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Self-Healing Polymer Nanocomposites for Composite Structure Applications

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Abstract

There has been an increased research demand as potential applications emerge with the synthesis of self-healing nano-composites. Here a novel approach for using the self-healing capable nanocomposites as a sacrificial layer in carbon-fibre reinforced structures is proposed. The idea is very innovative and easily scalable to composite structures, it helps in both detection and healing of the induced damages. Firstly, the nanoparticles were coated using tri-phasic reverse emulsion method, and then used in the synthesis of polymer-nanocomposite (PNC) using in-situ polymerisation; this ensured and aided in the formation of designed interfaces and effective dispersion of nanoparticles. The PNC was characterised using FT-IR, DSC, XRD and TEM. Testing of the concept was done using synthesized nanocomposite as a sacrificial layer sandwiched between two carbon fibre reinforced unidirectional tapes, and the damaged region of carbon-fibre was effectively healed upon the heat stimuli, hence hinting its applicable potentiality to improve life and endurance of various composite structure.

Keywords — Self-Healing, Intelligent Material, Polymer, Nanocomposite, Composite Structures, Iron Oxide, Nanoparticles, In-Situ Polymerization, Tri-Phasic Reverse Emulsion.

Introduction

The traditional approach of damage detection and subsequent manual repair/replacement result into a costly and time consuming affair; despite being completely reliable [1]. The research in the quest of stronger and better materials have reached its extent, and only the way further for demanding applications is to implement simultaneous detection and repair mechanism in the materials. These materials are inspired by the nature's arrangement of healing, particularly in the human bones. The human body can be considered as colossal supported by the feeble bone structure, if talking in terms of weight-ratio for instance, and bones are considered as extraordinary structural material, not because they are very strong but have the tendency to self-heal. It has been reported that up to 80% crack arrestment and optimum performance for first 5-6 times, is readily possible with self-healing concept [2].

Over the years, there are many techniques proposed for achieving self-healing, broadly classified as extrinsic and intrinsic. In the extrinsic system, the healing agent is supplied externally, either via vascular networks or embedded in form of capsules in the polymer matrix itself. The amount of supply of healing agent is not a problem here, though there is a tendency of the network getting blocked over a period of time, rendering the whole thing useless. Additionally, the dense network severely degrades the strength of the entire structure, hence limiting their applications [3]. Though this limitation is overcome by using the nanoparticles (NP's) dispersed intrinsic system. Here, the healing occurs by the nanoparticle's response to an external stimuli and bringing about bond reformation in the area of application. Repetitive healing is not a concern, as the polymer with dispersed NP's can be melted multiple times to fill the crack.

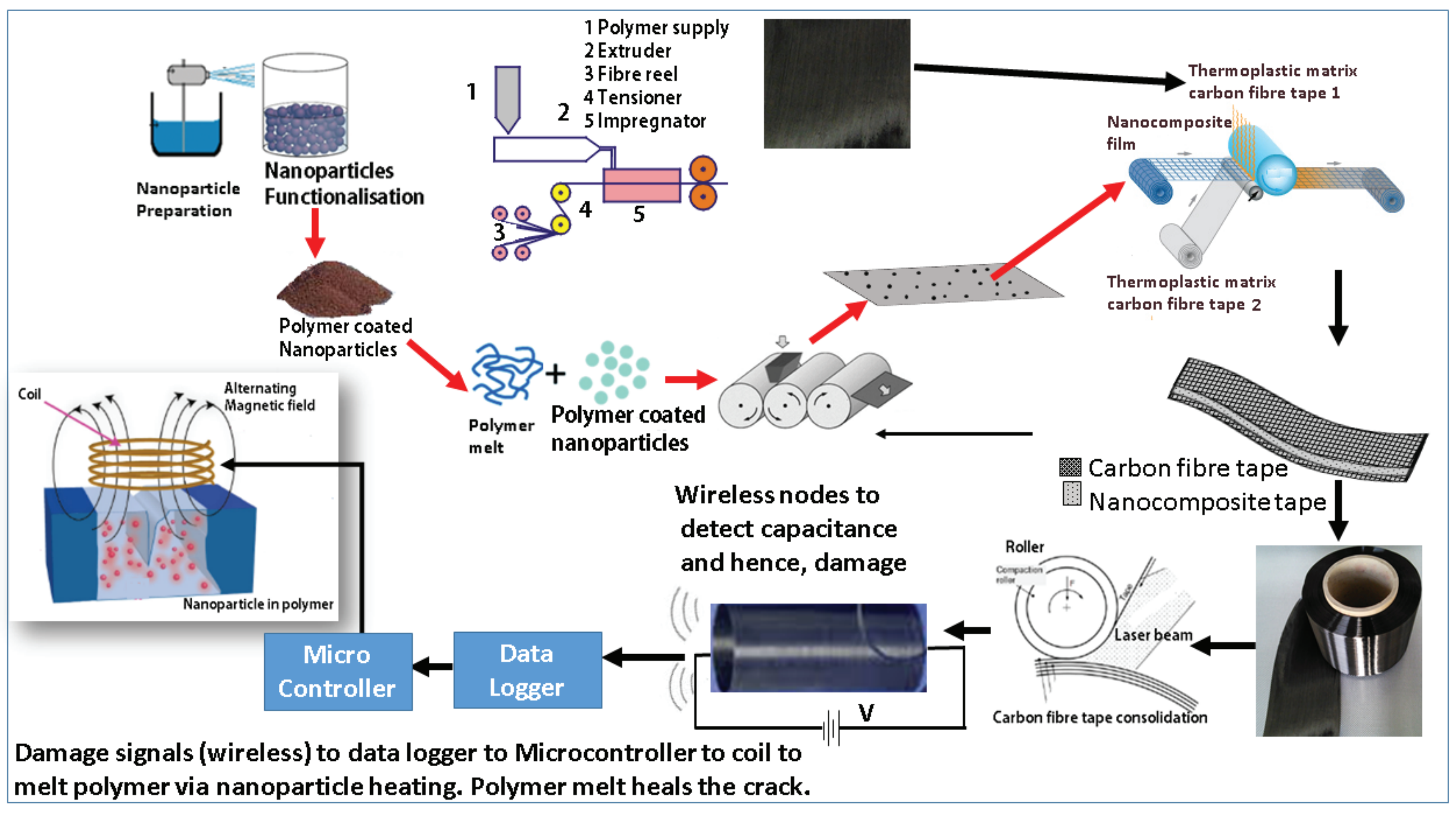

***Figure 1**: Schematic showing concept of bulk sandwich tapes with processing steps to prepare tubular structure and its intelligent healing process using magnetic flux stimuli.*

The process schematic is represented in the figure 1. Sandwiching the polymer nanocomposite (PNC) in between the carbon fibre reinforced tapes, creates a similar network as that of the vascular system, hence we get the benefits of both – the extrinsic vascular system and the intrinsic nanoparticle system. Hence, the novelty as a hybrid healing system. The iron oxide NP's were coated by tri-phasic reverse emulsion (TPRE) method, in-order to create designed interfaces for interpolating the ionic surface charges and enhancing adhesion with the base polymer matrix.

Methods

Firstly, 150 mg of iron oxide particles were introduced into a mixture of 30ml toluene and 5g of span-85 and shaken to form a TPRE. 3-Aminopropyl triethoxy silane was added to a final concentration of 2% w/v and allowed to react in condenser at 50 °C in an oil bath for 5 hrs under constant stirring; then decanted and washed three times with coupling solution of 0.8% (v/v) glacial acetic in dry methanol. Now, 15g of ε-caprolactam (CL) was taken and melted at 90 °C, then the coated NPs were introduced and sonication at 20 KHz for 20 minutes, to break down any agglomeration. Further the mixture was brought to 155 °C, and 0.43ml of catalyst ethylmagnesium bromide (EtMgBr), followed by 0.47ml of initiator N-acetyl caprolactam (NACL) were introduced under inert gas flush. Because, EtMgBr is an efficient anionic initiator, the polymerisation of CL was very quick. Therefore, the nanoparticles didn't settle down at the bottom of the flask and most were captured in polymer as uniformly dispersed.

Results

The peaks observed in FT-IR, as shown in figure 2(a), the amine peak at 3293 cm^{-1} attributed to N-H bond, and methylene stretch at 2934 cm^{-1} match well with that of a standard sample; hence confirming successful polymerisation of PA6. DSC results, figure 2(b), depict the effect of NP's addition on the shift in glass transition temperature (T_g) and melting temperature (T_m).

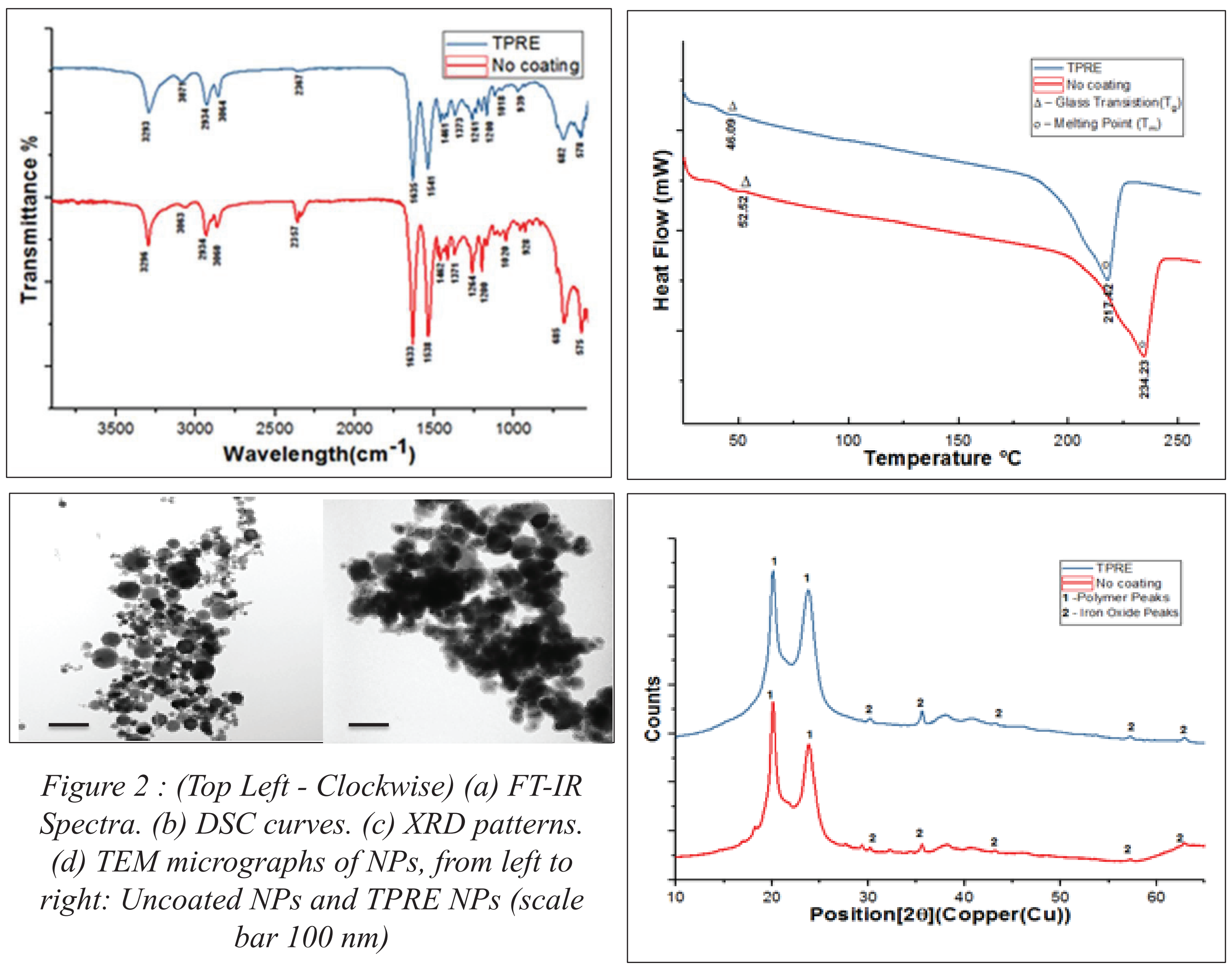

Figure 2 : (Top Left - Clockwise) (a) FT-IR Spectra. (b) DSC curves. (c) XRD patterns. (d) TEM micrographs of NPs, from left to right: Uncoated NPs and TPRE NPs (scale bar 100 nm)

The noticeable endothermic peak the drop in T_g 52.52 °C to 46.09 °C and the T_m is shifted to 217.42 °C from 234.23 °C after using TPRE prepared NP's; hence indicating suitability of this PNC for self-healing applications as compared with a regular PNC. Also, the heat fusion from the thermogram gave the percentage crystallinity of 54.67% and 51.36% for no-particles and the TPRE sample; which are comparable with a standard PA-6 sample [4]. In the XRD pattern, Figure 2(c) the two-dominant monoclinic crystallite phases viz. the α-phase indexed as (200) and (002)/(202), and γ-phase with corresponding indexes of (020), (001) and (200)/(201), are seen to appear at around 21° and 24°; confirming the prominent PA-6 presence in the sample. Using FWHM the crystallite sizes of the NP's was found as 41.76 nm and 30.93 nm for uncoated and coated NP's respectively. TEM images, figure 2(d), were taken to confirm the nature of NP's; and it confirms that the NP's are coated and are much more distributed, rather than getting ionically attracted.

From impedance measurement of the carbon fibre tape, the capacitive change before and after induced crack can be noted. The synthesised PNC is made into fine films and fixed between two carbon fibre tapes. The prepared sample is as shown in the figure 3. Upon heat stimuli the sacrificial PNC layer, sandwiched between the two carbon fibre tapes melted and filled the crack area, rearranging the melt volume.

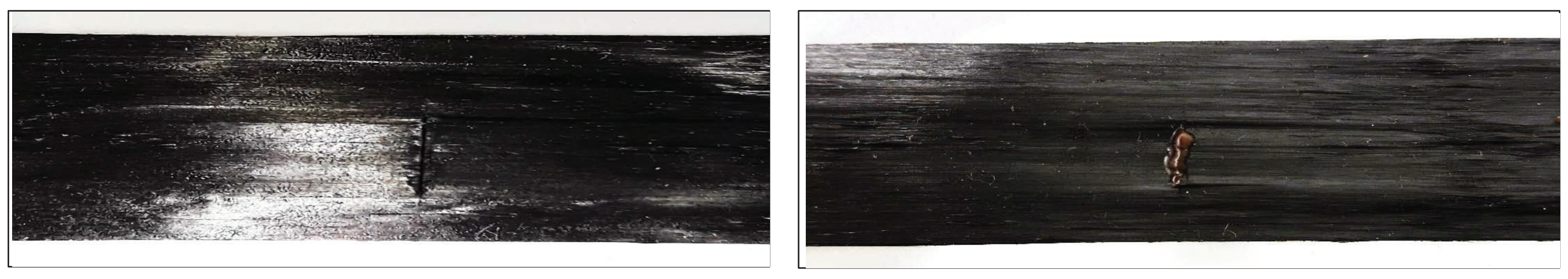

***Figure 3**: Damaged sample and repair after heat stimuli. (Left to Right).*

Conclusions

The quick response of the PNC is due to inclusion of the NP's, as the NP's absorb more heat and bring about the localized melting of the polymer. Also, for uniform melting the NP's are needed to be uniformly dispersed along the polymer matrix. This was achieved by first of all coating the NP's, so they don't agglomerate when brought together; and secondly by involving in-situ polymerisation of the PNC, here using sonicator the NP's are dispersed well and then quickly captured in dispersed positions by quick polymerisation.

The application of such technique can be helpful in both, detection and repair of cracks. And can be easily scaled to all types of composite structures, leading to sustainable designs with very long life.

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