Self-Healing of Polyimide Films. Challenges & Perspectives

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ABSTRACT

Since the pioneer works of S.R. White concerning the development of self-healing for polymeric products and composites, auto reparation, which practically imitates self-healing of wounds, has been a new challenge for damage structures which could not be reachable and repaired at distance.

The concept developed by our team (NATO project SPP # 982837) was to incorporate in the same microcapsule, both difunctional monomer and photoinitiator which, upon exposure to UV light, will crosslink the multi functional monomer.

Some preliminary works have been realized considering the encapsulation of TMPTA and radical photoinitiator in silica microcapsules disseminated in a Polyimide film based on dianhydride of dicyclodecene tetracarbonic acid and ODA. The feasibility of the concept has been demonstrated in absence of oxygen, for space devices working in sub-orbital spaceflight, i.e. above 100 km or a low Earth orbit (LEO) space flight i.e. 300 km and above .

INTRODUCTION

The development of self-healing polymeric materials, those that practically imitate self-healing process of wounds is a new and challenging problem for space applications to protect different types of devices made with composite materials. The pioneer works in auto-reparation of composites were developed by White S. R et al [1-4]. Their originality was to suggest the encapsulation of monomer – dicyclopentadiene, and Grubbs catalysor disseminated uniformly into the composites. Under loading cracks are formed and microcapsules open up releasing monomer and initiator which fulfill the cracks by polymerization and crosslinking reactions and allow the composite to retrieve his original structure without losing its initial mechanical properties - Figure 1.

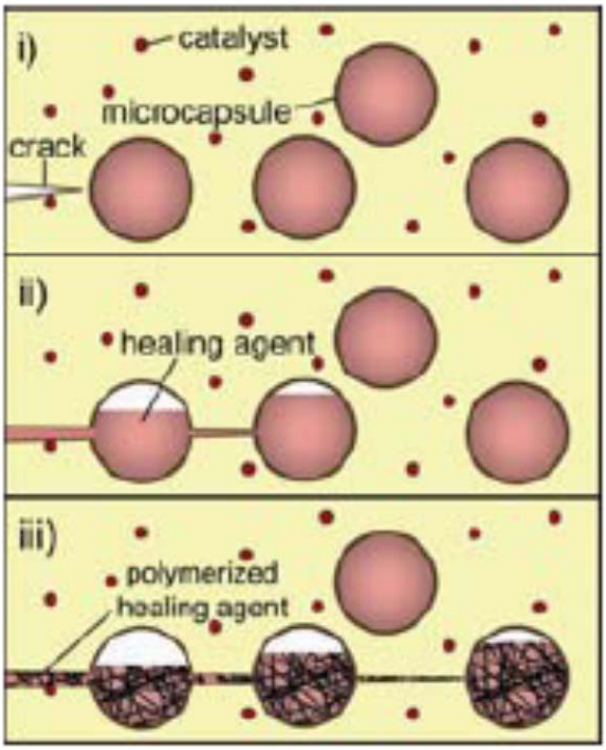

Figure 1. Concept of reservoirs developed by White S. R et al

The concept is strongly dependant on the reactivity of the monomers used as well as the initiator systems [5].

A sub-orbital spaceflight (above 100 km) or a low Earth orbit (LEO) impose on the composites the following conditions : absence of oxygen, temperature variable from - 120°C (dark side) to +300°C (solar side), UV radiation and heavy ions, low pressure 10^{-4} Pa.

The methodology developed was to test the feasibility of self-healing by using a encapsulated multifunctional acrylates, i.e. trimethylolpropanetriacrylate (TMPTA) in presence of radical photoinitiator.

The novelty of the work was to develop new polymeric film composites, based on Polyimide containing microencapsulated active monomer and generator of active species, to prevent destruction of the damaged sample.

The new concept tested was to encapsulate in the same microcapsule used as reservoir, both the monomer and the initiator. Active species are produced upon exposure to UV light using a radical photoinitiator such as Darocur® 1173 [6].

Two major issues have been studied :

a) Develop a suitable microcapsule which could, under loading, liberate the active principle in presence of initiator.

b) Distribute homogeneously the microcapsules into the polymeric film used as coatings

I. EXPERIMENTAL

Microencapsulation

Microcapsules shell should be resistant to high temperatures (> 300 °C) and have average diameters ranging 1-20 µm in order to put them in the host material.
Silica gel microcapsules have been tested

1.1- Synthesis of Silica Gels Microcapsules by Sol-Gel Polymerization Process - The TMPTA monomer and the Darocur® 1173 photoinitiator are encapsulated in silica gels microcapsules by sol-gel polymerization. 3-(trimethoxysilyl)propyl methacrylate (MPTS), tetraethoxysilane (TEOS), trimethylolpropane triacrylate (TMPTA), Darocur 1173, silica surfactant (PEGSi), compatibility agent to increase the stability between the shell and the aqueous solution) and ethanol are placed and are mixed with a magnetic stirrer in a bottle. Then, an aqueous solution of ammoniac (16 wt. %) is added drop by drop to the mixture. After 10 minutes of continuous agitation, this solution is added to an aqueous solution of polyoxyethylene (12) nonylphenyl ether (Igepal CO-720 (NP12), 1 wt. %). After 2 hours of reaction, the suspension is filtered under vacuum. Microparticles are collected and are dried in air at room temperature for 24-48 h. Figure 2 illustrates the schematic road to synthesis of silica gels microcapsules loaded with TMPTA monomer [7].

1.2- Scanning Electron Microscopy - Silica microcapsules are studied by ESEM. The spherical particles have average diameters ranging from 1-30 µm, shown in – Figure 3. The shells of micro particles present a smooth surface.

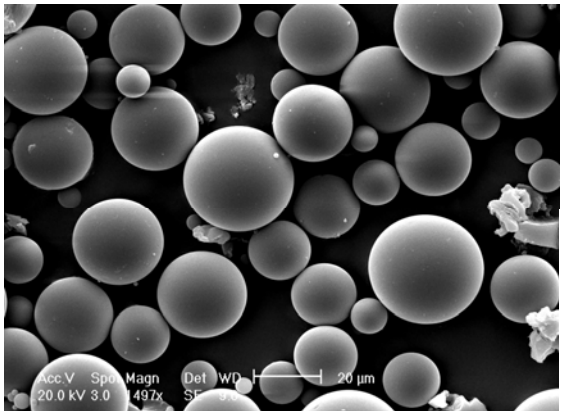

Figure 3. ESEM image of Silica gels microcapsules loading in TMPTA monomer and Darocur ®1173 photoinitiator

1.3- Infrared Analysis - The comparison of IR spectra of empty silica-gels microparticules and silica-gels microparticles loaded in TMPTA do not enable us to prove the encapsulation of the TMPTA. In effect, the two spectra present the same absorption bands because silica-gels shell contains a methacrylate compound – Figure 4.
For that we used silica gels microcapsule (empty microcapsules and microcapsules loaded in TMPTA) with TEOS precursor alone (not methacrylate chain in this compound). The comparison between Infrared spectra of the empty silica gels microparticles with TEOS precursor alone and silica gels microparticles loaded with TMPTA, shows the presence of new bands, in particular at 1721, 983 and 807 cm^{-1}. These bands characteristic of the TMPTA monomer indicates that this compound is encapsulated in silica gel microcapsules.

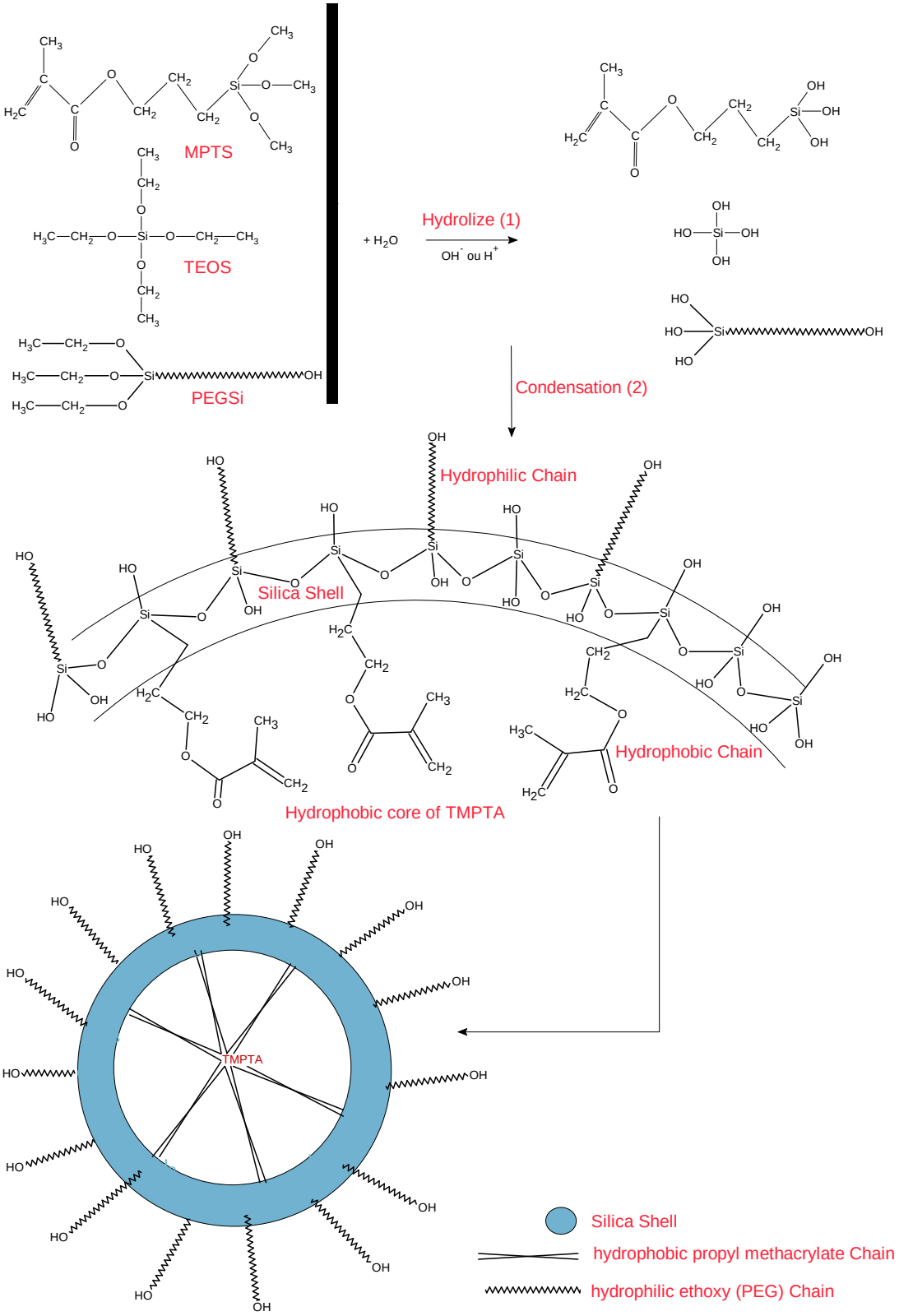

Figure 3. Schematic Road for Synthesis of Silica Gel Microcapsules Loaded in TMPTA

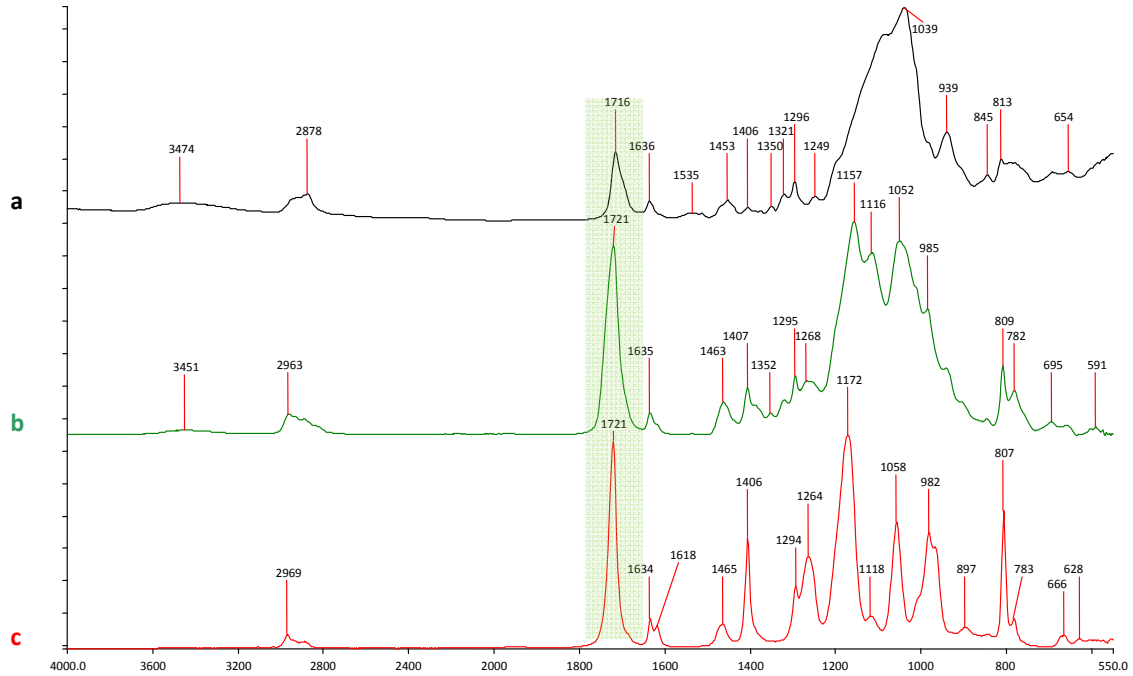

Figure 4. Infrared spectrum of (a) Empty silica gels microcapsules (b) silica gels microcapsules loaded in TMPTA monomer and (c) TMPTA

1.4- Thermogravimetric Analysis - The thermogravimetric analysis of silica-gels particles (without TMPTA) indicates a good thermal resistance (above 320°C) of silica-gels membrane – Figure 5.

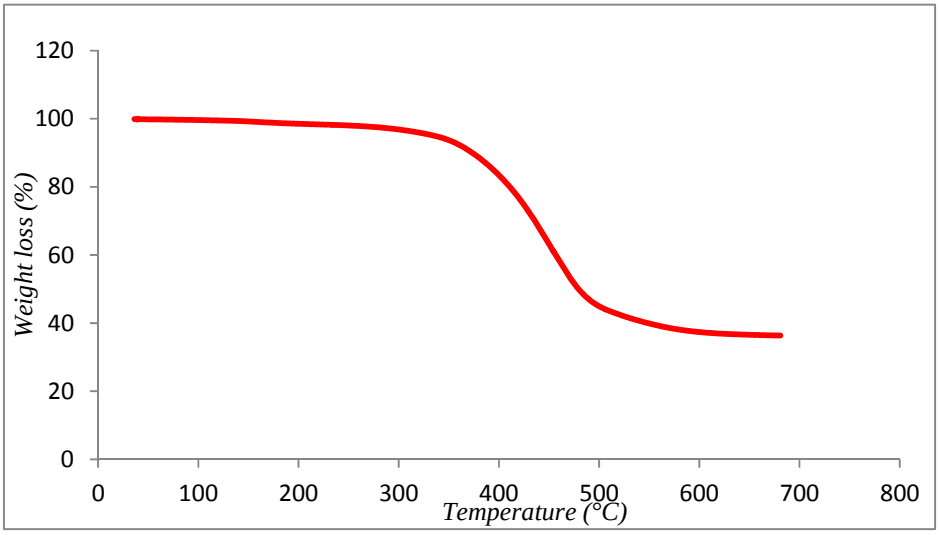

Figure 5 : Thermogravimetric Analysis of Empty Silica Gels Microcapsules

We have encapsulated with success TMPTA monomer by different processes of microencapsulation. Two of three techniques used cannot be applicable for aerospace application as the microcapsules are not thermal resistant above 300 °C presenting a temperature of degradation below 200°C. However, silica membrane is much more resistant due to their degradation temperatures exceeding 300°C.

Dispersion into the Polyimide Film

Polyimide films are based on dianhydride of dicyclodecene tetracarbonic acid and ODA –Figure 7. The dianhydride was synthesized by Solar-irradiation technology of a mixture of benzene/toluene fraction with maleic anhydride to produce highly reactive monomer – benzene adduct (AB) – Figure 6.

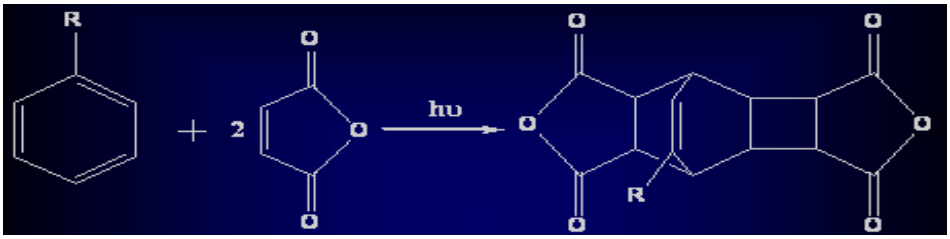

Figure 6. Photosynthesis of the dianhydride of dicyclodecene tetracarboxylic acid

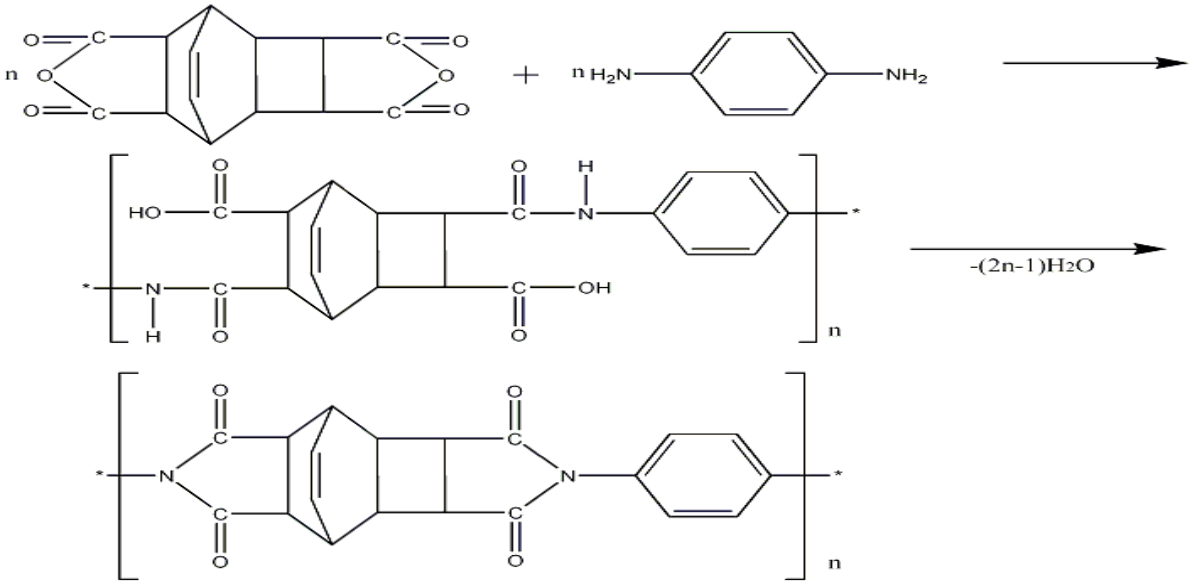

Figure 7. Polyimide based on dianhydride of dicyclodecene tetracarbonic acid and ODA

Microcapsules loaded with TMPTA and the radical photoinitiator are mixed in 5 to 15 wt. % in solution of PI in DMF, cast and dry, and then subjected tp 100 °C for 4 hours, followed by 4 hours at 180 °C.

Environmental scanning electronic microscopy coupled with RX (ESEM/EXD) show a good dispersion of the microcapsules along the polyimide film and confirms their presence.

EDX of polyimide film does not show any silicium peak but is present in the analysis of the polyimide with silico-gel microcapsules.

II. RESULTS AND DISCUSSIONS

Auto-reparation of Polyimide Film

Different formulation of Polyimide films have been loaded with variable concentration of microcapsules from 5 wt. % to 15 wt. %. Then the films casted are exposed to UV light (365 nm) once cracks were produced.

Self-healing process was followed by morphological analysis by scanning electron microscopy ESEM. Figures 8 and 9 clearly show the auto-reparation, upon exposure to UV radiation, of the film loaded with silica-gel microcapsules containing both radical photoinitiator and multifunctional acrylate monomer.

Figure 10. Auto-repairing after cracks

Figure 8. Effect of UV after cracking micro-gel capsules on Polyimide film

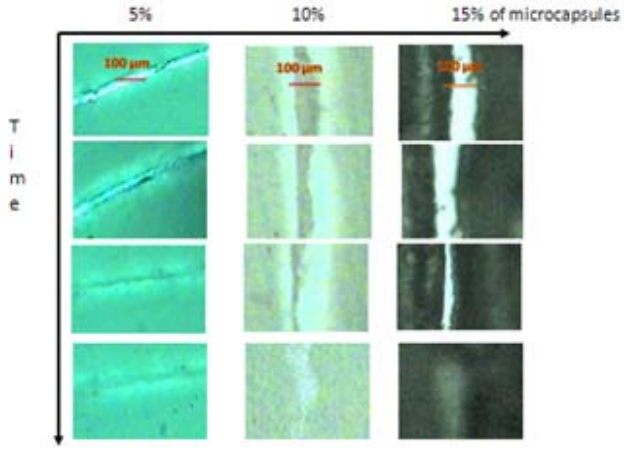

Figure 9. Sel-healing after cracks

Figures 9 and 10 show the reconstitution of the Polyimide film for different concentration of silica-gel microcapsules versus time of exposure to UV radiation, 0 min, 5 min, 10 min and 15 min respectively for intensity of 100 mW/cm^2.

PI films loaded with 15 wt. % of Si-microcapsules loaded with TMPTA monomer and exposed 5 min are equivalent to 1 month exposure at the real space condition over geostationary orbit of the earth.

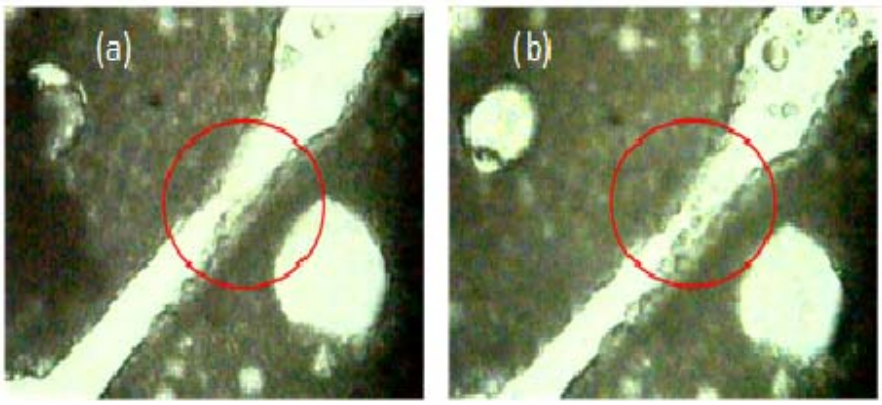

Figure 10. Cracks at time zero (a) – Cracks at exposure time 5 min

CONCLUSIONS

Silica-organic microcapsules based on 50 wt. % MPTS and 50 wt. % TEOS have been selected to encapsulate monomer TMPTA and the photoinitiator Darocur 1173. The microcapsules prepared have diameter size of 4.00 ± 0.30 mm in optimal synthesis conditions : reaction time of 2.0h and stirring rate of 450.0 rpm.

Silica-organic microcapsules have been chosen over other systems [8] due to their thermal stability up to 375 °C.

Feasibility of self-healing of Polyimide films has been demonstrated using a photo-radical mechanism.

Further experiments in presence of epoxies should complete this study showing the feasibility of self-healing by photo-cationic mechanism [9, 10] for low orbital with presence of oxygen.

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