring for 24 h at 25 °C. The surfactant concentration was fixed at 5 wt%, which is significantly larger with respect to the critical micellar concentration (CMC) of F127 copolymer. Consequently, the surfactant dissolved in water generates the formation of the PNPs with an hydrophobic pocket. Moreover, F127/PEG aqueous mixtures were prepared in order to study the influence of the PEG presence on the characteristics of PNPs. To this purpose, the F127 concentration (5 wt%) was not altered while the amount of PEG was systematically changed within a wide interval. In detail, the F127/PEG weight ratio ranges between 0 and 1.67.