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Preparation of self-healing acrylic latex coatings using novel oil-filled ethyl cellulose microcapsules



S.M. Mirabedini a,b,*, I. Dutil c, L. Gauquelin d, N. Yan e, R.R. Farnood b

- ^a Color, Resin & Surface Coatings Department, Iran Polymer and Petrochemical Institute, Tehran, Iran
- ^b Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada
- ^c Department of Materials Science and Engineering, University of Toronto, Toronto, ON, Canada
- d Department of Chemical Engineering, Institute National Polytechnique de Toulouse ENSIACET, Toulouse Cedex, France
- ^e Faculty of Forestry, University of Toronto, ON, Canada

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ABSTRACT

Novel oil-filled microcapsules were prepared by introducing a phase separation method using ethyl cellulose as a shell-forming containing rapeseed oil. The prepared oil-filled microcapsules were evaluated by optical microscopy, scanning electron microscopy and particle size analysis. Results showed that spherical microcapsules with a diameter of 10 to 45 µm and a rough porous shell were obtained. Carboxylated styrene/butadiene copolymer latex films containing various levels of these microcapsules were subjected to various levels of pre-elongation and their tensile properties were examined. The addition of oil-filled microcapsules resulted in a significant improvement in the modulus, strain-to-break, and toughness of the films. The self-healing mechanism of latex films was examined through the colorimetric measurements of the release of dye-containing following the pre-elongation of the samples. These measurements confirmed that pre-elongation of samples resulted in the release of oil within the latex films, hence plasticizing the surrounding polymeric network and partly restoring the mechanical properties of the pre-elongated films.

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1. Introduction

Water-based polymeric coatings are used in a wide variety of applications ranging from decorative wall paints to packaging materials. However, due to the low strain-to-failure exhibited by these materials, unexpected damages and cracks often incur during their service life [1]. In many cases, physical and mechanical damages of polymeric coatings occur within the manufacturing and converting processes. In addition, water-based coatings usually provide relatively poor barrier properties against gases, high sensitivity to water and moisture, and inferior mechanical properties [2]. Some of conventional methods for improving these properties include; increasing the coating thickness [3], applying multiple coating layers [1], adding functionalized nanoparticles [4–6], increasing the crosslinking density of polymer [7] and introducing functionalized core–shell latexes into the coating formulation [8].

Among the aforementioned available methods [3–8], application of healable materials in coating formulations shows great potential for improving the durability and enhancing bulk mechanical properties of the coating layers. Such self-healing coatings possess the ability to repair in response to damage in the material [9].

In 2001, White and co-workers [10] introduced a novel method to repair the mechanical properties of thermosetting polymers following crack propagation through the micro-encapsulation of self-healing materials. Repairing has been obtained via the addition of urea-formaldehyde microcapsules containing dicyclopentadiene (DCPD) healing agent and through the ring opening polymerization of DCPD in the presence of Grubbs' catalyst [11]. Micro-encapsulation is an approach that consists of isolating a dispersed phase from an external medium by surrounding or coating it with a protective sell material having sizes typically ranging from submicron up to 1 mm [12]. The microcapsules containing healing agents have the capability of self-repairing upon crack propagation [13,14]. As the healing agent flows within the crack lines, it comes into contact with the active materials inducing polymerization and hence sealing up the crack [15]. The repairing of mechanical damage is particularly useful to coatings or composites where subsurface damage occurs that is difficult to detect and fix [15-18].

^{*} Corresponding author at: Iran Polymer & Petrochemical Institute, Color, Resin and Surface Coatings, Pajouhesh Blv., Exit 15, Tehran-Karaj, Tehran 14965-115, Iran. Tel.: +98 21 4866 2401; fax: +98 21 4458 0023..

E-mail addresses: m.mirabedini@utoronto.ca, sm.mirabedini@ippi.ac.ir (S.M. Mirabedini).

A variety of self-healing chemistries have been introduced to enhance the interaction between the healing agent and a polymeric matrix. These include epoxy [10,19,20], isocyanate [21] and solvent welding [22] siloxane chemistries for vinyl ester matrices [23] and poly dimethyl siloxine (PDMS) [24].

An alternative to self-healing using chemical bonding agents is self-healing by plasticizing mechanism. This approach is a promising method for enhancing mechanical properties of polymeric coatings via increasing tensile strength and elongation at break.

In the current study, rapeseed oil was encapsulated in ethyl cellulose microcapsules using a robust phase separation route and the mechanical properties of the water-based latex coatings containing these oil-filled microcapsules were investigated. Latex films containing 1–3 wt% microcapsules and two microcapsule sizes were studied. The deformation and disruption of latex films containing microcapsules filled with colored rapeseed oil were examined under applied tensile load using color coordinate measurements.

2. Experimental

2.1. Materials

Ethyl cellulose (EC), rapeseed oil (RO), sodium dodecyl sulfate (SDS), Sudan Red 7B solvent dyestuff, and ethyl acetate were purchased from Sigma Aldrich (Oakville, Ontario, Canada). A non-ionic surfactant, Dynol 604, was provided by Air Products USA. A commercial carboxylated styrene–butadiene latex, Styronal ND 656 was supplied by BASF Corporation. This latex is an emulsion-type latex commonly used for paper coating applications for its filmforming properties, resistance to water and moisture, and relatively rapid drying with low porosity [25]. All chemicals were analytical reagent grade and used as received.

2.2. Microcapsules preparation

Microcapsules with oil to ethyl acetate ratio of 70:30 were prepared via a two-stage solvent evaporation method [2] following

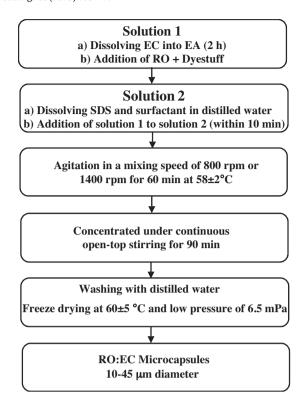


Fig. 1. Microencapsulation procedure.

the methodology reported elsewhere [26,27]. The flowchart for the synthesis of microcapsules is provided in Fig. 1. In brief, in the first stage, ethyl cellulose powder was dissolved in ethyl acetate (5 wt%) under magnetic stirring for at least 2 h at ambient temperature. RO and 0.005 wt% of red solvent dyestuff were then added to the above-mentioned solution and system was magnetically stirred for further 30 min. In the second stage, the solution was added drop wise to an aqueous solution of 1 wt% SDS and 0.05 wt%

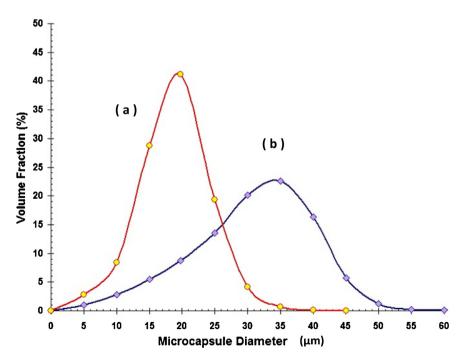


Fig. 2. Volume fraction (%) and the average diameter of 70:30 RO:EC microcapsules: (a) 1400 rpm ($d_m = 18.8 \text{ } \mu\text{m}$, C.V. = 8.1%), and (b) 800 rpm ($d_m = 34.0 \text{ } \mu\text{m}$, C.V. = 8.5%).

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