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Preparation and Characterisation of Self-Healing Polyuretahne Composites Replacing Conventional Curing Catalysts

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Abstract—*Polyurethane matrix were modified with microcapsules which enable it to become a self healing material. The paper studies the effects of different catalyst which could act as cheap substitutes in self-healing technology. Transition metal compounds with excellent predetermined catalytic properties like Chromium trichloride and manganese dichloride are chosen for the study instead of Grubb's catalyst, which is a ruthenium chloride, transition metal complex for the crosslinking of liquid resin after crack formation. A much simpler version of catalyst was tried in the work to study the healing characteristics. Manganese has diagonal similarity with ruthenium from the periodic table location, hence selected. Urea-formaldehyde microcapsules were prepared using in-situ polymerization technique, and embedded into the polymer matrix, such that the mixture is about 10 weight percentage of the entire polymer matrix. Characterization tests like optical microscopy, SEM and FTIR are done to analyze the matrix for the incorporation. These tests show the presence of the microcapsules containing the self-healing agent. The amount of healing agent present in the microcapsules, the composition of the microcapsules and the structure of the microcapsules is also determined using the above mentioned tests.*

Keywords—Catalyst, Self assembling, Polyurethanes, microencapsulation

INTRODUCTION

The ability of any material to heal itself whenever and wherever any damage occurs is known as self-healing. Due to various reasons a material might undergo changes in their physical properties one of which is the formation of cracks on their surface [1, 2]. The formation of cracks not only reduces the efficiency of the material but also increases the overall cost of repairing and replacement and sometimes might prove to be fatal. To avoid such instances, it has become necessary for us to come up with a solution that will not only be efficient but also cost effective. One such solution is the concept of Self-Healing Material [3, 4]. Self-healing materials are a class of smart material which can heal itself when cracks are formed [5]. The ability of the material to heal itself will reduce the

cost of repairing and replacement, reduce inefficiency due to degradation and ensure prolonged material life [6]. Self-healing materials are divided into three categories, namely: capsule based, intrinsic and vascular [7]. Each healing mechanism depends on the nature of damage that triggers the process. This determines the damage volume to be healed and the recovery rate [8, 9].

In capsule based self-healing, the healing agent is trapped inside the microcapsules and once a crack occurs, it results in the rupturing of the microcapsule releasing the healing agent [10]. In vascular self-healing materials, the healing agent is stored in hollow channels or fibers. When damage occurs, these channels or fibers are ruptured and the healing agent flows out. In intrinsic self-healing materials, thermally reversible reactions, hydrogen bonding or molecular diffusion triggers the self-healing process [11-14].

This paper proposes the development of self-healing polyurethane matrix. The healing and mechanical performances of the self-healing composites are to be analyzed as well as related to various fabrication techniques. This work will concentrate on polyurethane matrix, but similar concepts can also be applied to other material systems, such as concrete and ceramics. The most general and simple concepts are used to make the project.

Experimental

Materials used: Urea, Formaldehyde (37%), diphenylmethane diisocyanate (MDI),propylene glycol polyol, Dicyclopentadiene (DCPD), Chromium Trichloride, formaldehyde, Resorcinol, Ammonium chloride, Citric acid, Triethylamine, 1-Octanol, Polyvinyl alcohol, Manganese Dichloride, NaOH, Sodium do decyl benzene sulfonate, Deionised water are all SD fine laboratory grade.

TABLE I
formulations

No	Ingredients	Function	Quantity
1	Urea	To prepare UF resin-monomer	5gm
2	Formaldehyde (37%)	To prepare UF resin-monomer	11.7ml
3	Triethylamine	Adjust the pH	10ml
4	Sodium do decyl benzene sulfonate	Emulsifier	0.5gm
5	Polyvinyl alcohol	Emulsion stabiliser	0.5gm
6	Dicyclopentadiene	Healing agent	60ml
7	Resorcinol	Crosslinking agent	0.5gm
8	Ammonium chloride	To maintain pH	0.5gm
9	Citric acid	To maintain ph to acidic	0.5gm
10	Deionised water	solvent	200ml
11	1-Octanol	Bubble elimination	1-2 drops
12	Triethylenediamine	Catalyst for PU	1-2 drops

Urea Formaldehyde microcapsules preparation:

The healing agent encapsulated in this system of microcapsule is Dicyclopentadiene (DCPD). Microcapsules were composed of a smooth inner membrane and a rough, porous outer surface of agglomerated urea-formaldehyde nanoparticles. Surface morphology is influenced by pH of the emulsion.

There were 2 steps carried out during microcapsule formation. The first step is emulsion of Dicyclopentadiene (DCPD) in urea-formaldehyde resin solution, in which DCPD is as a dispersed phase. High rotation speed of stirring was conducted to emulsify DCPD. The second step is microcapsule shell formation. In this step, the pH of emulsion liquid was adjusted into acidic condition. This promotes the reaction of urea with formaldehyde in the interface of emulsion bubbles, producing a film of urea formaldehyde polymer as a microcapsule shell. Urea formaldehyde microcapsules were prepared by in-situ polymerization, using the ingredients in the Table 1.Urea-formaldehyde microcapsules were formed by in-situ polymerization in an oil-in-water emulsion. At room temperature (20-24OC) 200ml of deionised water was added in a 1000ml beaker. The beaker was suspended in a temperature controlled water bath on a programmable hot plate. The solution was agitated with a digital mixer placed just above the bottom of the beaker. Under agitation, 5g urea, 0.5g ammonium chloride and 0.5g resorcinol were dissolved in the solution. The pH was increased from 2.60 to 3.50 by the addition of Sodium Hydroxide and Hydrochloric acid. 1 to 2 drops of 1-Octanol were added to prevent surface bubbles. A slow stream of 60ml of Dicyclopentadiene was added to form an emulsion and allowed to stabilize for 10minutes. After stabilization, 12.67g of 37wt% of aqueous solution of Formaldehyde was added to obtain 1:1.9 molar ratio of Formaldehyde to Urea (Sanghvi and Narin 1992). The emulsion was covered and heated at a rate 1OC per minute to the target temperature of 55OC for 4hours of continuous agitation. Once the mixture is cooled to ambient temperature, the suspension of microcapsules was separated under vacuum with a coarse-fritted filter. The microcapsules were rinsed with deionised water and air dried for 120 hours [15].

Embedment of Microcapsules

The prepared microcapsules and catalyst are embedded into the polymer matrix. The PU matrix was prepared by mixing aromatic isocyanates: diphenylmethane diisocyanate (MDI) and polyol: propylene glycol. First, the microcapsule and the catalyst mixture (once with chromium trichloride and another with manganese dichloride) was poured into polyol and then thoroughly mixed. In this step, the microcapsule and catalyst mixture is in the ratio 1:1 and constitute 10wt% of the overall PU matrix. Also, 2wt% of 1-Octanol is added for the removal of air bubbles. The microcapsule mixture was added to MDI containing curatives for polyurethanes and mixed thoroughly. This was then left to air dry until the PU blend hardened completely. The reaction leads to formation of urea formaldehyde polymer chain. This polymeric network provides high strength to the microcapsule shell and avoids breakage of the shell.

Characterization:

Optical Microscopy

Optical characterization was performed using the Olympus BLX microscope connected to a CCD camera and video system with which pictures could be taken. Magnifications of 100, 200, and 500X were used. Microscopy was done on samples of the microcapsules subjected to various amounts of filtration and on the polyurethane, which was embedded with silane washed microcapsules. The optical microscope uses visible light and a system of lenses to magnify images of small samples improve resolution and sample contrast. The image from an optical microscope can be captured by normal light-sensitive cameras to generate a micrograph. Originally images were captured by photographic film in CMOS and charge-coupled device (CCD) cameras allow the capture of digital images.

Scanning electron microscopy (SEM)

SEM can achieve resolution better than 1 nanometer. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. In SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be electrically heated for electron emission. The electron beam, has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. The beam current absorbed by the specimen can be detected and used to create images of the distribution of specimen current.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or em ission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

Physical properties of the composites

The polyurethane composites are tested for Compression Strength, Impact Strength and Rockwell Hardness tests. Test specimens were moulded for measuring Izod Impact (ASTM D 4812-93), Compression strength (ASTM D 6641-14) and Rockwell hardness (ASTM E18-16) with matrix materials with and without microcapsules. Test results were compared with PU mouldings without any microcapsules.

Results and Discussion

Microscopy

Characteristic particles of each filtration level are shown in figure 1 as well as a characteristic view of the polyurethane. Figure 1 a, b, & c is the microcapsules prepared and d shows the PU matrix with microcapsules incorporated. Notice that in part a of figure 1, the first level of filtration shows a particle that is approximately 200 μm in diameter, and

the particles shown in part b of figure are from the second level of filtration and have a diameter of approximately 100 μm. Part c of figure shows a particle from the maximally filtrated particles; notice a diameter for this particle is approximately 50 μm. Consequently, when subjected to more filtrations, the characteristic particle size of the representative samples decreases. Part d of figure 1 shows silane washed microcapsules in the polyurethane matrix. The matrix did not polymerize in the presence of the silane, and therefore light can be seen transmitting through the matrix. There are air bubbles present indicated by black rimmed spheres. There was extremely little crystallinity present in the sample. It also appears that the shell provide complete coverage of the DCPD as seen in figure.

Environmental Scanning Electron Microcapsule

Figure 2 shows the SEM images of microcapsules incorporated PU. Matrix with Microcapsules was studied using the environmental scanning electron microscope (ESEM). Note the appearance of a spherical particle with a relatively rough surface in part a with 50μm magnification. In part b, agglomerations of small, smooth, spherical particles are seen. They are tiny particles of UF since it seems that these spheres form the rough outside layer of the UF shell. The photograph confirmed the presence of microcapsules, shape and structure available in the PU matrix. These microcapsules can function as self healing materials as it contain the liquid resin to fill the cracks and get crosslinked after that to seal the gap.

Fourier Transform Infrared Spectroscopy

A reference spectrum for DCPD is shown in figure 3a. The results of the analysis of the product of our microcapsule synthesis are shown in figure 3 (b). To determine encapsulating process DCPD FTIR spectroscopy was conducted on the microcapsules. The microcapsules were prepared by urea formaldehyde was the shell with DCPD, healing agent was encapsulated. The curves show that there is very less DCPD as available free when it is compared with original DCPD curves, which is the major proof that DCPD is encapsulated into the urea shell. The major peaks confirmed are 3335 for O-H stretch also for amine, medium (primary amines have two bands; secondary have one band, often very weak), 3052 for C-H, 2924 for C-H, 1075 for C-O also for C-N stretch, 1408 for C-H , 865 for C-H alkene bending, 1646 for C=C also for N-H bonds and 1025 C=O etc. Thus FTIR is very clearly giving the proof that DCPD is not available as free but encapsulated in urea resin. The peeks related to N-H are giving the confirmation for urea and also formaldehyde related peaks.

Figure .1: Characterisation microcapsules from (a) One filtration, (b) Two filtration, (c) Multiple filtration and (d) microcapsule (washed in silane) embedded in Polyurethane.

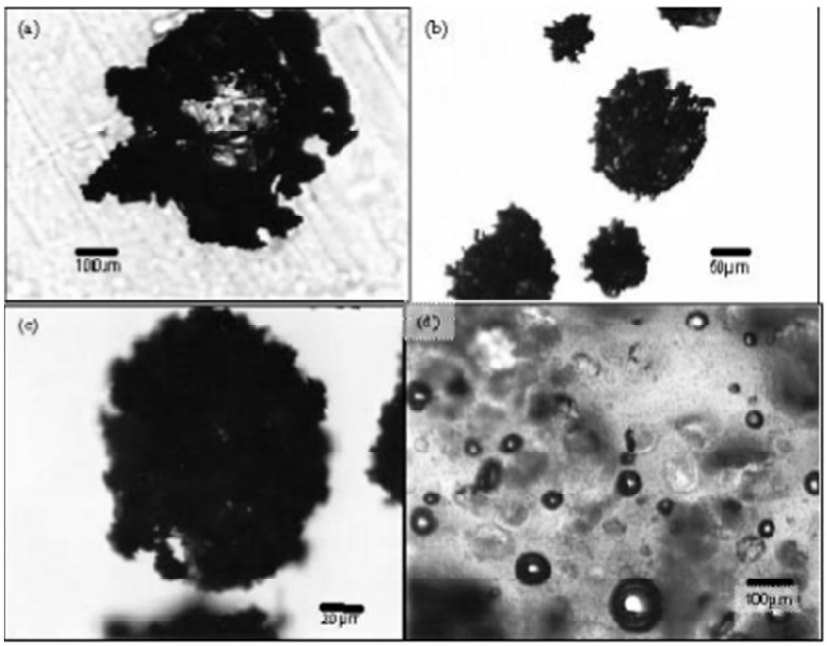


Figure 2: The SEM images of microcapsules incorporated PU.

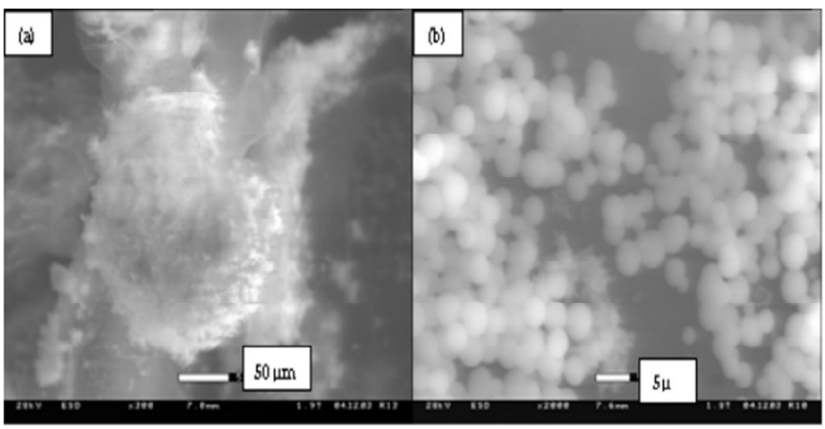
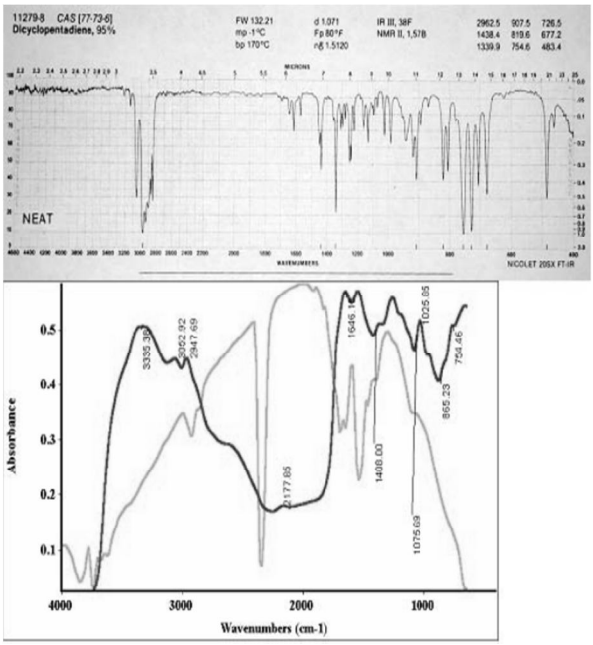


Figure 3: a) Reference FTIR for Dicyclopentadiene, (b) FTIR spectrum for microcapsule powder (dark lines), background (light grey)



Physical properties like Compression Strength, Impact Strength and Rockwell Hardness of the matrices were found to be promising and out of the two catalysts Chromium trichloride were performing 15 % better than manganese dichloride as chromium is more reactive and have multiple valancies compared to manganese. Both the catalysts were performing 20 -25% better than the original PU matrices without sealing agents.

CONCLUSIONS

The concept of a self□healing is a relatively new area of technological interest with many potential applications to fields ranging from electronics to biomedical interest. The inherently complex interaction of design parameters in a composite system makes it difficult to apply theoretical models to explain macroscopic properties. A variety of experimental techniques were used to understand various aspects of materials science and engineering challenges necessary to fabricate a composite material. The observations of microstructure suggest that a general microencapsulation process can be adapted to diverse polymer matrices with careful attention to surface characterization. DCPD encapsulated urea formaldehyde microcapsules were prepared and shows the chemical characteristics and surface study shows the consistency of the microcapsules. SEM and optical microscopy results confirms the presence of the microcapsules in the PU matrix. These microcapsules can be initiated for self healing of the matrices and repair the crack by itself when damaged. The Grubb's catalyst was replaced by much simpler and easily available catalyst looking into the similar working as per the chemical configuration of the transition metals. Grubb catalyst belongs to ruthenium chloride based structure. Physical properties of the composites

were studied and the working of the healing agents with the catalysts were analyzed for self healing characteristics.

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