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Bioinspired Material Design Based On Switching of Dynamic Properties of Materials

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Since early days scientists have been inspired by nature. Even today inspiration is drawn from nature to fabricate bio-friendly and mechanically responsive nano-composites. Such materials can have biomedical applications such as in tissue engineering, artificial organs and in management of diseases like Parkinson's disease and spinal cord injuries.

The sea cucumber Cucumaria frondosa, (figure-I) an echinoderm, has unique abilities to rapidly and reversibly alter its passive mechanical properties viz. tensile strength and stiffness within few seconds in response to the signals from the nervous system. This feature is attributed to the mutable collagenous tissue (MCT) present in the inner dermis. The MCT comprises of discontinuous collagen fibrils connected by a viscoelastic matrix. Recently, Capadona et al. have reported a family of nano-composites which can mimic this architecture and display similar adaptability to external stimuli. They synthesized a viscoelastic matrix composed of a rubbery copolymer consisting of 1:1 ethylene oxide/epichlorohydrin (EO/EPI) and collagen fibrils (figure-II) held by cellulose nanofiber "whiskers". Its stiffness and dimensions (26nm×2.2μm) can be exploited for use as composite filler. The nanocomposites were prepared in two steps. First, a nanofiber template was synthesized through sol-gel process which was subsequently filled with a desirable polymer. The nanocomposites were then processed by solution casting and compression modelling [1].

Figure I: A picture of a sea cucumber

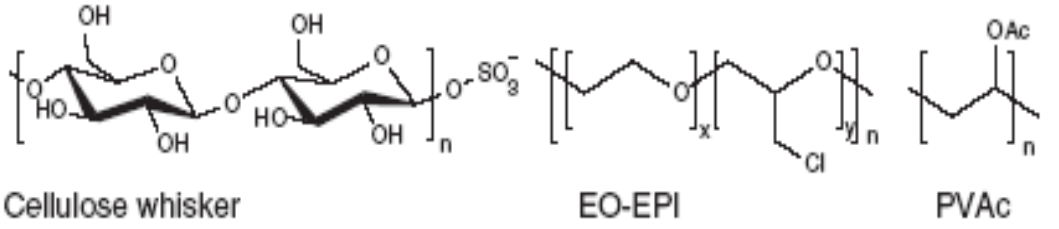

Figure II: Chemical structure of cellulose whiskers and the EO-EPI and PVC matrix polymers.

The loading of whiskers was reported to change the tensile storage modulus from 3.7 MPa (for neat sample) to 800 MPa (approximately 200 times, for loaded sample). It also resulted in decrease in the elongation at break from 360±20 to 6.7±0.8 % and increase in tensile strength from 0.27±0.04 to 1.71±0.23. This can be accredited to the formation of a homogeneous percolated network within the rubbery EO/EPI–cellulose matrix, capable of transferring the stress directly from whiskers to whiskers [2]. This stress transferring capability arises from the hydrogen bonding interactions between hydroxyl groups of cellulose. Hydrogen bonding interactions between the cellulose whiskers were investigated using solvents such as water and iso-propyl alcohol (IPA) [1, 2]. Whiskers' self-interaction was "switched off" by the introduction of these hydrogen bonding solvents and upon removal of solvents the interactions among the whiskers were "switched on" (figure-III). In other words, strong hydrogen bonding interactions between the solvent (water and IPA) with the hydroxyl groups of celloluse inhibited self-interactions. This decoupling and coupling behaviour upon introduction and removal of the solvent formed the basis of stress transferring property and dynamic mechanical adaptability. When these nanocomposites were immersed in water for two days, the tensile storage modulus decreased from 800MPa to 20 MPa (40 fold at 19% v/v whisker composite), while the tensile strength decreased from 1.71±0.23 to 0.37±0.11 MPa for 14.3 % v/v whisker, along with increase in

elongation at break from 6.7±0.8 to 17.8±0.39%. However, the nanocomposite regained its original stiffness when it was dried.

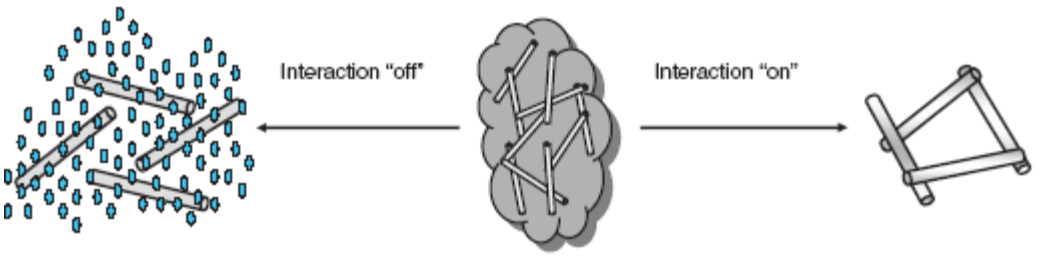

Figure III: Schematic representation of the switching mechanism of hydrogen bond in the designed nanocomposites on introduction and removal of the hydrogen bonding solvent

High interactions between hydroxyl groups cause the aggregation of cellulose whiskers. Therefore a few alterations have also been tried such as introduction of sulphate groups (to moderate hydrogen bonding interactions) and replacement of EO/EPI with PVAc [Poly(vinylacetate)] in the matrix. The thermo-mechanical properties were established by dynamic mechanical analysis experiments which shows that glass transition temperature (T_g) of neat PVAc is 42°C whereas that of EO/EPI is -37°C (independent of the whiskers loading between 0 to 19 %). The mechanical properties of the PVAc-cellulose whiskers are dependent on temperature changes from ambient (ca. 23°C) to physiological temperature (37°C). On heating the tensile storage modulus of neat PVAc polymer reduced from 1.8 GPa (at 23°C) to 0.39 MPa at 56°C (Tg + 16°C). When PVAc nanocomposites were made by varying the whisker loading (from 0 to 16.5 % v/v) no significant change (5.1 GPa for 16.5 % v/v) in tensile storage modulus was observed below Tg. Whereas at 56°C(T_g + 16°C) the tensile storage modulus increased from 1.0 MPa (for neat) to 814 Mpa (for 16.5% v/v whiskers). Disassembling of whiskers network occur upon exposure to the physiological condition due to phase transition. Lowering of T_g below physiological temperature (19 to 23°C) and tensile storage modulus were observed when these nanocomposites were introduced to solvent. PVAc – cellulose whisker swollen in artificial cerebrospinal fluid (ACSF) for 15 min. showed decrease in tensile storage modulus from 4.2 GPa (required for easy insertion into the cortex) to 1.6 MPa at physiological temperature. This mechanical transition is compatible to the soft brain tissue since micro motion leads to tissue damage and microelectrodes failure.

In spite of having sufficient activity it is necessary to decrease the response time of synthetic materials to few seconds as observed in C. frondosa. The effects of non-chemical stimuli viz. optical and electrical are also to be explored. Loss of signal quality in current microelectrodes within a few months has made long term applications challenging. To alleviate this problem it is required to design mechanically adaptive microelectrode devices.

This article features one application where in the inspiration has been drawn from nature, however, there are many more on-going challenges in this field of research.

References:

1. Angew. Chem. In. Ed., 2008, 47, DOI: 10.1002/anie.20080233.

2. Science, 319, 1370, 07-mar-2008.