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High performing smart hyperbranched polyurethane nanocomposites with efficient self-healing, self-cleaning and photocatalytic attributes

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1. Characterization

UV spectrophotometer, Hitachi (U2001, Tokyo, Japan) was employed to record UV-visible absorption spectra of nanomaterial and nanocomposites in aqueous solution. X-ray diffraction analysis of the purified nanoparticles and nanocomposites were conducted by using a D8 FOCUS P-XRD machine (Bruker AXS, Germany) operating at a wavelength of 1.5 Å, over the range of 2θ = (10-80)°, at a scanning rate 2.0 min^{-1}. An EDX spectrophotometer (JEOL-JSM 6390, Japan.) was used to confirm the elemental composition of the nanoparticles and nanocomposites. A JEOL JEMCXII transmission electron microscope (TEM) at an operating voltage of 200 kV was employed to determine the size and state of dispersion of the nanomaterials in the nanocomposites. The FTIR spectra of the prepared nanocomposites and nanomaterials were recorded on a Nicolet FTIR spectrophotometer (Impact-410, Madison, USA) using KBr pellets. Mechanical properties (tensile strength and elongation at break) of the nanocomposite films were measured by a Universal Testing Machine (UTM, Zwick Z010, Germany) equipped with a 500 N load cell operated at a crosshead speed of 50 mm/min (ASTM D 638). The scratch hardness of the polymeric films was determined by a scratch hardness tester, Model No. 705 (Sheen instrument limited, UK) with a stylus accessory at a travel speed of (30-40) mm/s. Thermal properties were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies. Thermogravimetric study was carried out by means of a PerkinElmer 4000 thermal instrument, in the temperature range of (25-700) °C, at a scanning rate of 10 °C/min, keeping up an inert atmosphere of nitrogen at a gas flow rate of 30 mL/min. The differential scanning calorimetric study was conducted by a PerkinElmer DSC 6000 (USA) instrument in the temperature range of (-50 to +200) °C (starting temperature = 0 °C) following a cycle of heating-cooling-heating under an atmosphere of nitrogen (at 30 mL/min flow rate) and at a scanning rate of 3 °C/min.

2. Shape memory test

To study the shape-memory behavior of HPU and its nanocomposites, strip samples were heated at 60 °C for 5 min and transformed into a spiral shape. Immediately, the spiral samples were immersed in an ice-water salt bath at -(15 ± 5) °C for 10 min to fix the temporary shape. The shape fixity of the cooled films was observed by drying them under vacuum followed by placing at room temperature (25 °C) for 30 min. Consequently, the fixed films were exposed to non-contact stimuli such as MW irradiation of 360 W for 20-30 s and under direct sunlight (11 am - 2 pm, at Tezpur University campus, altitude: 26.63 °N 92.8 °E in the month of June at sunny days, average temperature: 34 + 1 °C and humidity: 74 + 1%) under ambient condition. The shape recovery and the time required to retain original shape was noted. The shape recovery and shape fixity were calculated from the subsequent equations:[1-3]

Shape recovery (%) = $[(90-\theta)/90] \times 100$ …….. (i)

Shape fixity (%) = $[\theta/90] \times 100$ …….. (ii)

Where θ (degree) = Angle between the tangential line at the midpoint of the film and the line connecting the midpoint and the end of the curved film. The results are consistent as the test is repeated for five times.

3. Self-healing test

To determine the healing performance, films with a thickness of 0.5 mm of the nanocomposite were cut (10 x 0.2 x 0.015 mm^3 in dimension) in a transverse direction by a razor blade, and the cracked was healed by sunlight or MW, separately.

The optical images of the damaged, partially healed and completely healed films were captured at 10X magnification by Motic polarising microscope (BA310Pol, China). The healing efficiency was calculated as the ratio of the tensile strength values of the nanocomposites before and after healing.[2] The tensile strengths of the pristine and the healed samples were measured by the same UTM. Samples were cut into strips of 80 mm x 10 mm x 0.50 mm for testing. The tensile strengths of pristine HPU, as well as the nanocomposites with different loadings of the nanohybrid were measured for at least four samples in each case, before and after the healing process. The optimal healing time for each case was defined as the shortest time required achieving the best healing efficiency under the given conditions. For MW healing, a domestic microwave oven (360 W) operating at a frequency of 2.45 GHz was used. Sunlight healing was performed under direct sunlight (11 am-2 pm) at Tezpur University campus (altitude: 26.631N 92.81E) in the month of November on sunny days [average temperature (29 ± 1 °C) and humidity (65 ± 1%)], with a light intensity of 90,000-100,000 lux.

References

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