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Mechanical and self-healing properties of a water-based acrylic latex containing linseed oil filled microcapsules: Effect of pre-silanization of microcapsules' shell compound

H. Es-haghi [a], S.M. Mirabedini [a, b, *], M. Imani [a], R.R. Farnood [b]

[a] Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965-115, Tehran, Iran
[b] Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada

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ABSTRACT

In this study, mechanical properties and self-healing performance of a water-based acrylic coating containing linseed oil-filled ethyl cellulose (EC) microcapsules were evaluated. In order to improve interfacial interactions between microcapsules' shell and their surrounding latex matrix, EC was treated with three different trimethoxysilane coupling agents before microencapsulation process. Water-based acrylic coatings containing various amounts of different microcapsules were prepared and their tensile properties were studied. The effect of silane pre-treatment of microcapsules' shell on the self-healing performance of the coating was also evaluated via optical microscopy, UV–visible spectroscopy, AFM and SEM. Water vapor transmission (WVT) of intact and healed scratched coating samples was measured and their healing efficiency values calculated.

It was found that the addition of microcapsules with pre-silanized shell compound has a positive effect on the tensile and mechanical properties of the coating. The degree of this effect depended on the silane type and microcapsules' loading wt% in the coating material. Sample containing microcapsules with amino-based silane treatment revealed appropriate tensile properties among the others owing to better compatibility with polymeric matrix, improving barrier properties of scratched area by releasing of hydrophobic oil and therefore, minimizing the penetration of water and water vapor through the coating layer.

1. Introduction

During the recent years, research and development for new and more efficient self-healing materials has been widespread. Some of the methods used for providing self-healing characteristics to the coating materials are included, but do not limit to systems containing hollow glass fibers [1], microvascular networks [2], supramolecular structures [3] and finally microencapsulation of healing agent(s) [4–9]. Among those methods, microcapsules filled with healing materials seem to be a promising method for repairing their substrate coatings in response to an external mechanical stimulus causing damage to the coating. Incorporated microcapsules in a polymeric matrix are ruptured with external stress, released the healing materials within the cracked area and restored the mechanical properties of the coating layer [9]. In first generation of trials to use microencapsulated healing agents for self-healing purposes in coatings, White and co-workers [5] embedded urea-formaldehyde microcapsules containing dicyclopentadiene (DCPD) and solid phase Grubbs' catalyst in an epoxy matrix. In their work, when a micro-crack propagated and reached the microcapsules, the healing agent was released into the cracked region and caused a ring opening polymerization of DCPD in the presence of the Grubbs' catalyst that led to restore the mechanical properties of the host polymeric matrix [5,6].

Microencapsulated self-healing systems are widely used in thermosetting resins like epoxy matrix [4–11] and limitedly in water-based paints [12–15] in contrast to widespread application of water-based polymeric coatings ranging from decorative paints to packaging purposes [5]. It is evident that water-based coatings, similar to any other coating systems, are in the risk of developing micro-cracks during their service life due to external mechanical

* Corresponding author. Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965-115, Tehran, Iran. Tel.: +98 21 4866 2401; fax: +98 21 4458 0023.
E-mail addresses: sm.mirabedini@ippi.ac.ir, m.mirabedini@utoronto.ca (S.M. Mirabedini).

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forces which subsequently exposes newly formed surfaces of the substrate to atmospheric moisture and oxygen. This fact describes why curable chemical compounds such as DCPD or oxidizing linseed oil can be used for self-healing purposes to provide longer durability for the host polymeric coatings.

In self-healing applications, the microcapsules are designed to break at a prescribed level of external stimulus, resulting in the releasing of the healing material [4]. However, when the interfacial of microcapsules/polymeric matrix is weak, external stress is passed from the weakest part of the matrix, i.e. the intersection of microcapsules/matrix, and consequently, the number of ruptured microcapsules is diminished resulting in decreasing of healable materials [16]. Hence, enhancing the chemical and/or physical interactions between microcapsule shells and the surrounding polymer matrix could significantly improve the self-healing characteristics [12,16]. Effect of microcapsule shell/polymeric matrix interactions on the mechanical properties and self-healing efficiency has been previously studied only by a few of researchers [5,12,17]. In particular, silane coupling agents (SCA) have gained more attention because of their special structures that can enhance physicochemical interactions between the microcapsules and polymeric matrix [17].

In our previous work [18], preparation and characterization of oil-filled ethyl cellulose microcapsules with pre-silanized shell was reported. Here, the mechanical properties and self-healing performance of silane modified microcapsules embedded water-based latex coating are studied. Optical microscopy, UV–visible spectroscopy, SEM and AFM were used to record the crack-filling property of scratched coating films.

2. Experimental

2.1. Materials

Ethyl cellulose (EC), linseed oil (LO), sodium dodecyl sulfate (SDS), Triton X-100, Sudan Red 7B, and chloroform were purchased from Sigma Aldrich (Oakville, Ontario, Canada). Silane coupling agents (SCA) consisting of; (3-aminopropyl)-trimethoxysilane (APS), [3-(methacryloyloxy)-propyl]-trimethoxysilane, (MPS), and [3-(2,3-epoxy-propoxy)-propyl]–trimethoxysilane, (EPS), were purchased from Merck Chemicals Co. (Darmstadt, Germany). Acrylic emulsion resin (SH-305, 50 wt% solid content) was obtained from Simab Resin Co. (Tehran, Iran). All materials were used as received without further purification.

2.2. Silanization of EC

EC powder was chemically modified by three different trimethoxysilane derivatives for enhancing possible interfacial interactions between the microcapsules' shell and polymeric matrix. The procedure details were reported in our previous work [18]. Briefly, EC modification was accomplished in solution state using acetone as a solvent and APS, MPS, and EPS as the silane coupling agents under magnetic stirring for 7 h. The ratio of the three different SCAs to EC was selected as 1:2 (wt:wt). Upon completion of the process, the treated EC samples were washed with deionized water several times and were filtered and dried subsequently in a vacuum oven for 24 h at 25 °C.

2.3. Microcapsules preparation

The EC Microcapsules with core to shell ratio of 70:30 were prepared via a robust solvent evaporation method [4,18]. Neat or pre-silanized EC was used as the shell materials and linseed oil was considered as the core compound. 30 mL solution of shell and core materials (10 wt% in chloroform) was added drop wise into 30 mL of an aqueous solution of SDS (1 wt%) and Triton X-100 (0.2 wt%). The microcapsules were prepared under mechanical stirring at a constant speed of 1000 rpm with an axial three-bladed impeller stirrer (Heidolph RZR 2102, Germany) at 58 ± 2 °C for 90 min.

2.4. Preparation of acrylic latex/microcapsules samples

Various amounts of microcapsules (i.e. 0.5, 1 and 2 wt%) were gently added to the latex resin under magnetic stirring operating at speed of 250 rpm for 20 min. The mixture was placed in a vacuum oven for 10 min to remove trapped air. Coating samples with a wet thickness of 500 ± 20 μm were applied on a degreased glass substrate using a film applicator (Model 352, Erichsen Co.). The specimens were then left to dry for 24 h at ambient temperature. The dried films had thicknesses of about 240 ± 15 μm. The coated samples were immersed in deionized water for about 3 h, and film samples were easily detached from their substrate. The free-standing coating films were then dried at ambient temperature for further 24 h.

2.5. Mechanical properties of acrylic latex/microcapsules samples

Tensile properties of the free-standing samples containing various wt% of the microcapsules (unmodified and pre-silanized shell compound) were studied using a Santam SMT-20 Universal Testing Machine (Tehran, Iran), according to ASTM D 882 standard method. Rectangular test specimens (0.24 mm × 20 mm × 50 mm) were prepared by cutting the film to shape. Tensile tests were conducted at a speed of 50 mm min^{-1} and under the ambient temperature of 23 ± 2 °C at 50 ± 5% RH. The load cell used in the tensile tests had a 100 N load capacity. For each sample formulation, five specimens were tested and the average was reported.

DMTA was carried out under N_2 atmosphere with a 'Polymer Laboratory' Model PL. Measurement of the shear storage modulus (E′) and loss tangent (tanδ) of latex films containing 0.1, 1 and 2 wt% EC-microcapsules, were carried out at a frequency of $\omega = 1$ Hz at 50 ± 5% RH and working in single cantilever with rectangular samples. The temperature was increased from −20 °C to 100 °C at a constant rate of 5 °C min^{-1}.

The hardness of films was measured using a pendulum hardness tester (Elcometer 3034, UK) according to ASTM D 4366 test practice based on Persoz method. The test was performed using a 500 g mass ball with 8 mm diameter, and the starting deflection was set as 12° for the Persoz mode. The coating samples were applied on degreased glass plate (100 mm × 100 mm) with 120 ± 10 μm wet film thickness. The dried films had thicknesses of about 50 ± 5 μm. For each sample, five individual tests were carried out and the average value reported.

2.6. Healing performance of the microcapsules

Crack healing performance of the microcapsules in the coating sample was studied by incorporating 1 wt% of various microcapsules (neat or pre-silanized shell materials) in the coating sample, creation of an artificial crack in the coating (using scalpel blade No. 11) and inspection of the crack under an optical microscope and evaluating mechanical properties of the host polymeric matrix. For enhanced visibility and improved contract, LO was stained using 0.05 wt% Sudan Red 7B solvent dyestuff during microcapsules preparation and 3 wt% TiO_2 pigment was added to the resin, respectively. The coating samples were applied on a degreased glass plate using a film applicator (Model 352, ERICHSEN Co.) with a wet film thickness of 500 ± 20 μm. The specimens were left to dry for 24 h at ambient temperature. The dried films had thicknesses of