The present invention generally relates to self healing polymer nanocomposites and to a process for the preparation of the self healing polymer nanocomposites. The nanocomposite may comprise a macromolecule, a crosslinking agent for non-covalent bonding with the macromolecule and a nano filler. The crosslinking agent may be urea and the macromolecule may be a condensation polymer such as polyamide. The nanocomposites exhibit autonomous self-healing behaviour.
SELF-HEALING POLYMER NANOCOMPOSITES AND PROCESS FOR THE PREPARATION THEREOF

FIELD OF THE INVENTION

[0001] The present invention generally relates to self-healing polymer nanocomposites and to a process for the preparation of the self-healing polymer nanocomposites.

BACKGROUND

[0002] A rapidly rising field of polymer technology is that of nanocomposites. Nanocomposites can be prepared by dispersing nanometre sized particulate material throughout a host polymer matrix. Such nanocomposites can demonstrate superior chemical or physical properties compared with conventional polymer composites, or the host polymer in absence of any reinforcing particles, and often these improved properties can be attained using a moderately small quantity of nanoparticles.

[0003] Nanocomposites are of commercial interest to a number of industries, including the aerospace industry and the packaging industry, because of the superior properties exhibited by many nanocomposites.

[0004] However, nanocomposite materials can be subject to failure due to damage initiated by various external factors. For example, the physical or chemical behaviour of a nanocomposite may be altered under the influence of elevated temperature, pressure, mechanical stress or impact, chemical degradation, or other external stresses. Such changes in physical or chemical behaviour can trigger the appearance of cracks in the nanocomposite, resulting in damage of the material so it can no longer perform as required or fulfil its intended utility. Such damage is particularly problematic when nanocomposites are used in high performance parts, such as for the aerospace industry. For this reason, parts need to be frequently checked and may need to be repaired or replaced on many occasions, leading to increased cost.
Polymer materials capable of "self-healing" in response to damage are of increasing interest. One self-healing composite material has been described by White, et al (Nature, 2001, 409, 794-797). This material includes microcapsules containing healing promoting agents embedded in a polymer composite matrix, and a catalyst that is also incorporated in the polymer matrix. When damage occurs to the material, the healing agents are released into presence of the catalyst, promoting a polymerisation reaction that generates a polymer to fill in the damaged area. This filling arrests fracture dissemination and reduces the fatal damage of the material. However, one disadvantage with this material is that even under ordinary stresses and normal use, the microcapsules can open and the healing agent and catalyst can react with each other. A further disadvantage is that the material is not able to readily self heal again if damage occurs again at the same site.

It would be desirable to provide a self-healing nanocomposite that addresses one or more of the above disadvantages.

The above discussion of the background to the invention is intended to facilitate an understanding of the invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was published, known or part of the common general knowledge as at the priority date of the application.

SUMMARY

In accordance with a first aspect of the present invention there is provided a self healing nanocomposite including:

- a crosslinked matrix, said matrix including a macronnuclele including a plurality of functional groups and a crosslinking agent including a plurality of functional groups, wherein the functional groups of the macronnuclele interact with the functional groups of the crosslinking agent by non-covalent bonding interactions to form non-covalent bonds between the macronnuclele and the crosslinking agent; and

- a nanofiller dispersed in the matrix.
In embodiments of a self-healing nanocomposite of the invention, the non-covalent bonds may be hydrogen bonds.

In embodiments of a self-healing nanocomposite of the invention, the functional groups of the macromolecule are selected from the group consisting of hydrogen donating functional groups, hydrogen accepting functional groups, and mixtures thereof. In some embodiments, the functional groups of the macromolecule may each be independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups. In some embodiments, the functional groups of the macromolecule may each be independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups.

In embodiments of a self-healing nanocomposite of the invention, the macromolecule may be a condensation polymer. In one such embodiment, the macromolecule may be formed from the condensation polymerisation of two or more monomers including compatible reactive functional groups. For example, the macromolecule may be formed from the condensation polymerisation of a polyacid monomer and a polyamine monomer. In another such embodiment, the macromolecule is formed from the condensation polymerisation of a monomer including two or more compatible reactive functional groups.

In embodiments of a self-healing nanocomposite of the invention, the macromolecule may have a moiety having a structure of Formula (II):

\[
\begin{align*}
\left( \begin{array}{c}
\vdots \\
R^1
\end{array} \right) & \quad \left( \begin{array}{c}
X \\
\vdots \\
A
\end{array} \right)^m \quad \left( \begin{array}{c}
\vdots \\
A
\end{array} \right)^n \\
\end{align*}
\]

(II)

where

\( X \) at each occurrence is independently selected from the group consisting of \( O \) and \( N \);
A at each occurrence is independently selected from the group consisting of O and NH, where R is H or alkyl (preferably Ci-C₄ alkyl);
R¹ represents the remainder of a first monomer unit;
R² represents the remainder of a second monomer unit;
m represents the number of repeating units for the first monomer and is at least 1; and
n represents the number of repeating units for the second monomer is an integer and is at least 1.

[0013] In embodiments of a self-healing nanocomposite of the invention, the macromolecule may be a polyamide including a plurality of amine functional groups.

[0014] In embodiments of a self-healing nanocomposite of the invention, the functional groups of the crosslinking agent may each be independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups. In some embodiments, the functional groups of the crosslinking agent may each be independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups. In one embodiment, the functional groups of the crosslinking agent are each amide functional groups. An exemplary crosslinking agent may be a diamide crosslinking agent, such as urea.

[0015] In embodiments of a self-healing nanocomposite of the invention, the nanofiller may include one or more selected from the group consisting of nanofibres, nanosheets, nanoparticles, nanotubes, graphitic nanofillers, nanowhiskers, metal phosphates, layered double hydroxides, nanocalcium, and metal chalcogenides.

[0016] In embodiments of a self-healing nanocomposite of the invention, the nanofiller includes a plurality of nanoparticles. In such embodiments, the nanoparticles may be nanoclay particles. The nanoclay particles may be derived from a clay selected from the group consisting of pristine clays and organically-modified clays. In one embodiment, the nanoclay particles may be
capable of cation exchange. In another embodiment, the nanoclay particles may be layered silicate clay particles.

[0017] When used in a self-healing nanocomposite of the invention, nanoclay particles may be selected from the group consisting of montmorillonite, mica, bentonite, kaolinite, saponite, halloysite, hectorite, fluoro mica, fluoro hectorite, vermiculite, and magadiite particles.

[0018] In embodiments of a self-healing nanocomposite of the invention, the nanofiller may present in an amount in a range selected from the group consisting of from about 0.5% to about 50%, from about 2% to about 10%, and from about 3% to about 5%, by weight of the nanocomposite.

[0019] In some embodiments, a self-healing nanocomposite of the invention has a structure selected from the group consisting of an intercalated structure, an exfoliated structure, and a flocculated structure.

[0020] In some embodiments, a self-healing nanocomposite of the invention self heals at a temperature in the range of from about 0 °C to about 300 °C.

[0021] In some embodiments, a self-healing nanocomposite of the invention self heals within a time period selected from the group consisting of about 72 hours, about 48 hours, about 24 hours, about 6 hours, about 2 hours, about 1 hour, about 30 minutes, about 5 minutes, and about 1 minute.

[0022] Desirably, a self-healing nanocomposite of the invention exhibits repeated self-healing.

[0023] In accordance with a second aspect of the present invention there is provided a process for the preparation of a self-healing nanocomposite including the steps of:

- providing a macromolecule including a plurality of functional groups, a crosslinking agent including a plurality of functional groups, and nanofiller in a reaction vessel; and
forming non-covalent bonds between the functional groups of the macromolecule and the functional groups of the crosslinking agent in the presence of the nanofiller to provide a nanocomposite including a crosslinked matrix and a nanofiller dispersed in the matrix.

[0024] In embodiments of a process of the invention, the non-covalent bonds may be hydrogen bonds.

[0025] In embodiments of a process of the invention, the functional groups of the macromolecule may be selected from the group consisting of hydrogen donating functional groups, hydrogen accepting functional groups, and mixtures thereof. In some embodiments, the functional groups of the macromolecule may be each independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups. In one embodiment, the functional groups of the macromolecule may each be independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups.

[0026] In embodiments of a process of the invention, the process may include the step of forming a macromolecule in the reaction vessel to provide the macromolecule in the reaction vessel. In such embodiments, the macromolecule may be a condensation polymer.

[0027] Where the macromolecule is a condensation polymer, one embodiment of the process of the invention may include the step of reacting two or more monomers having compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more monomers to form the macromolecule in the reaction vessel.

[0028] Where the macromolecule is a condensation polymer, another embodiment of the process of the invention may include the step of reacting a monomer having two or more compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more reactive functional group to form the macromolecule in the reaction vessel.
[0029] In one embodiment of the process of the invention, the macromolecule may be a polyamide polymer. In one form of such an embodiment, the process of the invention may include the step of reacting a polyacid monomer and a polyamine monomer to form a polyamide macromolecule in the reaction vessel.

[0030] In embodiments of a process of the invention, the process may include the step of adding a crosslinking agent to the reaction vessel to provide the crosslinking agent in the reaction vessel, wherein the crosslinking agent is added during or after formation of the macromolecule in the reaction vessel.

[0031] In embodiments of a process of the invention, the functional groups of the crosslinking agent may each be independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups. In some embodiments, the functional groups of the crosslinking agent may each be independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups. In one embodiment, the functional groups of the crosslinking agent may each be amide functional groups. An exemplary crosslinking agent is a diamide crosslinking agent, such as urea.

[0032] In embodiments of a process of the invention, the process may include the step of adding a nanofiller to the reaction vessel to provide the nanofiller in the reaction vessel. The nanofiller may be added before, during, or after the addition of the crosslinking agent in the reaction vessel. In one form of this embodiment, the crosslinking agent and the nanofiller are added to the reaction vessel at approximately the same time.

[0033] In embodiments of a process of the invention, the nanofiller includes a plurality of nanoparticles. In some embodiments, the nanoparticles are nanoclay particles.

[0034] Where nanoclay particles are used in the process of the invention, the nanoclay particles may be derived from a clay selected from the group
consisting of pristine clays and organically modified clays. In one embodiment, the nanoclay particles are capable of cation exchange. The nanoclay particles may be layered silicate clay particles.

[0035] Where nanoclay particles are used in the process of the invention, the nanoclay particles may be selected from the group consisting of montmorillonite, mica, bentonite, kaolinite, saponite, halloysite, hectorite, fluoromica, fluorohectorite, vermiculite, and magadiite particles.

[0036] In embodiments of a process of the invention, the process may include the step of heating the reaction vessel containing the macromolecule, the crosslinking agent and the nanofiller. In such embodiments, the reaction vessel may be heated at a temperature in the range of from about 20 °C to about 300 °C. In some embodiments, the reaction vessel is heated at a temperature in the range of from about 140 °C to about 180 °C.

[0037] In accordance with a third aspect of the present invention there is provided a self healing product including a self-healing nanocomposite of any one of the embodiments described herein.

[0038] In accordance with a fourth aspect of the present invention there is provided a self healing coating including a self-healing nanocomposite of any one of the embodiments described herein.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0039] The present invention will now be described with reference to the figures of the accompanying drawings, which illustrate particular preferred embodiments of the present invention, wherein:

[0040] Figure 1 shows characteristic XRD patterns of a crosslinked polymer matrix (SMP), for montmorillonite clays Cloisite Na⁺ (CNa⁺), Cloisite 25A (C25A) and Cloisite 30B (C30B), and for modified layered silicate nanocomposites SMPNa⁺, SMPA and SMPB in accordance with one form of the invention.
[0041] Figure 2 shows optical microscope images of nanocomposite SMPB of one form of the invention taken (a) 2 seconds, (b) 10 seconds, (c) 20 seconds, (d) 40 seconds, (e) 60 seconds, and (f) 90 seconds after a cut is made on the surface of the nanocomposite material.

[0042] Figure 3 is a graph showing relaxation modulus as a function of time for various polymer nanocomposites (SMPNa+, SMPA and SMPB) in accordance with one form of the invention, when compared with a crosslinked polymer matrix (SMP), with a schematic representation of a DMA compression test on the polymer nanocomposite shown in inset.

[0043] Figure 4 is a graph showing stress-strain curves for an original and a healed polymer nanocomposite SMPNa+ in accordance with one form of the invention.

[0044] Figure 5 is a graph showing % weight loss versus temperature (°C) for samples of macromolecule pre-polymer, a crosslinked polymer matrix (SMP), and polymer nanocomposites SMPNa+, SMPA and SMPB in accordance with one form of the invention.

[0045] Figure 6 is a DSC thermogram of samples of macromolecule pre-polymer, a crosslinked polymer matrix (SMP), and polymer nanocomposites SMPNa+, SMPA and SMPB in accordance with one form of the invention.

[0046] Figure 7 is a DSC thermogram comparing results obtained for nanocomposites containing Cloisite 25A (C25A) and a crosslinked polymer matrix prepared with various polyamide pre-polymers in accordance with embodiments of the invention.

[0047] Figure 8 is a graph showing % weight loss versus temperature (°C) for nanocomposites containing Cloisite 30B (C30B) and a crosslinked polymer matrix prepared with various polyamide pre-polymers in accordance with embodiments of the invention.
[0048] Figure 9 shows characteristic XRD patterns of nanocomposites containing Cloisite 25A (C25A) and a crosslinked polymer matrix prepared with various polyamide pre-polymers in accordance with embodiments of the invention.

[0049] Figure 10 shows characteristic XRD patterns of nanocomposites containing Cloisite 30B (C30B) and a crosslinked polymer matrix prepared with various polyamide pre-polymers in accordance with embodiments of the invention.

**DETAILED DESCRIPTION**

[0050] Various terms that will be used throughout the specification have meanings that will be well understood by a skilled addressee. However, for ease of reference some of these terms will now be defined.

[0051] As used herein, the term "macromolecule" refers to molecular species that may be oligomeric or polymeric. Oligomers and polymers are generally formed from the polymerisation of one or more monomers. Oligomers contain fewer monomer units than polymers and therefore, are generally of lower molecular weight. As an example, oligomers may contain from 2 to 10 monomer units, while polymers may contain more than 10 monomer units.

[0052] As used herein, the term "crosslinking agent" refers to a compound that promotes intermolecular bonding between macromolecule chains. The intermolecular bonding interactions result in the formation of a three-dimensional crosslinked matrix.

[0053] As used herein, the term "compatible reactive functional group" refers to a chemical functional group that is capable of undergoing reaction with another chemical functional group to form a covalent intermolecular bond there-between.
As used herein the term "optionally substituted" is taken to mean that a group may or may not be substituted or fused (so as to form a condensed polycyclic group) with one, two, three or more of organic and inorganic groups (i.e. the optional substituent) including those selected from: alkyl, alkenyl, alkynyl, carbocyclyl, aryl, heterocyclyl, heteroaryl, acyl, aralkyl, alkaryl, alkheterocyclyl, alkheteroaryl, alkcarbocyclyl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, halocarbocyclyl, haloheterocyclyl, haloheteroaryl, haloacry, haloaryalkyl, hydroxy, hydroxylalkyl, hydroxyalkenyl, hydroxyalkynyl, hydroxycarbocyclyl, hydroxyaryl, hydroxyheterocyclyl, hydroxyheteroaryl, hydroxyacyl, hydroxyaralkyl, alkoxyalkyl, alkoxyalkenyl, alkoxyalkynyl, alkoxyacyl, alkoxyaralkyl, alkoxy, alkenyl, alkynyl, alkenyloxy, alkynloxy, aryloxy, carbocyclyloxy, aralkyloxy, heteroaryloxy, heterocyclyloxy, acyloxy, haloalkoxy, haloalkenyl, haloalkynyl, haloaryl, halocarbocyclyloxy, haloheterocyclyloxy, haloheteroaryloxy, haloheterocyclyloxy, haloacyloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, nitroheteroaryl, nitrocarbocyclyl, nitroacyl, nitroaralkyl, amino (NH$_2$), alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, aralkylamino, diaralkylamino, acylamino, diacylamino, heterocyclamino, heteroarylamino, carboxy, carboxyester, amido, alkylsulphonyloxy, aryl sulphenyl, alkoxysulphenyl, arylsulphenyl, thio, alkylthio, alkenythio, alkynylthio, arylthio, aralkylthio, carbocyclythio, heterocyclythio, heteroarylothio, acylthio, sulfoxide, sulfonyl, sulfonamide, aminoalkyl, aminocyclyl, aminoalkenyl, aminoalkynyl, aminocarbocyclyl, aminoaryl, aminoheterocyclyl, aminoheteroaryl, aminocyclyl, aminoaralkyl, thioalkyl, thioalkenyl, thioalkynyl, thiocarbocyclyl, thioaryl, thioheterocyclyl, thioheteroaryl, thioacyl, thioaralkyl, carboxyalkyl, carboxyalkenyl, carboxyalkynyl, carboxyacyl, carboxycarbocyclyl, carboxyaryl, carboxyheterocyclyl, carboxyheteroaryl, carboxyacyl, carboxyaryl, carboxyesteralkyl, carboxyesteralkenyl, carboxyesteralkynyl, carboxyestercarbocyclyl, carboxyesteraryl, carboxyesterheterocyclyl, carboxyesterheteroaryl, carboxyesteracyl, carboxyesteraralkyl, amidoalkyl, amidoalkenyl, amidoalkynyl, amidocarbocyclyl, amidoaryl, amidoacyl, amidoaryl, amidoacyl, amidoalkyl, amidoalkenyl, amidoalkynyl, amidocarbocyclyl, amidoaryl, amidoacyl, formylalkyl, formylalkenyl, formylalkynyl, formylcyclyclyl, formylaryl, formylheterocyclyl,
formylheteroaryl, formylacyl, formylaralkyl, acylalkyi, acylalkenyl, acylalkynyl, acylcarbocyclyl, acylaryl, acylheteroaralkyl, acylacyl, acylheterocyclyl, acylheteroaryl, acylacyl, acylaralkyl, sulfoxidealkyl, sulfoxidealkenyl, sulfoxidealkynyl, sulfoxidecarbocyclyl, sulfoxidearyl, sulfoxideheterocyclyl, sulfoxideheteroaryl, sulfoxideacyl, sulfoxidearalkyl, sulfonylalkyl, sulfonylalkenyl, sulfonylalkynyl, sulfonylcarbocyclyl, sulfonylaryl, sulfonylheterocyclyl, sulfonylheteroaryl, sulfonylacyl, sulfonylaralkyl, sulfonamidoalkyl, sulfonamidoalkenyl, sulfonamidoalkynyl, sulfonamidocarbocyclyl, sulfonamidoaryl, sulfonamidoheterocyclyl, sulfonamidoheteroaryl, sulfonamidoacyl, sulfonamidoaralkyl, nitroalkyl, nitroalkenyl, nitroalkynyl, nitrocarbocyclyl, nitroaryl, nitroheterocyclyl, nitroheteroaryl, nitroacyl, nitroaralkyi, cyano, sulfate and phosphate groups.

[0055] Some desirable optional substituents include alkyl, (e.g. C₁-₆ alkyl such as methyl, ethyl, propyl, butyl, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl), hydroxyalkyl (e.g. hydroxymethyl, hydroxyethyl, hydroxypropyl), alkoxyalkyl (e.g. methoxymethyl, methoxyethyl, methoxypropyl, ethoxymethyl, ethoxyethyl, ethoxypropyl etc), alkoxy (e.g. C₁-₆ alkoxy such as methoxy, ethoxy, propoxy, butoxy, cyclopropoxy, cyclobutoxy), halo, trifluoromethyl, trichloromethyl, hydroxy, phenyl (which itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy, hydroxyCi-6 alkyl, Ci-6 alkoxy, haloCi-₆ alkyl, cyano, nitro OC(O)Ci-₆ alkyl, and amino), benzyl (wherein benzyl itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy, hydroxyCi-6 alkyl, Ci-6 alkoxy, haloCi-₆ alkyl, cyano, nitro OC(O)Ci-₆ alkyl, and amino), benzyl (wherein benzyl itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy, hydroxyCi-6 alkyl, Ci-6 alkoxy, haloCi-₆ alkyl, cyano, nitro OC(O)Ci-₆ alkyl, and amino), phenoxo (wherein phenyl itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy, hydroxyCi-₆ alkyl, C₁-₆ alkoxy, haloCi-₆ alkyl, cyano, nitro OC(O)Ci-₆ alkyl, and amino), benzyl (wherein benzyl itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy, hydroxyCi-6 alkyl, Ci-6 alkoxy, haloCi-6 alkyl, cyano, nitro OC(O)Ci-6 alkyl, and amino), amino, alkylamino (e.g. Ci-6 alkyl, such as methylamino, ethylamino, propylamino etc), dialkylamino (e.g. Ci-6 alkyl, such as dimethylamino, diethylamino, dipropylamino), acylamino (e.g. NHC(O)CH₃), phenylamino (wherein phenyl itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy hydroxyCi-6 alkyl, Ci-6 alkoxy, halo C₁-₆ alkyl, cyano, nitro OC(O)Ci-₆ alkyl, and amino), nitro, formyl, -C(O)-alkyl
(e.g. C1-6 alkyl, such as acetyl), O-C(O)-alkyl (e.g. C1-6 alkyl, such as acetyloxy), benzoyl (wherein the phenyl group itself may be further substituted e.g., by C1-6 alkyl, halo, hydroxy hydroxyCi-6 alkyl, Ci-6 alkoxy, haloCi-6 alkyl, cyano, nitro OC(O)Ci-6 alkyl, and amino), replacement of CH2 with C=O, CO2H, CO2alkyl (e.g. Ci-6 alkyl such as methyl ester, ethyl ester, propyl ester, butyl ester), CO2phenyl (wherein phenyl itself may be further substituted e.g., by Ci-6 alkyl, halo, hydroxy, hydroxyl Ci-6 alkyl, Ci-6 alkoxy, halo Ci-6 alkyl, cyano, nitro OC(O)Ci-6 alkyl, and amino), CONH2, CONHphenyl (wherein phenyl itself may be further substituted e.g., by C1-6 alkyl, halo, hydroxy, hydroxyl C1-6 alkyl, C1-6 alkoxy, halo C1-6 alkyl, cyano, nitro OC(O)Ci-6 alkyl, and amino), CONHbenzyl (wherein benzyl itself may be further substituted e.g., by C1-6 alkyl, halo, hydroxy hydroxyl Ci-6 alkyl, Ci-6 alkoxy, halo Ci-6 alkyl, cyano, nitro OC(O)Ci-6 alkyl, and amino), CONHalckyl (e.g. Ci-6 alkyl such as methyl ester, ethyl ester, propyl ester, butyl amide) CONHdialkyl (e.g. C1-6 alkyl) aminoalkyl (e.g., HN C1-6 alkyl-, Ci-6 alkylHN-Ci-6 alkyl- and (Ci-6 alkyl)2N-Ci-6 alkyl-), thioalkyl (e.g., HS Ci-6 alkyl-), carboxyalkyl (e.g., HO2CCI-6 alkyl-), carboxyesteralkyl (e.g., Ci-6 alkylO2CCI-6 alkyl-), amidoalkyl (e.g., H2N(O)CCI-6 alkyl-, H(Ci-6 alkyl)N(O)CCI-6 alkyl-), formylalkyl (e.g., OHCCI-6 alkyl-), acylalkyl (e.g., C1-6 alkyl(O)CCI-6 alkyl-), nitroalkyl (e.g., O2NCi-6 alkyl-), sulfoxidealkyl (e.g., R3(O)SCI-6 alkyl, such as Ci-6 alkyl(O)SCi-6 alkyl-), sulfonylalkyl (e.g., R3(O)2SCI-6 alkyl- such as C1-6 alkyl(O)2SCI-6 alkyl-), sulfonamidoalkyl (e.g., 2HRN(O)SCI-6 alkyl, H(Ci-6 alkyl)N(O)SCI-6 alkyl-).

[0056] As used herein, the term "alkyl", used either alone or in compound words denotes straight chain, branched or cyclic alkyl (or "cycloalkyl"), for example C1-40 alkyl, or C1-20 or C1-10. Examples of straight chain and branched alkyl include methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, f-butyl, n-pentyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methyl hexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethyl-pentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, octyl, 6-methylheptyl, 1-methylheptyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-, 2-, 3-,
4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-, 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methyleneoctyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-; 8- or 9-methyldodecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylnoundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propynonyl, 1-, 2-, 3- or 4-butyloctyl, 1,2-pentylheptyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonoacdecyl, eicosyl and the like. Examples of cyclic alkyl include mono- or polycyclic alkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl and the like. Where an alkyl group is referred to generally as "propyl", "butyl" etc, it will be understood that this can refer to any of straight, branched and cyclic isomers where appropriate. An alkyl group may be optionally substituted by one or more optional substituents as herein defined.

[0057] The term "alkenyl" as used herein in relation to a moiety or group denotes a hydrocarbon group containing at least one carbon-carbon double bond. The alkenyl may be straight or branched preferably having 2-14 carbon atoms, more preferably 2-12 carbon atoms, most preferably 2-6 carbon atoms, in the normal chain. The alkenyl may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. Alkenyl includes, but is not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl and eicosenyl hydrocarbon groups with one or more carbon to carbon double bonds. Alkenyl may be optionally substituted by one or more optional substituents as herein defined.

[0058] As used herein, the terms "alkylene", "alkenylene", "arylene" and "heteroarylene" are intended to denote the divalent forms of "alkyl", "alkenyl", "aryl", and "heteroaryl" respectively, as herein defined.

[0059] As used herein, the term "aryl" (or "carboaryl") denotes any of single, polynuclear, conjugated and fused residues of aromatic hydrocarbon ring systems. Examples of aryl include phenyl, biphenyl, terphenyl, quaterphenyl, naphthyl, tetrahydroanaphthyl, anthracenyl, dihydroanthracenyl,
benzanthracenyl, dibenzanthracenyl, phenanthrenyl, fluorenyl, pyrenyl, idenyl, azulenyl, chrysenyl. Preferred aryl include phenyl and naphthyl. An aryl group may be optionally substituted by one or more optional substituents as herein defined.

[0060] As used herein, the term "halogen" ("halo") denotes fluorine, chlorine, bromine or iodine (fluoro, chloro, bromo or iodo).

[0061] The term "carbocyclyl" (or "carbocyclic") as used herein in relation to a moiety or group denotes a non-aromatic monocyclic, polycyclic, fused or conjugated hydrocarbon ring system. The carbocyclyl moiety or group may be C3-20 (e.g. C3-10 or Cs-s). Exemplary carbocyclyl moieties are 5-6-membered or 9-10 membered ring systems. Examples of carbocyclyl include mono- or polycyclic hydrocarbon ring systems such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl and the like. The carbocyclyl may be optionally substituted by one or more optional substituents as herein defined.

[0062] As used herein, the term "heterocyclyl" when used alone or in compound words includes any of monocyclic, polycyclic, fused or conjugated hydrocarbon residues, preferably 03-20 (e.g. C3-10 or C3-8) wherein one or more carbon atoms are replaced by a heteroatom so as to provide a non-aromatic residue. Suitable heteroatoms include O, N, S, P and Se, particularly O, N and S. Where two or more carbon atoms are replaced, this may be by two or more of the same heteroatom or by different heteroatoms. The heterocyclyl group may be saturated or partially unsaturated, i.e. possess one or more double bonds. Suitable examples of heterocyclyl groups may include azridinyl, oxiranyl, thiiranyl, azetidinyl, oxetanyl, thietanyl, 2H-pyrrolyl, pyrrolidinyl, pyrrolinyl, piperidyl, piperezinyl, morpholinyl, indolinyl, imidazolidinyl, imidazolinyl, pyrazolidinyl, thiomorpholinyl, dioxanyl, tetrahydropyran, tetrahydropyranyl, tetrahydropyrrolyl, tetrahydrothiophenyl, pyrazolinyl, dioxalanyl, thiazolidinyl, isoxazolidinyl, dihydropyranyl, oxazinyl, thiazinyl, thiomorpholinyl, oxathianyl, dithianyl, trioxanyl, thiaiazinyl, dithiaazinyl, trithianyl, azepinyl, oxepinyl,
thiepinyl, indenyl, indanyl, 3H-indolyl, isoindolinyl, 4H-quinolazinyl, chromenyl, chromanyl, isochromanyl, pyranyl and dihydropyranyl.

[0063] The terms "carbocyclyl" and "heterocarbocyclyl" includes divalent forms of the groups defined herein.

[0064] As used herein, the term "heteroaryl" includes any of monocyclic, polycyclic, fused or conjugated hydrocarbon residues, wherein one or more carbon atoms are replaced by a heteroatom so as to provide an aromatic residue. Preferred heteroaryl have 3-20 ring atoms, e.g. 3-10. Suitable heteroatoms include, O, N, S, P and Se, particularly O, N and S. Where two or more carbon atoms are replaced, this may be by two or more of the same heteroatom or by different heteroatoms. Suitable examples of heteroaryl groups may include pyridyl, pyrrolyl, thienyl, imidazolyl, furanyl, benzothienyl, isobenzothienyl, benzofuranyl, isobenzofuranyl, indolyl, isoindolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, quinolyl, isoquinolyl, phthalazinyl, 1,5-naphthyridinyl, quinozalinyl, quinazolinyl, quinolinyl, oxazolyl, thiazolyl, isothiazolyl, isoxazolyl, triazolyl, oxadiazolyl, oxatriazolyl, triazinyl, and furazanyl.

[0065] As used herein, the term "amine" or "amino" includes groups of the formula NR^A^ R^B^ wherein R^A^ and R^B^ may be any independently selected from hydrogen, alkyl, alkenyl, alkynyl, aryl, carbocyclyl, heteroaryl, heterocyclyl, aralkyl, and acyl. R^A^ and R^B^, together with the nitrogen to which they are attached, may also form a monocyclic or polycyclic ring system e.g. a 3-10 membered ring. Examples of "amine" include NH^2^, NHalkyl (e.g. C_{1,2}alkyl), NHacyl (e.g. NHphenyl), NHaralkyl (e.g. NHbenzyl), NHacyl (e.g. NHC(O)Cl-2alkyl, NHC(O)phenyl), Nalkylalkyl (wherein each alkyl, for example Ci-2o, may be the same or different) and 5 or 6 membered rings, optionally containing one or more same or different heteroatoms (e.g. O, N and S).

[0066] As used herein, the term "amide" or "amido" includes groups having the formula C(O)NR^A^ R^B^, wherein R^A^ and R^B^ are as defined as above. Examples of amido include C(O)NH^2^, C(O)NHalkyl (e.g. C_{1,2}alkyl), C(O)NHaryl (e.g.
C(O)NHphenyl), C(O)NHaralkyl (e.g. C(O)NHbenzyl), C(O)NHacyl (e.g. C(O)NHC(O)Ci\textsubscript{2}oalkyl, C(O)NHC(O)phenyl), C(O)Nalkylalkyl (wherein each alkyl, for example Ci\textsubscript{2}o, may be the same or different) and 5 or 6 membered rings, optionally containing one or more same or different heteroatoms (e.g. O, N and S).

[0067] As used herein, the term "heteroatom" or "hetero" refers to any atom other than a carbon atom which may be a member of a cyclic organic group. Particular examples of heteroatoms include nitrogen, oxygen, sulfur, phosphorous, boron, silicon, selenium and tellurium, more particularly nitrogen, oxygen and sulfur.

[0068] All percentages used herein are percentages based on weight by weight (\% w/w), unless otherwise indicated.

[0069] The terms "polymer nanocomposite" and "nanocomposite" are interchangeably used herein to refer to a nanocomposite material including a crosslinked polymer matrix and a nanofiller, having features as described herein.

[0070] The present invention relates to a self-healing polymer nanocomposite. The nanocomposite of the invention includes a crosslinked matrix and a nanofiller dispersed in the matrix. Upon damage or failure of the nanocomposite material, the nanocomposite self heals without the need to apply additional force or the use of chemical reactants to promote self healing and damage repair.

[0071] The crosslinked matrix of the nanocomposite of the invention is a polymer matrix that is formed from a macromolecule and a crosslinking agent. In forming the matrix, macromolecule chains interact with a crosslinking agent to form a three-dimensional polymer network. The crosslinking agent extends between chains of the macromolecule to provide intermolecular links between the chains. In some embodiments, the three-dimensional polymer network may
be considered a supramolecular network that is held together by non-covalent bonds.

[0072] In the crosslinked matrix of the nanocomposite of the invention, the macromolecule interacts with the crosslinking agent by non-covalent bonding interactions. Accordingly, the crosslinked matrix is predominately held together by non-covalent bonds. In one form of the invention, it is desirable that the non-covalent bonds between the macromolecule and the crosslinking agent be hydrogen bonds. However, it is contemplated that other types of non-covalent bonding interactions, such as electrostatic or ionic bonding interactions, may occur in addition to, or instead of, hydrogen bonds.

[0073] The macromolecule used in the crosslinked matrix of the self-healing nanocomposite includes a plurality of functional groups. The macromolecule includes at least two functional groups and may include three, four or more, functional groups. The number of functional groups in the macromolecule may depend on the type of monomer used to prepare the macromolecule, as well as macromolecule molecular weight. The functional groups may be included in the backbone structure of the macromolecule, or they may be pendant functional groups attached to the backbone.

[0074] The functional groups enable the macromolecule to interact with the crosslinking agent by non-covalent bonding interactions. In some embodiments, the non-covalent bond interactions between the macromolecule and the crosslinking agent form hydrogen bonds.

[0075] Where hydrogen bonds are formed between the macromolecule and the crosslinking agent, it is desirable for the macromolecule to include hydrogen donating functional groups, hydrogen accepting functional groups, or a mixture of such groups. A person skilled in the relevant art would appreciate that functional groups containing a hydrogen atom bonded to an electronegative atom (such as nitrogen or oxygen) can act as hydrogen bond donors, while functional groups containing an atom with a lone pair of electrons can act as hydrogen bond acceptors. Direct interactions between a hydrogen bond donor
group and a hydrogen bond acceptor group results in the formation of a hydrogen bond.

[0076] In some embodiments, the functional groups of the macromolecule are each independently selected from the group consisting of halogen, oxygen, and nitrogen containing functional groups. In some particular embodiments, the functional groups of the macromolecule may each be independently selected from the group consisting of hydroxyl, amine, and carbonyl containing functional groups. The functional groups of the macromolecule may each be of the same type of functional group, or alternatively, they may be a mixture of different types of functional group. In one embodiment, the functional groups of the macromolecule are each carbonyl containing functional groups. Carbonyl containing functional groups include the moiety C=O. Examples of carbonyl containing functional groups include amide, ester and carboxylic acid functional groups. It is believed that the C=O moiety of carbonyl containing functional groups can act as hydrogen bond acceptors for the formation of hydrogen bonds, as the oxygen atom of the carbonyl group contains a lone pair of electrons.

[0077] The crosslinked matrix of the nanocomposite of the invention may include any type of macromolecule containing suitable functional groups. Macromolecules useful in the present invention may be prepared synthetically, or derived from natural sources. Synthetically prepared macromolecules can be obtained from the polymerisation of a single monomer, or from two or more co-monomers. Synthetic macromolecules may be formed using a number of different techniques, including free radical, ionic, ring opening, allyl addition or condensation polymerisation techniques. The macromolecules may also be formed using synthetic techniques, such as Diels-Alder or click chemistry techniques.

[0078] In one embodiment, the crosslinked matrix may include one type of macromolecule. In an alternative embodiment, the crosslinked matrix may include a mixture of two or more different types of macromolecule, such as for example, a blend of synthetic and naturally derived macromolecules.
In some embodiments, the macromolecule is a condensation polymer. A person skilled in the relevant art would appreciate that condensation polymers are macromolecules that are formed when compatible reactive functional groups present in one or more monomers react to join together via a covalent bond and liberate a small molecule, such as water. For example, carboxylic acid functional groups can react with amine functional groups to form amide functional groups, with the loss of water. Other compatible reactive functional groups that are capable of producing condensation polymers could be readily ascertained by one skilled in the relevant art. The term "compatible reactive functional group" therefore refers to terminal functionalities or groups such as hydroxyl, carboxylic acid, carboxylic acid halide, ester, anhydride, amine and amide functional groups, which are contained in monomers capable of participating in condensation reactions.

In some embodiments, the macromolecule includes at least one condensation polymer selected from the group consisting of polyamides and polyesters. Polyamides include a plurality of amide functional groups, while polyesters include a plurality of ester functional groups. In an exemplary embodiment, the macromolecule is a polyamide including a plurality of amide functional groups.

Where the macromolecule is a condensation polymer, the macromolecule may be prepared from the polymerisation of a single type of monomer, or from the polymerisation of two or more co-monomers.

When a single monomer is used to form the condensation polymer, typically two or more compatible reactive functional groups are contained in the same monomer unit. The compatible reactive functional groups in the monomer are generally of different types, however they are capable of reacting with one another under condensation polymerisation reaction conditions to produce the desired condensation polymer. Examples of a monomer containing two different types of reactive functional group include hydroxy-acids, which contain...
a carboxylic acid and a hydroxyl functional group, and amino acids, which contain a carboxylic acid and an amine functional group.

[0083] When two or more co-monomers are used to form the condensation polymer, one co-monomer unit can contain one type of reactive functional group, while another co-monomer unit contains a different type of reactive functional group. The reactive functional groups of each of the co-monomers are compatible with one another and are able to react together under conditions of condensation polymerisation. Generally, each monomer unit includes two or more reactive functional groups. At least two reactive functional groups are required in each monomer unit to enable the co-monomers to link together in the macromolecule chain.

[0084] In forming macromolecules by condensation polymerisation, a person skilled in the relevant art would appreciate that the nature of the reactive functional group in each monomer unit is important to the polymerisation reaction. The structure of the remaining portion of the monomer unit however is less critical. As a result, the invention contemplates that a variety of different moieties may be present in the remainder of each monomer unit.

[0085] According to one embodiment of the invention, the macromolecule in the crosslinked matrix is formed from the condensation polymerisation of a monomer including at least two compatible reactive functional groups. A macromolecule in accordance with this embodiment may have a monomer unit having a structure of Formula (I) as given below:

\[
\begin{align*}
\text{A} & \quad \text{R}^1 \\
\text{X} & \\
\text{m} & \\
\end{align*}
\]

where

- \(X\) is selected from the group consisting of \(O\) and \(N\);
- \(A\) is selected from the group consisting of \(O\) and \(NHR\), where \(R\) is \(H\) or alkyl (preferably \(C_1\) to \(C_4\) alkyl);
R$^1$ represents the remainder of the monomer unit; and
m represents the number of repeating units for the monomer and is at least 2.

[0086] According to another embodiment of the invention, the macromolecule in the crosslinked matrix is formed from the condensation polymerisation of at least two co-monomers. In this embodiment, each co-monomer includes at least two reactive functional groups that are compatible with the reactive functional groups of the other co-monomer. Each co-monomer provides a repeating monomer unit in the resulting macromolecule. A macromolecule in accordance with this embodiment may have a repeating unit having a structure of Formula (II) as given below:

\[
\left( \begin{array}{c}
X \\
R^1
\end{array} \right) \left( \begin{array}{c}
X \\
m
\end{array} \right) \left( \begin{array}{c}
A \\
R^2 \\
A
\end{array} \right) \]

(II)

where
X at each occurrence is independently selected from the group consisting of O and N;
A at each occurrence is independently selected from the group consisting of O and NR, where R is H or alkyl (preferably C1-C4 alkyl);
R$^1$ represents the remainder of a first monomer unit;
R$^2$ represents the remainder of a second monomer unit;
m represents the number of repeating units for the first monomer and is at least 1; and
n represents the number of repeating units for the second monomer and is at least 1.

[0087] In some embodiments of the invention, macromolecules with a repeating unit having a structure of Formula (I) or Formula (II) may be polyesters or polyamides.
In macromolecules having a repeating unit of structure of Formula (I) or (II), the structure of the groups \( R^1 \) and \( R^2 \) will depend on the monomer or monomers used to prepare the macromolecule. In some embodiments, the groups \( R^1 \) and \( R^2 \) may be the same or different at each occurrence and in each case, may independently include a moiety selected from the group consisting of optionally substituted linear or branched alkyne, optionally substituted linear or branched alkenylene, optionally substituted carbocyclyl, optionally substituted heterocarbocyclyl, optionally substituted arylene and optionally substituted heteroarylene.

In some embodiments of a repeating unit of Formula (I) or (II), \( R^1 \) is selected from the group consisting of optionally substituted linear or branched \( C_3 \) to \( C_{10} \) alkyne, optionally substituted linear or branched \( C_2 \) to \( C_6 \) alkenylene, and optionally substituted \( C_5 \) to \( C_6 \) arylene. In some exemplary embodiments of a repeating unit of Formula (I) or (II), \( R^1 \) is selected from the group consisting of optionally substituted linear or branched \( C_5 \) to \( C_{10} \) alkyne, optionally substituted linear or branched \( C_2 \) to \( C_4 \) alkenylene, and optionally substituted \( C_5 \) to \( C_6 \) arylene.

It may, in some instances, be desirable for at least one of the groups \( R^1 \) and \( R^2 \) in a repeating unit of Formula (I) or (II) to include a moiety having at least 4 carbon atoms. The use of monomers containing at least 4 carbon atoms to prepare the macromolecule can desirably enable better physical properties to be imparted to the macromolecule initially, and later to the nanocomposites as well. For example, bulk physical properties such as physical state (i.e. liquid to solid state) of the nanocomposite, and thereby the hardness, density, tensile strength and Young's modulus-like properties of the nanocomposite may be influenced by the nature of the monomer or monomers used to prepare the macromolecule used in the crosslinked matrix of the nanocomposite.

In some embodiments, it may be desirable for at least one of the groups \( R^1 \) and \( R^2 \) to include a moiety having at least one unsaturation. For example, at least of \( R^1 \) and \( R^2 \) may be selected from the group consisting of an optionally
substituted linear or branched alkenylene, an optionally substituted arylene or an optionally substituted heteroarylene. In some embodiments of a repeating unit of Formula (I) or (II), R1 may be selected from the group consisting of an optionally substituted linear or branched C2 to Cs alkenylene (preferably C2 to C4 alkenylene), and an optionally substituted C5 to C6 arylene. Nanocomposites formed with a macronnolecule including at least one unsaturation in the polymer chain may display different mechanical strength properties (e.g. lower mechanical strength).

[0092] In one form of the invention, the macronnolecule is derived from a co-monomer containing two or more carboxylic acid functional groups (a polyacid monomer) and a co-monomer containing two or more amine functional groups (a polyamine monomer). In this embodiment, the carboxylic acid containing co-monomer is capable of reacting with the amine containing co-monomer to form an oligomer, with an amide linkage between the monomer units of the oligomer. The oligomer, which now has a terminal carboxylic acid group and a terminal amine group, may subsequently react with further monomer units bearing an amine or carboxylic acid group so as to form one or more further amide linkages (amide functional groups) in the polymer backbone and extend the length of the macronnolecule chain. The reaction is desirably carried out under condensation polymerisation conditions.

[0093] The polyacid monomer may be at least one selected from the group consisting of sebacic acid, maleic acid, fumaric acid, malonic acid, glutaric acid, pimelic acid, azelaic acid, phthalic acid, isophthalic acid, and terephthalic acid. Esters, diesters and anhydrides of any one of the above polyacids are also suitable.

[0094] The polyamine monomer may be at least one selected from the group of diethylenetriamine (DETA), ethylamine, ethylenediamine, diethylamine, triethylenetetramine (TETA), cadaverine, spermidine, and p-phenylenediamine.

[0095] Mixtures of two or more of the above polyacid monomers and/or two or more of the above polyamine monomers may be used to prepare
macromolecules suitable for inclusion in a nanocomposite of the invention. The use of mixtures of monomers may allow the properties of the macronnolecule and resulting nanocomposite to be tailored for particular applications. For example, it has been found that a macronnolecule formed by reacting a polyamine monomer with a mixture of glutaric acid and pimelic acid exhibits elastic properties. Thus, a nanocomposite formed with such a macronnolecule may exhibit shape memory properties as well as self-healing properties.

[0096] In one embodiment, the macronnolecule is formed from the condensation polymerisation of a dicarboxylic acid monomer and a diamine or a triamine monomer. For example, the macronnolecule may be formed from the condensation polymerisation of sebacic acid and diethylenetriamine, as shown in Scheme 1.

![Scheme 1](image)

[0097] A person skilled in the art would appreciate however, that other monomers with different numbers and/or types of reactive functional groups may also be used. For example, a polyol monomer can be used in place of the polyamine monomer. When the polyol reacts with a polyacid monomer under condensation polymerisation conditions a polyester macronnolecule is formed. An exemplary polyol is polyethylene glycol, such as PEG 600.

[0098] To provide the crosslinked matrix of the nanocomposite of the invention, the functional groups of the macronnolecule interact with functional groups present in a crosslinking agent by non-covalent bonding interactions. The
bonding interactions result in the formation of a crosslinked matrix that is predominantly held together by intermolecular non-covalent bonds between the crosslinking agent and at two chains of the macromolecule. The intermolecular non-covalent bonding interaction is reversible. Accordingly, reversible crosslinks are formed between the macromolecule and crosslinking agent. It is one advantage of the present invention that upon disruption of the non-covalent bonding interactions, the reversible crosslinks between the macromolecule and crosslinking agent are able to readily re-form under appropriate conditions.

[0099] In order to interact with the macromolecule, the crosslinking agent includes a plurality of functional groups which are capable of participating in non-covalent bonding interactions. Accordingly, the crosslinking agent includes at two functional groups, and may include three, or four, or more functional groups, that are capable of participating in non-covalent bonding interactions with the functional groups of the macromolecule. Desirably, the functional groups of the crosslinking are terminal functional groups as such groups would be more readily available for interaction with the macromolecule.

[0100] In one form of the invention, non-covalent bonding interactions between the functional groups crosslinking agent and the functional groups of the macromolecule form hydrogen bonds. Without wishing to be limited by theory, it is believed that hydrogen bonds can promote the self-healing capability of the nanocomposite of the invention. The desire of the functional groups of the macromolecule and the crosslinking agent to associate by intermolecular hydrogen bonds can provide the driving force for nanocomposite self-healing.

[0101] Where hydrogen bonds are formed, it is desirable for the crosslinking agent to include hydrogen donating functional groups, hydrogen accepting functional groups, or a mixture of such groups. The nature of functional group that is present in the crosslinking agent may be dictated by the nature of functional group present in the macromolecule. For example, where the macromolecule includes hydrogen bond acceptor groups, it would be desirable for the crosslinking agent to include hydrogen bond donating groups to ensure that a hydrogen bond can then be formed between the crosslinking agent and
the macromolecule. Conversely, where the macromolecule includes hydrogen bond donor groups, the crosslinking agent may include hydrogen bond accepting groups.

[0102] In some embodiments, the functional groups of the crosslinking agent are each independently selected from the group consisting of halogen, oxygen, and nitrogen containing functional groups. In some particular embodiments, the functional groups of the crosslinking agent may each be independently selected from the group consisting of hydroxyl, amine, and carbonyl containing functional groups. The functional groups of the crosslinking agent may each be of the same type of functional group, or alternatively, they may be a mixture of different types of functional group. In one embodiment, the functional groups of the crosslinking agent are selected from the group consisting of amine and amide functional groups. Amine and amide functional groups can contain the moiety -NHR. The moiety -NHR is capable of acting as a hydrogen bond donor in the formation of hydrogen bonds, as it contains a hydrogen atom bonded to an electronegative nitrogen atom.

[0103] The crosslinked matrix of the nanocomposite of the invention may include any type of crosslinking agent, provided the crosslinking agent contains suitable functional groups that are capable of participating in non covalent bonding interacting with the functional groups of the macromolecule. In one embodiment, the crosslinked matrix includes one type of crosslinking agent. In an alternative embodiment, the crosslinked matrix includes a mixture of two or more different types of crosslinking agents.

[0104] In one form of the invention, the crosslinked matrix of the nanocomposite of the invention may include at least one diamide crosslinking agent. Diamide crosslinking agents include two -NHR functional groups, which are each capable of interacting with the functional groups of the macromolecule. Examples of diamide crosslinking agents include urea, 1,3-dimethylurea, 1,1-diethylurea, 1-acetyl-1-phenylurea, isopropylideneurea, 2-(3-methylureido)-1-naphthoic acid, allophanic acid, hydantoic acid, allophanoyl, and 4,4'-ureylenedi-1-naphthalenesulfonic acid, 2-ethyl-1,1-diphenylisourea, 2-ethyl-1-
phenylisourea, 2-ethyl-3-phenylisourea, 4-(2-ethyl-1,1-dimethyl-3-isoureido)-1-naphthol, 2-(2-naphthyl)uronium picrate, thiourea, N-methylselenourea, 1-methyl-2-selenourea, 1-methyl-2-propylisothiourea, N-methyl-S-propylisothiourea, N,N-diethyl-S-phenylthiouuronium, biuret, thiobiuret, dithiobiuret, triuret, 4-thiotriuret, and 1-methyl-2-thiobiuret. Mixtures of diamide crosslinking agents may be present in the crosslinked matrix.

[0105] In embodiments of the nanocomposite of the invention, the macromolecule and the crosslinking agent are held together in mutual association in the crosslinked matrix by hydrogen bonds. An example of a hydrogen bonded crosslinked matrix that is formed with a polyamide macromolecule and urea crosslinking agent is shown in Scheme 2. The association between the macromolecule and the crosslinking agent results in the formation of reversible crosslinks in the matrix.

[0106] The number of crosslinks and crosslink density can be varied to obtain a matrix and nanocomposite of desired characteristics. One skilled in the relevant art would understand that a variation in the number or density of crosslinks may be achieved by varying the concentration and/or type of crosslinking agent used to prepare the crosslinked matrix.

[0107] The self-healing polymer nanocomposite of the present invention also includes a nanofiller dispersed in the matrix. As used herein, the term
"nanofiller" refers to a material with at least one dimension in the nanometer scale. The nanofiller of the nanocomposite of the invention may include one or more materials selected from the group consisting of nanofibres, nanosheets, nanoparticles, nanotubes, graphitic nanofillers, nanowhiskers, metal phosphates, layered double hydroxides, nanocalcium, and metal chalcogenides. Desirably, the nanofiller is compatible with, and capable of being substantially homogeneously dispersed in, the crosslinked matrix of the nanocomposite. Accordingly, it is desirable that little or no phase separation of the nanofiller from the crosslinked matrix be observed.

[0108] Any type of nanofiller conventionally employed in the preparation of nanocomposites may be used. Some specific examples of nanofillers that may be used to in the self-healing nanocomposite of the invention include the following:

- Nanofibers, such as carbon nanofibers or ceramic nanofibers. Ceramic nanofibers can include pristine or modified titanium dioxide (TiO₂), silicon dioxide (SiO₂), zirconium dioxide (ZrO₂), lanthanum oxide (La₂O₃), aluminium oxide (Al₂O₃), lithium titanate (Li₄Ti₅O₁₂), titanium nitride (TiN) or platinum (Pt).
- Graphitic nanofillers, such as pristine graphite and modified graphite.
- Nanosheets, such as graphite nanoplatelets or graphite flakes, graphene and stacked graphene sheets.
- Carbon nanotubes and inorganic nanotubes.
- Nanotube / nanofiber compositions.
- POSS (Polyhedral oligomeric silsesquioxanes)
- Metal phosphates, such as Zr(HPO₄)₂.
- Layered double hydroxides, such as Mg₆Al₂(OH)i₆CO₃.
- Nanocalcium, such as calcium carbonate nanoparticles.
- Cellulose nanowhiskers.
- Metal chalcogenides such as (PbS)i₄₈ (TiS₂)₂, MoS₂.
- Nanoparticles, such as nanoclay particles and layered silicate particles, including montmorillonite, hectorite, saponite, fluoroica, fluorohectorite, vermiculite, kaolinite, magadiite.
The type of nanofiller and its properties may influence the properties of the resulting nanocomposite.

In one form of the self-healing nanocomposite of the invention, the nanofiller comprises a plurality of nanoparticles. Nanoparticles are particles of a material that have a size measured on the nanometer scale. Nanoparticles may have a size of from about 1 nm up to about 1000 nm. Nanoparticles useful in the nanocomposite of the invention may have a size of from about 10 nm to about 500 nm.

When the nanofiller includes a plurality of nanoparticles, the type of nanoparticles necessary for a given nanocomposite can vary depending on the nature of the polymer matrix material and the particulate matter. Nanoparticles can help to impart desirable mechanical properties to the nanocomposite. In one form of the invention, the nanoparticles are nanoclay particles.

Nanoclay particles used in the nanocomposite of the invention may be selected from the group consisting of pristine clays and organically-modified clays. Organically-modified clays are clays modified with one or more functional groups. Organically-modified clays may be clays modified with hydroxyl (-OH) groups, which can enhance the hydrogen bonding capacity of the self-healing nanocomposite.

In some embodiments, the organically-modified clays are clays modified with one or more groups selected from the group consisting of alkyl ammonium ions such as dodecyl ammonium, octadecyl trimethyl ammonium, bis(2-hydroxyethyl) octadecyl methyl ammonium, bis(2-hydroxyethyl) methyl tallow ammonium, bis(2-hydroxyethyl) methyl hydrogenated tallow ammonium, octadecyl benzyl dimethyl ammonium, dimethyl, dehydrogenated tallow, 2-ethylhexyl quaternary ammonium salt (2MHTL8) or methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt (MT2EtOH) and the like or mixtures thereof.
In other embodiments, the organically-modified clays are clays modified with one or more organic cations. Examples of organic cations include but are not limited to alkyl ammonium ions, such as tetramethyl ammonium, hexyl ammonium, butyl ammonium, bis(2-hydroxyethyl) dimethyl ammonium, hexyl benzyl dimethyl ammonium, benzyl trimethyl ammonium, butyl benzyl dimethyl ammonium, tetrabutyl ammonium, di(2-hydroxyethyl) ammonium, and the like, and alkyl phosphonium ions such as tetrabutyl phosphonium, trioctyl octadecyl phosphonium, tetraoctyl phosphonium, octadecyl triphenyl phosphonium, and the like or mixtures thereof.

In other embodiments, the organically-modified clays are clays modified with one or more alkoxylated ammonium compounds. Alkoxylated ammonium compounds may include mono-alkoxylated, di-alkoxylated, tri-alkoxylated, and tetra-alkoxylated ammonium compounds, wherein the alkoxylate group comprises at least one alkyleneoxide group having from 2 to 10 carbon atoms. Alkoxylate groups may be hydroxyalky groups, having at least one terminal hydroxyl (-OH) group bound to any one of the carbon atoms.

In some embodiments, the nanofiller is montmorillonite nanoclay modified with an organic modifier selected from the group consisting of dimethyl, dehydrogenated tallow, 2-ethylhexyl quaternary ammonium salt (2MHTL8), and methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt (MT2EtOH). Such organic modifiers have the following structures:

![Chemical structures](image)

The presence of hydroxy groups (-OH) in nanofillers such as MT2EtOH can enhance hydrogen bonding interactions between the nanofiller and the
polymer matrix and may lead to the ability to alter the mechanical properties and self-healing capability of the polymer nanocomposite.

[01 18] In other forms of the self-healing nanocomposite of the invention, the nanofiller includes layered silicate clay particles. As used herein, the term "layered silicate" is intended to be a reference to clays which have as part of their molecular structure (SiO4)\(_n\) repeating units. Layered silicates may contain individual platelet particles that are closely stacked together. Upon being dispersed through the crosslinked matrix material, the layered silicate particles can exfoliate or delaminate to provide smaller aggregates in the matrix material.

[01 19] Nanoclay particles useful as a nanofiller in the nanocomposite of the invention may be selected from the group consisting of montmorillonite, mica, bentonite, kaolinite, saponite, halloysite, hectorite, fluoromica, fluorohectorite, vermiculite, and magadiite particles.

[01 20] In some embodiments, the nanoclay particles may be capable of cation exchange. An example of a nanoclay capable of cation exchange is montmorillonite with cation exchange capacity, such as Na\(^+\) montmorillonite, K\(^+\) montmorillonite, Ca\(^{2+}\) montmorillonite and Na\(^+\)-Ca\(^{2+}\)-montmorillonite. Such nanoclays can provide nanocomposites with cation exchange capacity, which may be useful in some biomedical applications.

[01 21] A self-healing nanocomposite of the invention may have a structure selected from the group consisting of an intercalated structure, an exfoliated structure, and a flocculated structure. The nature of the physical and chemical interactions between the nanoclay particles and the crosslinked matrix can influence the structure of the nanocomposite and consequently, the mechanical properties of the nanocomposite. The structure of the nanocomposite may be analysed using techniques, such as XRD.

[01 22] The nanofiller may be present in the self-healing nanocomposite in an amount in the range of from about 0.5% to about 50% by weight of the
nanocomposite. Higher concentrations of nanofiller may provide a more brittle nanocomposite than if a lower concentration of nanofiller is used. In some embodiments, the nanofiller may be present in the nanocomposite in an amount in the range of from about 2% to about 10%, or from about 3% to about 5%, by weight of the nanocomposite. In some forms of the self-healing nanocomposite of the invention, only a relatively low concentration of nanofiller may be required.

[01 23] The self-healing nanocomposite of the invention may also include conventional additives, such as plasticizers, antioxidants, and colourants such as tints, pigments and dyes. Such additives may be included in the nanocomposite where it is desired to customise the nanocomposite for a particular application.

[01 24] Another aspect of the present invention provides a process for the preparation of a self-healing nanocomposite including the steps of:

providing a macromolecule including a plurality of functional groups, a crosslinking agent including a plurality of functional groups, and a nanofiller in a reaction vessel; and

forming non-covalent bonds between the functional groups of the macromolecule and the functional groups of the crosslinking agent in the presence of the nanofiller to provide a nanocomposite including a crosslinked matrix and a nanofiller dispersed in the matrix.

[01 25] In embodiments of the invention, the non-covalent bonds are hydrogen bonds. Other non-covalent bonds may be formed in addition to, or instead of, hydrogen bonds.

[01 26] In carrying out the process of the invention, a macromolecule including a plurality of functional groups, a crosslinking agent including a plurality of functional groups, and a nanofiller are provided in a reaction vessel. The macromolecule and the crosslinking agent are then treated under conditions allowing the formation of non-covalent bonds. In one embodiment, the process of the invention includes the step of heating the reaction vessel containing the
macromolecule, crosslinking agent and nanofiller. The reaction vessel may be heated at a temperature in the range of from about 20°C to about 300°C. In some embodiments, the reaction vessel may be heated at a temperature in the range of from about 140°C to about 180°C. The reaction vessel may be heated for a period of time sufficient to form the nanocomposite. In some embodiments, the reaction vessel is heated for a period in the range of from about 8 to 12 hours to form the nanocomposite.

[0127] Prior to its interaction with the crosslinking agent, the macromolecule may be regarded as pre-polymer, which is useful for the formation of the crosslinked matrix of the nanocomposite. However, following the interaction of the macromolecule with the crosslinking agent, a polymer host matrix is then generated.

[0128] In some embodiments of the process, a macromolecule is formed in the reaction vessel. In one embodiment, the process of the invention may include the step of reacting a single monomer having two or more compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more reactive functional groups to form the macromolecule in the reaction vessel. In another embodiment, the process may include the step of reacting two or more co-monomers (e.g. a first monomer and a second monomer) having compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more monomers to form the macromolecule in the reaction vessel. Examples of monomers containing compatible reactive functional groups are described herein.

[0129] The reaction conditions required for condensation polymerisation of appropriate monomers to form the macromolecule would be understood by one skilled in the relevant art. Such condensation polymerisation conditions may be dictated by the nature of the monomers used to form the macromolecule. With polycondensation reactions it is possible to some extent to control the molecular weight of the resulting macromolecule, its degree of branching (through control of monomer functionality) and its end group functionality by adjustment of the molar ratios and the functionality of the monomers used in the reaction.
[01.30] Where the macromolecule is a polyamide, the macromolecule may be prepared by mixing a polyacid monomer and a polyamine monomer together with heating and continued stirring. A condensate such as water may be liberated from the reaction between the polyacid and the polyamine and if desired, the condensate may be removed from the reaction mixture using techniques such as distillation. To promote further reaction to produce a higher molecular weight macromolecule the temperature may be increased and vacuum applied, or a polycondensation catalyst may be used. A polyamide macromolecule useful in the preparation of a self-healing nanocomposite in accordance with the invention may be a viscous polymer. In one embodiment, a polyamide macromolecule suitable for the formation of a nanocomposite of the invention may be formed by reacting a polyacid monomer with a polyamine monomer at a temperature in the range of from about about 100°C to about 120°C for a time period in the range of from about 3 to 5 hours.

[01.31] In order to provide a crosslinking agent in the reaction vessel, the process of the invention may include the step of adding a crosslinking agent to the reaction vessel. In embodiments where the macromolecule is formed in the reaction vessel, the crosslinking agent may be added before, during or after the macromolecule is formed in the vessel. In some embodiments, the process of the invention may include the step of preparing a macromolecule in the reaction vessel, then adding a crosslinking agent to the vessel after the desired macromolecule has been synthesised. In some embodiments, an excess of crosslinking agent, relative to the quantity of macromolecule, is added to the reaction vessel. An excess of crosslinking agent may be used to ensure that the crosslinked matrix is formed. In some embodiments, the amount of crosslinking agent employed in the formation of the polymer matrix may be selected from the group consisting of at least 5%, at least 15%, least 15% and at least 25% by weight, relative to the weight of macromolecule pre-polymer.

[01.32] In order to provide the nanofiller in the reaction vessel, the process of the invention may include the step of adding a nanofiller to the reaction vessel. In embodiments where the macromolecule is formed in the reaction vessel, the
nanofiller may be added before, during or after the macromolecule is formed in the vessel. In some embodiments of the process of the invention, where a crosslinking agent is added to the reaction vessel to provide the crosslinking agent in the vessel, the nanofiller may be added to the reaction vessel at approximately the same time as the crosslinking agent. Where the nanofiller includes a plurality of nanoparticles, the process of the invention may include the step of adding nanoparticles to the reaction vessel. An amount of nanofiller in the range of from about 0.5% to about 50% by weight by be added to the reaction vessel. In some embodiments, the amount of nanofiller added to the reaction vessel may be in the range of from about 2% to about 10%, or from about 3% to about 5%, by weight, relative to the weight of macromolecule pre-polymer.

[0133] To disperse the nanofiller throughout the crosslinked matrix it may be desirable to disperse the nanofiller in a composition including a macromolecule and a crosslinking agent, then treat the resulting nanofiller containing mixture under conditions allowing formation of non-covalent bonds between the macromolecule and the crosslinking agent. In one embodiment, the process of the invention includes the step of heating the reaction vessel containing the macromolecule, crosslinking agent and nanofiller. The reaction mixture may be heated at a temperature in the range of from about 20°C to about 300°C for a desired period of time. The mixture may also be stirred to disperse the nanofiller in the mixture. In some embodiments, a mixture containing the macromolecule, crosslinking agent and nanofiller is stirred at a temperature in the range of from about 50°C to about 200°C for a time period in the range of from about 4 to about 24 hours. In one embodiment, a mixture containing the macromolecule, crosslinking agent and nanofiller is stirred at a temperature in the range of from about 140°C to about 180°C for a time period in the range of from about 8 to about 12 hours.

[0134] When the mixture of macromolecule, crosslinking agent and nanofiller is heated at elevated temperature, any excess crosslinking agent that may be present may be decomposed and removed. For example, when urea is used as the crosslinking agent, excess urea may be decomposed to ammonia and
isocyanic acid. The decomposition products may then be removed from the mixture.

[0135] The macromolecule used in the process of the invention may be selected from any one of the macromolecules described herein. In one embodiment, the macromolecule is a condensation polymer. An exemplary macromolecule is a polyamide polymer including a plurality of amide functional groups. Such amide polymers may be formed from the condensation polymerisation of a carboxylic acid containing monomer (for example, a polyacid such as a dicarboxylic acid) and an amine containing monomer (for example, a polyamine such as a triamine), as described above.

[0136] The crosslinking agent used in the process of the invention may be selected from any one of the crosslinking agents described herein. In one embodiment, the crosslinking agent includes a plurality of amine or amide functional groups. An exemplary crosslinking agent is a diamide crosslinking agent, such as urea.

[0137] The nanofiller used in the process of the invention may be selected from any one of the nanofillers described herein. In one embodiment, the nanofiller includes a plurality of nanoparticles. Suitable nanoparticles that may be used in the process are nanoclay particles. The nanoclay particles may be derived from pristine clays or organically-modified clays. In an exemplary embodiment, the nanoclay particles are selected from the group consisting of montmorillonite, mica, bentonite, kaolinite, saponite, halloysite, hectorite, fluoromica, fluorohectorite, vermiculite, and magadiite particles. In embodiments of the invention, very thin platelets of clay are dispersed in the crosslinked matrix material.

[0138] In another aspect of the present invention provides a process for the preparation of a self healing nanocomposite including the steps of:

  providing a mixture including a first monomer including at least two reactive functional groups, a second monomer including at least two reactive functional groups that are compatible with the reactive functional groups of the
first monomer, a crosslinking agent including a plurality of functional groups, and a nanofiller, in a reaction vessel;

reacting the first monomer and the second monomer under conditions of condensation polymerisation to form a macromolecule including a plurality of functional groups in the reaction vessel; and

forming non-covalent bonds between the functional groups of the macromolecule and the functional groups of the crosslinking agent in the presence of the nanofiller to provide a nanocomposite including a crosslinked matrix and a nanofiller dispersed in the matrix.

[0139] The first monomer and the second monomer may be selected from any one of the monomers described herein, and reaction conditions required for condensation polymerisation of appropriate monomers to form the macromolecule would be understood by one skilled in the relevant art. Furthermore, the crosslinking agent and nanofiller may be selected from those described herein.

[0140] To form the nanocomposite, the mixture containing the first and second monomers, crosslinking agent and nanofiller may be heated at a temperature in the range of from about 20°C to about 300°C for a desired period of time. In some embodiments, the mixture is stirred at a temperature in the range of from about 50°C to about 200°C for a time period in the range of from about 4 to about 24 hours. In such embodiments, the nanocomposite may be formed in situ, in a single step process, in the reaction vessel.

[0141] Nanocomposites produced via a single step procedure involving the in situ synthesis of a macromolecule in the presence of the crosslinking agent and nanofiller may exhibit different mechanical properties to nanocomposites produced in a two-step method with a pre-formed macromolecule. For example, it is has been found that nanocomposites formed from the in situ polymerisation of monomers in the presence of a crosslinking agent and nanofiller can be more viscous than nanocomposites produced using a pre-formed macromolecule that is subsequently crosslinked in the presence of nanofiller.
[0142] While processes of the invention may employ a solvent, it is desirable that processes in accordance with one or more embodiments described herein be free of added solvent. Accordingly, the nanocomposite of the invention can be formed without the use of a solvent. However, processes of the invention may be carried out in the presence of a relatively small amount of water or alcohol, which may be generated as a by-product of a condensation reaction used to prepare the macromolecule.

[0143] An exemplary embodiment of a process of the invention may utilise the reactants and reaction conditions detailed in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid monomer (e.g. sebacic acid)</td>
<td>50 mmol</td>
</tr>
<tr>
<td>Amine monomer (e.g. DETA)</td>
<td>80 mmol</td>
</tr>
<tr>
<td>Crosslinking agent (e.g. urea)</td>
<td>25% of prepolymer</td>
</tr>
<tr>
<td>Nanofiller (e.g. clay)</td>
<td>3-5% of prepolymer</td>
</tr>
<tr>
<td>Reaction time for pre-polymer formation</td>
<td>3-5 hours</td>
</tr>
<tr>
<td>Reaction time for nanocomposite formation</td>
<td>8-12 hours</td>
</tr>
<tr>
<td>Reaction temperature for pre-polymer formation</td>
<td>100-120°C</td>
</tr>
<tr>
<td>Reaction temperature for nanocomposite formation</td>
<td>140-180°C</td>
</tr>
</tbody>
</table>

[0144] The present invention can provide a facile method for the formation of a self-healing nanocomposite in situ in one pot. In some embodiments, the process of the invention is a single-step procedure, involving the in situ polymerisation of appropriate monomers in the presence of a crosslinking agent and a nanofiller to produce the nanocomposite in a single step. In other embodiments, the process of the invention is a two-step procedure, which involves formation of a macromolecule in a first step, then crosslinking of the pre-formed macromolecule in the presence of a nanofiller in a subsequent step, to produce the nanocomposite. The pre-formed macromolecule may be optionally isolated during the two-step procedure.
[0145] It is an advantage of the process of one or more aspects of the invention that the self-healing nanocomposite can be prepared in a relatively simple method that employs fewer steps than other methods described in the prior art. As a result, the process of the invention may be more commercially feasible than other methods for producing nanocomposite materials.

[0146] In another aspect, the present invention also provides a self-healing nanocomposite prepared by a process in accordance with any one of the embodiments as described herein.

[0147] One advantage of the self-healing nanocomposite of the invention is that its properties can be tuned to suit particular applications. For example, the nanocomposite may be a mouldable nanocomposite, or it may be brittle nanocomposite. Adjustments in the physical properties of the nanocomposite may be obtained by varying the type and/or concentration of nanofiller in the nanocomposite, as well as by varying the nature of the macromolecule and/or crosslinking agent used in the crosslinked matrix of the nanocomposite.

[0148] In one embodiment, the self-healing nanocomposite of the invention can be in the form of a liquid, such as a viscous liquid. In other embodiments, the self-healing nanocomposite may behave as a liquid when heated at an elevated temperature. For example, the nanocomposite may flow like a liquid at a temperature in the range of 100-250°C. This may be useful where it is desired to prepare products containing the nanocomposite by moulding techniques such as injection moulding. The fluidity of the material makes it promising to control the rate of this process and also to replicate the details of the mould. In other embodiments, the self-healing nanocomposite may be in the form of a solid or a gel. Self-healing nanocomposites of the invention may exhibit elastic properties, and may be deformable. The nanocomposites of the invention may exhibit shape memory properties as well as self-healing properties.

[0149] The self-healing nanocomposite of the invention may also be compatible with solvents. For example, the nanocomposite may be capable of swelling in
the presence of organic solvents such as dodecane and/or in the presence of water or moisture. The addition of water may provide a means of varying the nanocomposite properties mentioned above, as water may also participate in non-covalent bonding interactions, such as hydrogen bonding interactions.

[0150] The nanocomposite of the invention exhibits self-healing properties. That is, upon failure or damage of the nanocomposite, for example, by fracture, breakage, cuts, cracks, scratches etc., the damaged area can be readily repaired. One skilled in the art would appreciate that when the nanocomposite is damaged by a cut or a fracture, parts of the material separate from one another. This separation leads to the creation of interfaces at the damage site. The present invention enables the damage to be repaired as the interfaces are brought together in close proximity. Desirably, the interfaces are brought into direct contact with one another.

[0151] The nanocomposite of the invention may exhibit at least about 5% self healing, and may exhibit at least about 10%, at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, or at least about 90% self-healing. The nanocomposite may exhibit up to about 100% self-healing.

[0152] The self-healing nanocomposite of the invention may exhibit autonomic mending. In other words, the nanocomposite is capable of initiating its own self repair without the need to use catalysts, special surface treatments or harsh radiation or thermal treatments to induce or promote repair of the damage site.

[0153] Without wishing to be limited by theory, it is believed that the self-healing capability of the nanocomposite of the invention is promoted by the non-covalent bonding interactions between the macromolecule and the crosslinking agent used to form the crosslinked matrix of the nanocomposite. The non-covalent bonding interactions provide reversible crosslinks in the matrix. Upon failure or damage of the nanocomposite, crosslinks present in the matrix may be broken or disrupted as a result of the stress suffered by the nanocomposite during fracture or damage. The ability to reform the crosslinks through re-
establishment of the non-covalent bonding interactions enables the nanocomposite to be repaired.

[0154] The self-healing nanocomposite of the invention advantageously is capable of repeated self-healing. That is, the nanocomposite is re-mendable and may undergo repeated damage and repair at the same site without substantial loss or compromise of the physical and mechanical properties of the nanocomposite. Accordingly, the nanocomposite of the invention may self-heal more than once.

[0155] In some embodiments, the nanocomposite of the invention self-heals at a temperature in the range of from about 0 °C to about 300 °C. In some embodiments, the nanocomposite of the invention is able to self-heal at ambient temperature, or under mild thermal treatment. Mild thermal treatment may be treatment at a temperature in the range of from about 25 °C to about 80 °C.

[0156] The type of conditions under which the nanocomposite exhibits self-healing capability may be influenced by the nanofiller. Where the nanofiller includes a plurality of nanoparticles, such as nanoclay particles, varying the type of nanoparticles used can allow the nanocomposite to exhibit self-healing capabilities under different conditions. For example, a nanocomposite of the invention including organically-modified nanoclay particles may exhibit self-healing at ambient room temperature, while a nanocomposite of the invention including nanoclay particles derived from pristine clays may exhibit self-healing at an elevated temperature, such as a temperature in the range of from about 25°C to about 200°C. Functional groups on the nanoparticles may also influence self-healing behavior if such groups are capable of participating in non-covalent bonding interactions.

[0157] Reaction times for self-healing of the nanocomposite may range from hours to minutes, depending on the healing mechanism used. In some embodiments, the nanocomposite of the invention self-heals within a time period selected from the group consisting of about 72 hours, about 48 hours, about 24 hours, about 6 hours, about 2 hours, about 1 hour, about 30 minutes,
about 5 minutes, and about 1 minute. In some embodiments of the invention, the nanocomposites can self-heal quite rapidly. Temperature may play a role in healing time, with higher temperatures supporting faster healing processes and shorter healing time. Healing time and temperature may also have an influence on the mechanical properties of the healed nanocomposite. For example, the strength of healed nanocomposite material can increase with healing temperature and healing time.

[0158] The self-healing capability of the polymer nanocomposite of the invention may be observed visually, using techniques such as optical microscopy. Other techniques may also be used.

[0159] The self-healing properties of the polymer nanocomposite can be tuneable. Tuneable self-healing properties may be obtained by altering the macromolecule, crosslinking agent and/or nanofiller present in the nanocomposite. For example, organically modified nanoclays may provide polymer nanocomposites with decreased mechanical strength, while unmodified nanoclays may provide polymer nanocomposites with increased mechanical strength, compared to a base polymer matrix with no nanofiller. Accordingly, the choice of nanofiller can enable the mechanical properties of the polymer nanocomposite to be adjusted to suit particular applications. Self-healing properties may also be adjusted by varying the relative proportions of these components in the nanocomposite.

[0160] In some embodiments, the self-healing polymer nanocomposite of the invention is capable of being reconstructed or remodelled from one physical shape into another, desired physical shape. Accordingly, beside the self-healing capability, the polymer nanocomposites of the invention may exhibit properties of recyclability or reworkability, which could provide advantages from an economic point of view. The ability to alter the physical shape of the nanocomposite may be influenced by the types of monomers used to form the macromolecule employed in the nanocomposite.
[01.61] In a further aspect, the present invention provides a self-healing product including a self-healing nanocomposite as described herein. The self-healing product may take on a variety of forms as the nanocomposite of the invention is capable of being moulded or shaped to adopt a desired form. In some embodiments, the self-healing product is an article of manufacture.

[01.62] In a further aspect, the present invention provides a self-healing coating including a self-healing nanocomposite as described herein. The self-healing coating may be in the form of a film that is applied to a substrate surface. For example, the self-healing coating may be in the form of a self-healing paint coating. Such coatings may be susceptible to damage from scrapes or scratches and the ability of the coating to self-heal autonomously could represent a significant advantage.

[01.63] In a further aspect, the present invention provides a polymer composition including at least one polymer in combination with a self-healing nanocomposite as described herein. In some embodiments, the polymer composition includes a self-healing nanocomposite of the invention and at least one polymer selected from the group consisting of polycrylates (such as polymethyl acrylate), polymethacrylates (such as polymethyl methacrylate), acrylonitrile butadiene rubber, ethylene propylene diene rubber, polyolefins (such as polypropylene and polyethylene), polycarbonate, polystyrene, polyvinyl chloride and polyamides. To prepare the polymer composition, the self-healing nanocomposite may be combined with reactants used to form the polymer and in this manner, be combined with the polymer as the polymer is being synthesised. Alternatively, a pre-formed polymer may be introduced to a reaction mixture containing the macromolecule, crosslinking agent and nanofiller used to form the self-healing nanocomposite and in this manner, be combined with the nanocomposite as the nanocomposite is synthesised. In a further alternative, if diffusion properties are favourable, the self-healing nanocomposite and polymer may be physically blended together to provide the polymer composition.

[01.64] Polymer nanocomposites of the invention can be used in a wide range of applications due to the ability to tune the properties of the nanocomposite to suit
a particular application. In some embodiments, nanocomposite of the invention advantageously exhibit enhanced tensile strength. Nanocomposites with favourable tensile properties may be used to construct biomedical materials or products suitable for use in humans and other animals.

[0165] Polymer nanocomposites of the invention may also be used to in the preparation products such as high performance parts, coatings, cosmetics, dental materials, toys or seals. Such products may be vulnerable to damage such as cracks or failure due to the product being subjected to continued mechanical stress or from being in continued contact with liquids or other materials. In such circumstances it may be difficult to detect when the product has sustained damage. The inclusion of the nanocomposite of the invention in such products means that the products would have the ability to self-heal in a rapid and autonomous manner.

EXAMPLES
[0166] The present invention is described with reference to the following examples. It is to be understood that the examples are illustrative of and not limiting to the invention described herein.

Materials
[0167] Monomers and crosslinking agents were obtained from Sigma Aldrich Co., whereas the montmorillonite clays cloisite 25A (C25A), cloisite30B (C30B) and CloisiteNa+ (CNa+) were obtained from Southern clay products, Inc. All chemicals were used as received.

[0168] Unless stated otherwise, the terms 'CNa+', 'C25A' and 'C30B' as used herein denote Cloisite Na+, Cloisite 25A and Cloisite 30B, respectively. CNa+ is a natural sodium montmorillonite clay containing no organic modifier. C25A is an organically modified clay which is modified with dimethyl, dehydrogenated tallow, 2-ethylexyl quaternary ammonium salt (2MHTL8). C30B is an organically modified clay which is modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt (MT2EtOH).
Unless stated otherwise, the terms 'SMP', 'SMPNa+', 'SMPA' and 'SMPB' as used herein denote a supramolecular polymer (the crosslinked matrix) with no clay, nanocomposite with CNa+ clay, C25A clay and nanocomposite with C30B clay, respectively.

**Characterisation Methods**

X-ray diffraction (XRD) measurements were carried out on a Philips PW1 140/90 X-ray diffractometer with Cu Kα radiation target at 25 mA and 40 kV; scan rate of 1 deg/min; step size of 0.02 degree; 2θ scan range from 2 to 80.

Optical microscopy (OM) was used to analyse the morphology and self-healing capability of nanocomposite polymers using a Nikon TS100 optical microscope.

The Thermo gravimetric analysis (TGA) measurements were carrying out to determine the thermal stability of samples using a NETZSCH STA 409 PC/PG instrument. Initially, the sample was heated under Argon atmosphere up to 600 °C. The heating rate was 10 °C /min. For each sample, three tests were carried out under the same heating rate and the temperatures were reproducible. Experiments were conducted in an inert atmosphere under Ar gas at a flow rate of 30 ml/minute

Differential scanning calorimetry (DSC) experiments were carried out using a TA Q200 differential scanning calorimeter instrument. The measurement was performed using 5-10 mg of the sample under an atmosphere of nitrogen atmosphere. The samples were first heated to 170 °C and held at that temperature for 3 min to remove the thermal history. Subsequently, the samples were cooled to -50 °C at the rate of 10 °C /min, held for 5 min and again heated to 170 °C at 20 °C /min. The glass transition temperature (Tg) was taken as the midpoint of the second heating scan of the plot in the DSC thermo grams.

For the mechanical property studies, tensile properties of the polymer nanocomposites were measured on a Lloyd LR 30 K testing machine. The tests
were conducted on specimens which were technically made according to ASTM standard D 638-03. The tests were conducted at 25°C. At least five specimens were tested to obtain the average values of tensile properties for the entire nanocomposites and its healed samples.

[0175] Differential mechanical analysis was carried out on a dynamic mechanical thermal analyzer (DMTA) on a TA Q800 machine at compression mode under room temperature. The frequency used was 1.0 Hz and the force ramp rate was 0.01 N/sec. The round specimen dimensions were 3.5mm x 1.5mm. The relaxation modulus, displacement were measured on the application of static load from 0.001 to 18 N.

General Procedure for the Preparation of Polymer Nanocomposites

[0176] Self-healing polymer nanocomposites in the following Examples are prepared using a one pot, two-step procedure in the absence of added solvent and under an inert atmosphere with controlled temperature. To a stirred solution of polyamine monomer (80 mmol) under a nitrogen atmosphere maintained under reflux, a polyacid monomer was added (50 mmol) in a slow fashion over a period of 30 minutes. The mixture was turbid at room temperature and was heated to 100°C under nitrogen flow. It was then heated for 1 hour under same gas flow and temperature which turned to a viscous solution. The resulting condensation product is a macromolecule polymer, sometimes known as a pre-polymer. To the hot mixture of pre-polymer, crosslinking agent (70 mmol) and a selected nanofiller (which is 3% of pre-polymer) was then added. As the reaction mixture is stirred, it is observed that gaseous ammonia is given off (verified with pH paper), accompanied by foaming of the reaction medium. When the ammonia being given off decreases, the reaction mixture was then heated to 165°C by 5°C increments every 60 minutes maintaining the same gas flow. Once the whole content of the reactor had raised, the reaction mixture becomes difficult to stir and the stirring was stopped. The resulting viscoelastic material was then cooled to 100°C and quickly collected while it is still hot and elastic. Once the material cooled to room temperature, it was then placed in a vacuum oven at 70 °C (vacuum of 5 mmHg) in order to remove any remaining ammonia. The resulting polymer nanocomposite material obtained is
hydraulically pressed, at 70 °C, in the form of plates that are 1 to 3 mm thick. The samples were then characterised using the techniques described above.

**Example 1 - Pristine Layered Silicate Nanocomposite SMPNa+**

[01 77] The pristine layered silicate was used in this example and it was Cloisite Na+ (Southern Clay Products). Nanocomposites containing layered silicate montmorillonite were formed by mixing 10.3 g (50.9 mmol) of sebacic acid and 8.99 g (87 mmol) of diethylenetriamine in a 100 ml round bottom flask. The flask was fitted with a condenser and flushed with nitrogen gas to maintain inert atmosphere. The contents were magnetically stirred at 120 °C (oil bath) for 4 hours. The mixture was then cooled to 90 °C. To the reaction mixture 4.9 g (81.5 mmol) of urea and 0.95 g Cloisite Na+ (Southern Clay Products) was added. The forming of reaction mixture along with evolution of ammonia was observed at 140 °C. The temperature was increased to 175 °C at slow increment rate of 10 °C per hour after the ammonia evolution has dropped down significantly. The reaction mixture was left at 175 °C for 12 hours for completion of reaction. When there was no phase separation in the reaction mixture the following procedure was used for getting the nanocomposite formed. The reaction mixture was transferred to a sheet of Teflon while hot at room temperature. The material obtained was hot pressed at 75 °C for 5 minutes to form sheets of 2 mm thickness.

**Example 2 - Modified Layered Silicate Nanocomposite SMPA**

[01 78] The organically modified layered silicate used in this example was Cloisite 25A (C25A) (Southern Clay Products). 10.1 g (50 mmol) of sebacic acid and 8.25 g (80 mmol) of diethylenetriamine are added in a 100 ml round bottom flask. The flask was fitted with a condenser and flushed with nitrogen gas to maintain inert atmosphere. The contents were magnetically stirred at 120 °C (oil bath) for 4 hours. The mixture was then cooled to 90 °C. To the reaction mixture 4.58 g (76.3 mmol) of urea and 0.55g Cloisite 25A was added. The forming of reaction mixture along with evolution of ammonia was observed at 130 °C. The temperature was increased to 165 °C at slow increment rate of 10 °C per hour after the ammonia evolution has dropped down significantly. The reaction mixture was left at 165 °C for 10 hours for completion of reaction. When there
was no phase separation in the reaction mixture the following procedure was used for getting the nanocomposite formed. The reaction mixture was transferred to a sheet of Teflon while hot at room temperature. The material obtained was hot pressed at 75 °C for 5 minutes to form sheets of 2 mm thickness.

Example 3 - Modified Layered Silicate Nanocomposite SMPB

[0179] The organically modified layered silicate used in this example was Cloisite 30B (C30B) (Southern Clay Products). This nanocomposite was formed using the following synthetic step. 10.1 g (50 mmol) of sebacic acid and 8.25 g (80 mmol) of diethylenetriamine are added in a 100 ml round bottom flask. The flask was fitted with a condenser and flushed with nitrogen gas to maintain inert atmosphere. The contents were magnetically stirred at 120 °C (oil bath) for 4 hours. The mixture was then cooled to 90 °C. To the reaction mixture 4.58 g (76.3 mmol) of urea and 0.55 g Cloisite 30B was added. The forming of reaction mixture along with evolution of ammonia was observed at 130 °C. The temperature was increased to 165 °C at slow increment rate of 10 °C per hour after the ammonia evolution has dropped down significantly. The reaction mixture was left at 165 °C for 10 hours for completion of reaction. When there was no phase separation in the reaction mixture the following procedure was used for getting the nanocomposite formed. The reaction mixture was transferred to a sheet of Teflon while hot at room temperature. The material obtained was hot pressed at 75 °C for 5 minutes to form sheets of 2 mm thickness.

[0180] Following the general procedure described above, polymer nanocomposites were prepared using the components detailed in Table 2. A comparative polymer matrix without nanofiller (SMP) was also prepared for comparative experiments.
Table 2

<table>
<thead>
<tr>
<th>Example No</th>
<th>Polyacid monomer</th>
<th>Polyamine monomer</th>
<th>Crosslinking agent</th>
<th>Nanofiller</th>
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</thead>
<tbody>
<tr>
<td>Comparative Ex. 1 (SMP)</td>
<td>Sebacic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>-</td>
</tr>
<tr>
<td>4 (SMPA)</td>
<td>Sebacic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 25A</td>
</tr>
<tr>
<td>5 (SMPB)</td>
<td>Sebacic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite 30B</td>
</tr>
<tr>
<td>6 (SMPNa+)</td>
<td>Sebacic acid</td>
<td>DETA</td>
<td>Urea</td>
<td>Cloisite Na+</td>
</tr>
<tr>
<td>7</td>
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<td>DETA</td>
<td>Urea</td>
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</tr>
<tr>
<td>8</td>
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<td>DETA</td>
<td>Urea</td>
<td>Cloisite 30B</td>
</tr>
<tr>
<td>9</td>
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<td>DETA</td>
<td>Urea</td>
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[01 81] Figure 1 shows characteristic XRD patterns of a crosslinked polymer matrix (SMP), montmorillonite clays Cloisite Na+ (CNa+), Cloisite 25A (C25A)
and Cloisite 30B (C30B), and modified layered silicate nanocomposites
SMPNa+, SMPA, SMPB produced from SMP with CNa+, C25A, C30B,
respectively, in accordance with embodiments of the invention. The XRD
patterns clearly indicate the shift or absence of diffraction peaks for
montmorillonite clays CNa+, C25A and C30B in SMPNa+, SMPA and SMPB
nanocomposites, indicating the formation of delaminated nanocomposite
materials.

[0182] When montmorillonite is modified by organic modifier, the gallery of
montmorillonite is intercalated and expanded by the molecular chain of the
organic modifier. In compound samples shown in Figure 1, the increased clay
spacing due to the addition of the modifier between the platelets is evident. The
gallery spacing of organoclay in polymer nanocomposites generally depends on
the interaction between the polymer matrix and the organoclay.

[0183] As seen in Figure 1, the peaks correspond to the (001) plane reflection of
the clay, the d001 peak of pristine montmorillonite at 2Θ = 4.2 (C25A), and 4.8
(C30B) corresponds to 1.8 nm interlayer spacing for SMPA and SMPB
nanocomposite compounds. While 2Θ = 7.4 (CNa+) corresponds to 1.19 nm
interlayer spacing which was completely shifted to 1.39 nm interlayer spacing in
the diffraction peaks of SMPNa+ nanocomposite compound, indicating the
silicate layer are completely exfoliated in the polymer matrix and thus form
delaminated nanocomposites. The inset peak shown in Figure 1 shows a peak
for the montmorillonite clay at 21.7 and this corresponds to the intergallery
spacing of 1.4 nm which is being shifted to 19.7. Moreover, the characteristic
peaks of C25A at 1.86 and of C30B at 1.85 have completely disappeared in
SMPA and SMPB. This is also a clear indication of intercalated montmorillonite
nanoclay into the polymer matrix.

[0184] Figure 2 shows optical microscope images of nanocomposite SMPB in
accordance with an embodiment of the invention taken (a) 2 seconds, (b) 10
seconds, (c) 20 seconds, (d) 40 seconds, (e) 60 seconds, and (f) 90 seconds
after a cut is made on the surface of the nanocomposite material. The optical
microscope images demonstrate the self-healing capability of the
nanocomposite following mechanical damage. The healing response occurs automatically without any manual involvement, indicating the existence of an automatic self-healing behaviour.

[01.85] Figure 3 shows the results of dynamic mechanical analysis (DMA) of the macromolecule pre-polymer, SMP and polymer nanocomposites SMPNa+, SMPA and SMPB, in accordance with embodiments of the invention. Dynamic mechanical analysis enables the transition and relaxation behaviour of polymer systems to be studied. The DMA curves of Figure 3 illustrates the variation in the mechanical strength of nanocomposites SMPNa+, SMPA and SMPB compared to the base material SMP and confirms that the addition of nanoclay has a significant role in altering mechanical properties. It was observed that polymer nanocomposites with the same 3 wt % nanoclay loading but with different organo-modifiers or no organic modifier show a difference in behaviour as SMPB behaves with more strength compared to SMPA, which may be due to the presence of -OH groups in SMPB providing greater hydrogen bonding capability. The nanocomposite SMPNa+ with sodium montmorillonite nanoclay exhibited a linear straight line indicating its stronger and stiffer nature and thereby higher modulus.

[01.86] The results of tensile testing of SMPNa+ in accordance with an embodiment of the invention is shown in Figure 4.

[01.87] Figure 4 shows stress-strain curves on a tensile testing machine for original and healed nanocomposite SMPNa+ in accordance with an embodiment of the invention. The curves demonstrate the comparable efficiency of 'original' polymer nanocomposite, and 'healed' polymer nanocomposite after a cut was made in the original nanocomposite and then healed at 90 °C for 5 minutes followed by air cooling for 15 minutes. As seen in Figure 4, the nanocomposite retained mechanical strength after damage and healing, and also exhibited temperature-responsive self-healing behaviour.

[01.88] The healing efficiency (%) of the self-healing nanocomposite can be expressed using the tensile strength of the healed sample (tensile strength
healed) and tensile strength of the original sample (tensile strength original) according to the following equation:

\[
\text{Healing efficiency} = 100\% \times \frac{\text{tensile strength healed}}{\text{tensile strength original}}.
\]

[01.89] The study of SMPNa+ showed an 81% healing efficiency upon application of a thermal stimulus (85-95 °C).

[01.90] Thermogravimetric analysis (TGA) provides information on the thermal stability and thermal degradation behaviour of the polymer nanocomposites. The results of TGA analysis of the macromolecule pre polymer, pristine (SMP) and clay modified nanocomposites (SMPNa+, SMPA, SMPB) is shown in Table 3 and Figure 5.

<table>
<thead>
<tr>
<th>Macro-molecule</th>
<th>SMP</th>
<th>SMPNa+</th>
<th>SMPA</th>
<th>SMPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset Degradation Temperature (°C)</td>
<td>285</td>
<td>415</td>
<td>420</td>
<td>440</td>
</tr>
<tr>
<td>Residual mass at 900°C (%)</td>
<td>18</td>
<td>11</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

[01.91] The peak decomposition temperatures (the temperature where the thermal decomposition rate is maximum), and the corresponding peak decomposition rates (the maximum rate of decomposition at peak decomposition temperatures) are indicators of the thermal stability of the samples. As seen in Figure 5, it was observed that the peak decomposition temperature of SMP is almost same as that of SMPNa+. However, thermal properties changed in case of SMPA and SMPB, suggesting that the type of organic modifier can affect thermal decomposition trends.
The presence of residue at 900°C in the TGA curves is due the presence of the inorganic clay in the polymer nanocomposites. The observed increase in the thermal stability of SMPA and SMPB nanocomposites may be due to the high thermal stability of clay and the interfacial reactions between the clay layers and the polymer matrix through intercalation/exfoliation.

Differential Scanning Calorimetry (DSC) was used to measure the thermal properties of SMP, SMPA, SMPB and SMPNa* samples prepared in accordance with the invention, and the results are shown in Figure 8. The glass transition ($T_g$) temperature of compound SMPB was observed at -24°C, SMPA exhibited $T_g$ at -30.5°C while SMPNa* gave $T_g$ peak at 18.5°C and for the pristine compound SMP at -26°C, respectively. The macromolecule pre-polymer gave a $T_g$ peak at -5.5°C. The results can be explained on the basis of easy mobility of the clay chains within the polymer matrix layers thereby demonstrating the intercalated nature of the modified clay nanocomposites. The increase in $T_g$ of nanocomposites is in agreement with the results obtained from DMA.

Nanocomposites prepared with different polyamide macromolecules were also characterised by DSC, TGA and XRD.

Figure 7 compares DSC results obtained for the nanocomposites of Examples 4, 10, 13 and 16. The nanocomposites contain C25A nanoclay and a crosslinked polymer matrix including pre-polymers derived from dicarboxylic acid monomers of varying chain length. The DSC results show how glass transition temperature ($T_g$) varies for the different nanocomposites.

Figure 8 compares TGA results obtained for the nanocomposites of Examples 5, 11, 14 and 17. The nanocomposites contain C30B nanoclay and a crosslinked polymer matrix including pre-polymers derived from dicarboxylic acid monomers of varying chain length. The TGA results compare the decomposition temperatures of the different nanocomposites. The temperature at which 50% mass loss occurs ($T_{50%}$) is also given in the figure.
[0197] The above DSC and TGA results indicate that nanocomposite thermal stability can vary when different pre-polymers are used.

[0198] Figure 9 provides XRD patterns of the nanocomposites of Examples 4, 10, 13 and 16, which are prepared with C25A nanoclay. Figure 10 provides XRD patterns of the nanocomposites of Examples 5, 11, 14 and 17, which are prepared with C30B nanoclay. The XRD results indicate the formation of nanocomposites.

[0199] Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope of the present invention.

[0200] Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification (including the claims) they are to be interpreted as specifying the presence of the stated features, integers, steps or components, but not precluding the presence of one or more other feature, integer, step, component or group thereof.
CLAIMS:

1. A self healing nanocomposite including:
   a crosslinked matrix, said matrix including a macromolecule including a plurality of functional groups and a crosslinking agent including a plurality of functional groups, wherein the functional groups of the macromolecule interact with the functional groups of the crosslinking agent by non-covalent bonding interactions to form non-covalent bonds between the macromolecule and the crosslinking agent; and
   a nanofiller dispersed in the matrix.

2. A nanocomposite according to claim 1 wherein the non-covalent bonds are hydrogen bonds.

3. A nanocomposite according to claim 1 or claim 2 wherein the functional groups of the macromolecule are selected from the group consisting of hydrogen donating functional groups, hydrogen accepting functional groups, and mixtures thereof.

4. A nanocomposite according to any one of claims 1 to 3 wherein the functional groups of the macromolecule are each independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups.

5. A nanocomposite according to any one of claims 1 to 4 wherein the functional groups of the macromolecule are each independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups.

6. A nanocomposite according to any one of claims 1 to 5 wherein the macromolecule is a condensation polymer.

7. A nanocomposite according to any one of claims 1 to 8 wherein the macromolecule has a moiety having a structure of Formula (II):
where

\[ X \text{ at each occurrence is independently selected from the group consisting of O and N;} \]

\[ A \text{ at each occurrence is independently selected from the group consisting of O and NR, where R is H or alkyl (preferably } c_{1-4} \text{ alkyl}); \]

\[ R^1 \text{ represents the remainder of a first monomer unit;} \]

\[ R^2 \text{ represents the remainder of a second monomer unit;} \]

\[ m \text{ represents the number of repeating units for the first monomer and is at least 1;} \]

\[ n \text{ represents the number of repeating units for the second monomer and is at least 1.} \]

8. A nanocomposite according to claim 6 or claim 7 wherein the macromolecule is a polyamide including a plurality of amine functional groups.

9. A nanocomposite according to any one of claims 6 to 8 wherein the macromolecule is formed from the condensation polymerization of two or more monomers including compatible reactive functional groups.

10. A nanocomposite according to any one of claims 6 to 9 wherein the macromolecule is formed from the condensation polymerisation of a polyacid monomer and a polyamine monomer.

11. A nanocomposite according to any one of claims 8 to 8 wherein the macromolecule is formed from the condensation polymerization of a monomer including two or more compatible reactive functional groups.
12. A nanocomposite according to any one of claims 1 to 11 wherein the functional groups of the crosslinking agent are each independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups.

13. A nanocomposite according to any one of claims 1 to 12 wherein the functional groups of the crosslinking agent are each independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups.

14. A nanocomposite according to any one of claims 1 to 13 wherein the functional groups of the crosslinking agent are each amide functional groups.

15. A nanocomposite according to any one of claims 1 to 14 wherein the crosslinking agent is a diamide crosslinking agent.

16. A nanocomposite according to any one of claims 1 to 15 wherein the crosslinking agent is urea.

17. A nanocomposite according to any one of claims 1 to 16 wherein the nanofiller includes one or more selected from the group consisting of nanofibres, nanosheets, nanoparticles, nanotubes, graphitic nanofillers, nanowhiskers, metal phosphates, layered double hydroxides, nanocalcium, and metal chalcogenides.

18. A nanocomposite according to any one of claims 1 to 17 wherein the nanofiller includes a plurality of nanoparticles.

19. A nanocomposite according to any one of claims 1 to 18 wherein the nanoparticles are nanoclay particles.

20. A nanocomposite according to claim 19 wherein the nanoclay particles are derived from a clay selected from the group consisting of pristine clays and organically-modified clays.
21. A nanocomposite according to claim 19 or claim 20 wherein the nanoclay particles are capable of cation exchange.

22. A nanocomposite according to any one of claims 19 to 21 wherein the nanoclay particles are layered silicate clay particles.

23. A nanocomposite according to any one of claims 19 to 22 wherein the nanoclay particles are selected from the group consisting of montmorillonite, mica, bentonite, kaolinite, saponite, halloysite, hectorite, fluoromica, fluorohectorite, vermiculite, and magadiite particles.

24. A nanocomposite according to any one of claims 1 to 23 wherein the nanofiller is present in an amount in the range of from about 0.5% to about 50% by weight of the nanocomposite.

25. A nanocomposite according to any one of claims 1 to 24 wherein the nanofiller is present in an amount in the range of from about 2% to about 10% by weight of the nanocomposite.

26. A nanocomposite according to any one of claims 1 to 25 wherein the nanofiller is present in an amount in the range of from about 3% to about 5% by weight of the nanocomposite.

27. A nanocomposite according to any one of claims 1 to 26 wherein the nanocomposite has a structure selected from the group consisting of an intercalated structure, an exfoliated structure, and a flocculated structure.

28. A nanocomposite according to any one of claims 1 to 27 wherein the nanocomposite self heals at a temperature in the range of from about 0 °C to about 300 X.

29. A nanocomposite according to any one of claims 1 to 28 wherein the nanocomposite self heals within a time period selected from the group
consisting of about 72 hours, about 48 hours, about 24 hours, about 6 hours, about 2 hours, about 1 hour, about 30 minutes, about 5 minutes, and about 1 minute.

30. A nanocomposite according to any one of claims 1 to 29 wherein the nanocomposite exhibits repeated self-healing.

31. A process for the preparation of a self-healing nanocomposite including the steps of:

   providing a macromolecule including a plurality of functional groups, a crosslinking agent including a plurality of functional groups, and nanofiller in a reaction vessel; and

   forming non-covalent bonds between the functional groups of the macromolecule and the functional groups of the crosslinking agent in the presence of the nanofiller to provide a nanocomposite including a crosslinked matrix and a nanofiller dispersed in the matrix.

32. A process according to claim 31 wherein the non-covalent bonds are hydrogen bonds.

33. A process according to claim 31 or claim 32 wherein the functional groups of the macromolecule are selected from the group consisting of hydrogen donating functional groups, hydrogen accepting functional groups, and mixtures thereof.

34. A process according to any one of claims 31 to 33 wherein the functional groups of the macromolecule are each independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups.

35. A process according to any one of claims 31 to 34 wherein the functional groups of the macromolecule are each independently selected from the group consisting of hydroxyl, amine, amide, and carboxylic acid functional groups.
36. A process according to any one of claims 31 to 35 including the step of forming a macromolecule in the reaction vessel to provide the macromolecule in the reaction vessel.

37. A process according to claim 36 wherein the macromolecule is a condensation polymer.

38. A process according to claim 37 wherein the macromolecule is a polyamide polymer.

39. A process according to any one of claims 36 to 38 wherein the process includes the step of reacting two or more monomers having compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more monomers to form the macromolecule in the reaction vessel.

40. A process according to claim 39 including the step of reacting a polyacid monomer and a polyamine monomer to form the macromolecule in the reaction vessel.

41. A process according to any one of claims 36 to 38 wherein the process includes the step of reacting a monomer having two or more compatible reactive functional groups in the reaction vessel under conditions allowing condensation of the two or more reactive functional group to form the macromolecule in the reaction vessel.

42. A process according to any one of claims 36 to 41 including the step of adding a crosslinking agent to the reaction vessel to provide the crosslinking agent in the reaction vessel, wherein the crosslinking agent is added during or after formation of the macromolecule in the reaction vessel.

43. A process according to any one of claims 31 to 42 wherein the functional groups of the crosslinking agent are each independently selected from the group consisting of halogen, hydrocarbon, oxygen, and nitrogen containing functional groups.
44. A process according to any one of claims 31 to 43 wherein the functional groups of the crosslinking agent are each independently selected from the group consisting of hydroxy, amine, amide, and carboxylic acid functional groups.

45. A process according to any one of claims 31 to 44 wherein the functional groups of the crosslinking agent are each amide functional groups.

46. A process according to any one of claims 31 to 45 wherein the crosslinking agent is a diamide crosslinking agent.

47. A process according to any one of claims 31 to 46 wherein the crosslinking agent is urea.

48. A process according to any one of claims 42 to 47 including the step of adding a nanofiller to the reaction vessel to provide the nanofiller in the reaction vessel, wherein the nanofiller added before, during, or after the addition of the crosslinking agent in the reaction vessel.

49. A process according to claim 48 wherein the crosslinking agent and the nanofiller are added to the reaction vessel at approximately the same time.

50. A process according to any one of claims 31 to 49 wherein the nanofiller includes one or more selected from the group consisting of nanofibres, nanosheets, nanoparticles, nanotubes, graphitic nanofiilers, nanowhiskers, metal phosphates, layered double hydroxides, nanocaicium, and metal chalcogenides.

51. A process according to any one of claims 31 to 50 wherein the nanofiller includes a plurality of nanoparticles.

52. A process according to claim 51 wherein the nanoparticles are nanoclay particles.
53. A process according to claim 52 wherein the nanoclay particles are derived from a clay selected from the group consisting of pristine clays and organically modified clays.

54. A process according to claim 52 or claim 53 wherein the nanoclay particles are capable of cation exchange.

55. A process according to any one of claims 52 to 54 wherein the nanoclay particles are layered silicate clay particles.

56. A process according to any one of claims 52 to 55 wherein the nanoclay particles are selected from the group consisting of montmorillonite, mica, bentonite, kaolinite, saponite, halloysite, hectorite, fluoromica, fluorohectorite, vermiculite, and magadiite particles.

57. A process according to any one of claims 31 to 58 including the step of heating the reaction vessel containing the macromolecule, the crosslinking agent and the nanofiller.

58. A process according to claim 57 wherein the reaction vessel is heated at a temperature in the range of from about 20 °C to about 300 °C.

59. A self healing product including a nanocomposite according to any one of claims 1 to 30.

60. A self healing coating including a nanocomposite according to any one of claims 1 to 30.
FIG 4

Stress $\sigma$ (MPa) vs. Strain $\epsilon$ (cm)

Original
Healed
FIG 6

Temperature (°C)

Heat Flow (a.u.)

-70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80

Tg = 28 °C
Tg = 24 °C
Tg = 18.5 °C
Tg = -5.5 °C
Pre-polymer
SMPNa+
SMPA
SMPB
SMP
FIG 7

Heat Flow (a.u.)

Sebacic acid nanocomposite; Tg = 30.5 °C

Azelaic acid nanocomposite; Tg = 25.5 °C

Pimelic acid nanocomposite; Tg = 35.5 °C

Glutaric acid nanocomposite; Tg = 42.2 °C

Temperature (°C)
FIG 9

Graph showing the intensity vs. 2θ degree for different nanocomposites:
- Cloisite 25A
- Pimelic acid nanocomposite
- Azelaic acid nanocomposite
- Sebacic acid nanocomposite
- Glutaric acid nanocomposite
FIG 10
INTERNATIONAL SEARCH REPORT

International application No. PCT/AU2011/001459

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C08K 13/04 (2006.0 1)  C08K3/20 (2006.0 1)  C09D 5/00 (2006.01)
B82Y 30/00 (201.1.01)  C08L 77/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, epodoc, caplus: polymer? or polyamide?, hydrogen bond+, non_covalent bond+, self_heal+, self_repair+, healable, nano+ and +composite+; Inspec: polyamide or nano+, +composite, self heal+, self repair+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category*</th>
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<tr>
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<td>US 2008/0287638 A1 (REYNOLDS et al.) 20 November 2008 See abstract, [0034], [0039], Tables 1-2, Figures 2-4</td>
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<td>X</td>
<td>WANG QIGANG et al., &quot;High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder&quot;, Nature, 201 0, vol 463, pages 339-343 See abstract, Figure 1, col 1 page 339, page 342</td>
<td>1-6, 11-14, 17-39, 41-45, 48-60</td>
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[X] Further documents are listed in the continuation of Box C  [X] See patent family annex

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Date of the actual completion of the international search
3 January 2012

Date of mailing of the international search report
5 JANUARY 2012

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<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>CORDIER, PHILLIPPE et al., &quot;Self-healing and thermoreversible rubber from supramolecular assembly&quot;, Nature, 2008, vol 451, pages 977-980. See col 1 of page 977, Figure 2</td>
<td>1-60</td>
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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<td>US 2008287638</td>
<td>WO 2009023337</td>
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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX