

Competitive interactions and controlled release of a natural antioxidant from halloysite nanotubes

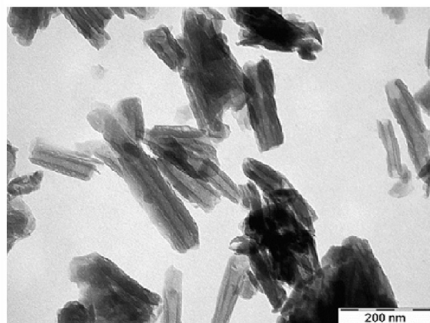
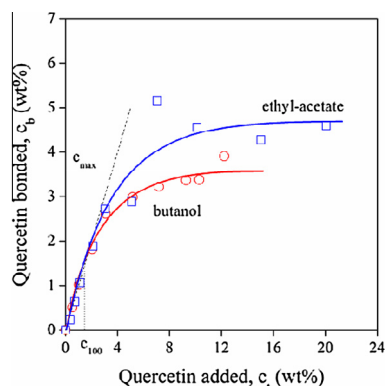


József Hári*, Ádám Gyürki, Márk Sárközi, Enikő Földes, Béla Pukánszky

Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

GRAPHICAL ABSTRACT



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ABSTRACT

Halloysite nanotubes used as potential carrier material for a controlled release stabilizer in polyethylene were thoroughly characterized with several techniques including the measurement of specific surface area, pore volume and surface energy. The high surface energy of the halloysite results in the strong bonding of the additive to the surface. Dissolution experiments carried out with eight different solvents for the determination of the effect of solvent characteristics on the amount of irreversibly bonded quercetin proved that adsorption and dissolution depend on competitive interactions prevailing in the system. Solvents with low polarity dissolve only surplus quercetin adsorbed in multilayers. Polyethylene is a very apolar polymer forming weak interactions with every substance; quercetin dissolves into it from the halloysite surface only above a critical surface coverage. Stabilization experiments confirmed that strong adhesion prevents dissolution and results in limited stabilization efficiency. At larger adsorbed amounts better stability and extended effect were measured indicating dissolution and controlled release.

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* Corresponding author at: Laboratory of Plastics and Rubber Technology, Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary.

E-mail addresses: jhari@mail.bme.hu (J. Hári), gyurkiadam@gmail.com (Á. Gyürki), fenuiww@gmail.com (M. Sárközi), foldes.eniko@ttk.mta.hu (E. Földes), bpukanszky@mail.bme.hu (B. Pukánszky).

1. Introduction

The dispersion of an active component in a matrix or the controlled release of a substance into a medium are major issues in several areas and applications. Accordingly, many combinations

of materials are explored both as supports or carriers as well as active components. A variety of materials and assemblies can be used as carriers like liposomes, polymer micelles and nanoparticles, nanogels, dendrites or silica nanoparticles. The complex structure and numerous hydrogen donor and acceptor groups of the cyclic saccharides, cyclodextrins, makes them ideal for use in delivery systems [1]. Metal, carbon and ceramic nanotubes also may be used as carrier materials. Halloysite is a naturally occurring mineral, which is available both in platelet like and tubular form as described in the review paper of Joussein et al. [2]. Numerous attempts have been made to use halloysite nanotubes as carriers for all kinds of bioactive molecules including drugs [3–15]. However, besides medical applications, halloysite nanotubes are used as supports in other areas as well. Shchukin et al. [16,17] developed an anticorrosion agent in which halloysite nanotubes contain the inhibitor that is released in a controlled way during a certain period of time. Fu et al. [18] used halloysite as a carrier for *N*-isopropyl-*N'*-*p*-phenylenediamine antioxidant to increase the stability of styrene-butadiene rubber. The approach resulted in improved homogeneity and stability, but at rather large, 2–3 wt.%, antioxidant content. Silver nanoparticles have been loaded onto the surface of halloysite [19], and magnetic nanotubes have been also prepared from this mineral [20] to create a simple separation technique by the application of the tubes in adsorption procedures. Halloysite nanotubes are used as adsorbents to bind organic and inorganic molecules mostly in water treatment [21,22].

Polyolefins usually contain a phenolic antioxidant as primary stabilizer. In the past decade, however, some concerns emerged on their possible negative effect on human health [23]. Natural antioxidants could be ideal candidates to replace synthetic phenolic stabilizers. Quercetin, a natural plant derived flavonoid with confirmed antiviral and anti-inflammatory effect, proved to be a very efficient melt stabilizer in polyethylene (PE) [24]. The compound protected PE from degradation during processing already at 50 ppm additive content and improved long term stability at 250 ppm compared to the 1000 ppm synthetic compound used routinely in industrial additive packages. However, quercetin has some drawbacks as well. Its melting temperature is 316 °C, thus it does not melt under the normal processing conditions of PE, it is very polar resulting in extremely limited solubility in PE, and it gives the polymer a very strong yellow color. The use of a support or a carrier material to disperse quercetin homogeneously in PE seemed to be an obvious solution to these problems and halloysite nanotube were selected for the purpose.

In order to check the possible use of halloysite nanotubes as support and controlled release device for the stabilization of PE, we characterized them as thoroughly as possible and studied the dissolution of the active molecule, quercetin, from their surface. The effect of the surrounding media on the characteristic concentrations related to the adsorption and desorption of quercetin were determined in eight solvents in order to predict the dissolution of the stabilizer in PE. Preliminary stabilization experiments were carried out and are reported here to check the stabilization efficiency of quercetin adsorbed on halloysite and its possible controlled release behavior.

2. Experimental

The quercetin used in the study was obtained from Sigma-Aldrich, USA and used as received. Its molecular weight is 302,24 g/mol, melting temperature 316 °C and purity >95%; its chemical formula is presented in Fig. 1. Stabilization experiments were carried out with the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow index of the powder:

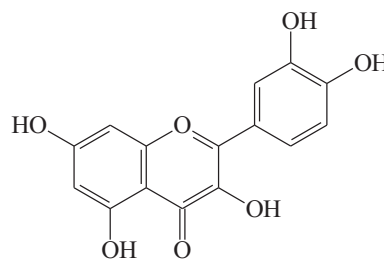


Fig. 1. The chemical structure of quercetin.

0.32 g/10 min, nominal density: 0.947 g/cm³) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by Tisza Chemical Ltd. (TVK), Hungary.

The halloysite nanotubes (Dragonite XR) were supplied by Applied Minerals, USA. The morphology of the mineral was characterized by scanning (SEM) and transmission (TEM) electron microscopy. SEM indicated the aggregation of the tubes to relatively large particles (Fig. 2). The average size of the particles was determined by a Horiba Partica LA950V2 particle size analyzer and proved to be 6.5 μm. The particles could be efficiently disintegrated by ultrasound. TEM micrographs verified tubular structure indeed (Fig. 3) and the average dimensions of the tubes could be determined from the images. The measurement of more than 70 particles yielded an average length of 203 ± 119 nm, outer tube diameter of 50 ± 23 nm and an inner diameter of 15 ± 6 nm. The specific surface area of the tubes, pore size and volume were determined by nitrogen adsorption using a NOVA2000 (Quantachrome, USA) apparatus. The measurements were done at −195 °C after evacuating the sample at 120 °C for 24 h down to 10^{−5} Hgmm. Nitrogen adsorption yielded a specific surface area of 57 m²/g and total pore volume of 0.181 cm³/g. Surface area was calculated also from the dimensions of the tubes determined from TEM micrographs. A specific surface area of 49 m²/g and a tube volume of 0.039 cm³/g was obtained from the calculations. The agreement in specific surface areas is reasonable, but the large difference in pore and tube volumes indicates that nitrogen adsorption measures also pores around and inside the particles and not only the volume of the tubes. The dispersion component of surface tension was determined by inverse gas chromatography (IGC). The filler was agglomerated with water and the 250–400 μm fraction was used for the packing of the column. The dispersion component of surface tension was determined by the injection of *n*-alkanes at

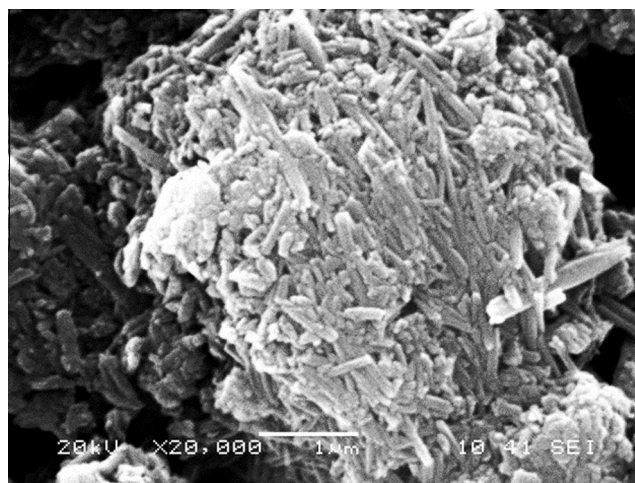


Fig. 2. Particle structure of aggregated halloysite nanotubes; a SEM micrograph.

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