Self Healing in Nanoparticle Reinforced Polymers and other Polymer Systems

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Abstract

This chapter aims at combining new insights in the field of (liquid encapsulated) self healing polymer systems as well as nanoparticle reinforced polymers to set the direction for the development of nanoparticle reinforced self healing polymers. In the case of self healing polymers the strategy is to minimise the volume fraction encapsulated healing agent for a desired healing performance. In the case of nanoparticle reinforced polymers the challenge is to maximise the mechanical property improvement for a certain fraction of nanoparticles.

For both systems the property to be optimised, i.e. the healing potential or the strengthening effect, is mathematically shown to depend on the aspect ratio of the added ingredient as well as its volume fraction. The chapter ends with a first exploration of the use of nanoparticle reinforcement to get attractive repetitive self healing behaviour in a polymer system still meeting minimal mechanical properties.

Table of Contents

1. **Introduction**

Two major developments in the field of structural polymer materials marked the turn of this century: i) the development of nano-particle reinforced polymers and ii) development of self healing polymers. Nano-particle reinforcement form a logical extension of the successful micro-particle reinforcement of engineering polymers aimed at increasing their mechanical properties, in particular stiffness and fracture strength even beyond the current high level. Self healing polymers form a new route in materials science aimed at creating materials with the ability to heal cracks more or less autonomously and to restore mechanical properties to their original, often lower, level. So, on the one hand mechanical properties were extended even further, while on the other hand mechanical properties were sacrificed in order to create a new functionality. In this chapter we will highlight the potential of nano-reinforced materials as suitable candidate materials demonstrating self healing behaviour in combination with acceptable mechanical properties.

Self healing materials are loosely defined as materials capable of restoring mechanical damage, i.e. a nano-, micro, or sometimes even macroscopic crack, in a more or less autonomous manner. While the mechanism of healing depends on the intrinsic character of the material to heal [Van der Zwaag, 2007, 2009], the common feature in all healing processes is that new material flows into the crack and restores the mechanical traction between both sides of the crack. So, in all self healing materials there is a local flow of 'reactive' material, i.e. material which transforms from a mobile and hence marginally load bearing state to a new immobile and load bearing state.

In the early days of self healing polymers and other self healing materials, the functionality of the mobile healing agent and the static matrix material were strictly separated and healing was obtained by inclusion of an encapsulated liquid 'glue' which would spread itself over the fracture surface as soon as the crack to be healed penetrated the micro-size capsules or sealed hollow fibres [Dry 1996, White 2001]. Provided the crack faces are not too far apart and the released healing agent is capable of connecting

both sides of the crack, a proper healing agent will lead to restoration of the load bearing capabilities of the former crack.

Of course, the presence of a liquid healing agent reduces the initial mechanical properties, in particular the modulus and the tensile strength, as liquids can only transfer loads under hydrostatic loading conditions and are incapable to sustaining tensile or shear forces. Hence, as will be demonstrated later in this chapter a major challenge is to maximize the availability of a liquid healing agent at the fracture surface at as low a liquid fraction present in the undamaged material. It will be shown that elongated capsules, i.e. capsules with a high aspect ratio, will be an important tool to achieve this target.

Of course, since the first demonstration of self healing behaviour via the liquid healing agent route, alternative routes have been identified to induce self healing behaviour such as elastic recovery in combination with reversible physical networks as employed in ionomers [Varley 2008], reversible hydrogen and other chemical bonds as employed in supra molecular materials [Sijbesma *et al* 1997], crack jamming by transport of particles under the influence of an electrical field [Ristenpart 2008], long distance reptation of dissolved linear molecules in a thermoset matrix [Hayes 2007], atomistic diffusion followed by local formation of strengthening precipitates in aluminium alloys [Lumley 2003],   local oxidation of the crack zone leading to the formation of new phases with a higher specific volume as in a very special high temperature ceramic [Song *et al* 2008] volumetric expansion of a nanostructure clay micro-layer to fill cracks in a multilayered coating [Micciche 2008, Hikasa 2004], and finally local deposits in the crack surface of bio-concrete grades due to bacterial excrements [Jonkers 2007].   In all the above examples the matrix is the more rigid phase and the healing agent is the mobile, i.e. less rigid, phase. For such systems, to get acceptable mechanical properties, the volume fraction healing agent should be kept relatively small and its configuration should be optimised to get the maximum effect at the lowest volume fraction.

In contrast, one could argue that in nano-reinforced polymers, consisting of a semi-crystalline polymer above its glass transition temperature, the matrix can be treated as the relatively mobile phase and the nano-particles as the phase to provide the rigidity and

flow stress to the system. So a nanoparticle reinforced polymer could be designed to become a self healing system, by tuning the mobility of the matrix and compensating the lower mechanical properties by nano-reinforcements. In this case the volume fraction of the rigid material is relatively small and again the challenge is to optimise its configuration in order to get the maximum effect at the lowest volume fraction. Again, particle aspect ratio is the key parameter to increase the efficiency of the reinforcement. Of course a key difference between the liquid based self healing polymer systems and self healing nanoparticle reinforced polymers is that in the first class of systems healing locally can happen only once and is lost upon the healing agent being used to fill and heal a crack. In contrast in the second class of systems, multiple healing can occur locally, since the molecular mobility is guaranteed at temperatures above the glass transition temperature.

While the current chapter focuses on the mechanical properties of bulk polymers and the healing of mechanical damage, it should be pointed out that nano-particles are also being used for the restoration of corrosive protection after scratching of the protective coating. Nanoparticle-filled silane films are named as a possible replacement for chromate containing anti-corrosion coatings for aluminum alloys [Palanivel 2003]. A small amount of silica particles (5 ppm) in the silane film changes the mechanism of cathodic reactions on the alloy surface such films behave as a cathodic barrier similar as also observable when Ce-compounds are used [Parkhill 2001]. The silica suppresses the cathodic reaction by reacting with the cathodically generated OH–ions, under the formation of water and SiO_3^{2-} ions. The as-formed SiO_3^{2-} ions subsequently react with Al^{3+} ions at the anodes forming a passive silicate film. With an increase in silica content (above 15 ppm) such a desirable cathodic inhibitive behavior disappears again, probably due to an enhanced porosity. .
Nanoreservoirs, homogeneously distributed in the film matrix can possess a controlled and corrosion-stimulated inhibitor release to corrosion defects without any negative effects on the stability of the passive corrosion protective coating matrix. The development of active corrosion protection systems for metallic systems is of prime importance for almost all applications. Oxide nanoparticles containing cerium ions were

explored as isolated, inhibitor-impregnated reservoirs to be incorporated inside the protective coatings providing prolonged release of the inhibitor and self-healing ability [Zheludkevich 2005]. In a fairly new contribution to the development of a new protective intelligent system with self-healing ability composed of hybrid sol-gel films doped with nanocontainers that release entrapped corrosion inhibitor by regulation of the permeability of the encapsulation shell in response to pH changes caused by corrosion process is described [Zheludkevich 2007]. Silica nanoparticles with a size of ca. 70 nm, covered layer-by-layer with polyelectrolyte layers and layers of the inhibitor (benzotriazole) were randomly introduced into the a silica-zirconia based hybrid film used work as an anticorrosion coating deposited on AA2024 aluminum alloy. The hybrid film with the nanocontainers reveals enhanced long-term corrosion protection in comparison with the undoped hybrid film. This effect is obtained due to regulated release of the corrosion inhibitor triggered by the started corrosion processes. The released benzotriazole forms a thin adsorption layer on the damaged metallic surface to sufficiently hinder the anodic and cathodic corrosion processes and passivate the alloy by replacing the damaged Al_2O_3 film.

2 Microstructured self healing polymer structures

2.1 Liquid-based self healing thermosetting polymers

The self-healing material development started with a landmark paper by White et al, who showed that a thermosetting epoxy material with embedment of 60-100 μm diameter spherical urea-formaldehyde capsules filled with dicyclopentadiene, in combination with a dispersed (Grubbs) catalyst can show substantial self-repair upon fracture. [White 2001] Upon cracking the released liquid monomer starts off a metathesis polymerisation with the dispersed catalyst, which leads to rebonding of the crack surfaces. Their results showed that the material regained about 75% of its original fracture load provided sufficient time for healing was allowed and crack surfaces were kept in contact during this healing period. Pang et al. (2005) published on the production of a self-healing fibre composite based on a similar self-healing principle, more in line to the concept presented by Dry [Pang 2005, Dry 1996]. They embedded hollow glass capillaries filled with either

of the two components of a two liquid-component epoxy-system. The results showed that their bleeding composites even re-establish around 97% of their original strength in compression tests after impact.

The original choice for a thermosetting polymer as the matrix material for self healing liquid-based system is rather logical and stems from the initial low viscosity of the thermosetting resin in combination with the low temperature imposes the most favourable conditions for mixing the liquid filled microcapsules in the matrix material without excessive premature rupture. However, the unavoidable consequence of the crosslinked nature of the matrix polymer is that the matrix itself is highly immobile and all healing action is related to the formation of a chemical bond between the healing agent, itself also a crosslinking system, and the matrix material present at the crack faces. So, the matrix material plays no role itself in the healing process other than providing adequate anchoring for the healing agent. An additional potential problem is the fact that the crack will be healed by a new material, having different (mechanical) properties than the matrix material, leading to undesirable stress concentrations upon reloading. More recently Caruso et al. [Caruso 2007] demonstrated self-healing in thermosetting epoxy resin by using a solvent as the encapsulated phase. This resulted in a significant healing efficiency of ca. 80%. The surprisingly high healing efficiency could be attributed to the presence of substantial amounts of uncured epoxy moieties within the matrix. The relatively lowly cured state of the epoxy was responsible for the low mechanical properties of the undamaged material. For a fully cured thermosetting polymer, healing via an encapsulated solvent would not lead to a measurable healing efficiency.

2.2 Liquid-based self healing thermoplastic polymers

In contrast to thermosets, thermoplastic polymers can show substantial molecular mobility, and hence self healing potential, provided the temperature is well above its glass transition temperature (for amorphous polymers) or above its melting temperature (for semi-crystalline polymers). Molecular mobility can also be enhanced by bringing the polymers in contact with a strong solvent. The enhanced mobility is used successfully in the case of solvent welding [Peng-Peng 1994, Wu 1994].

Very recently the concept of solvent welding has been merged with the liquid encapsulation concept for thermosets to generate liquid based self healing thermoplastics [Mookhoek et al, 2009]. These new systems are based on spherical urea-formaldehyde capsules containing o-dichlorobenzene (DCB) embedded in a mixture of polymethyl methacrylate (PMMA) and polystyrene (PS) since a PMMA/PS blend could be polymerised quickly from a 2:1 by weight ratio MMA/PS solution resin and had a low initial viscosity. The volume fraction of the capsules was 10-15%, at a typical capsule diameter of 60 μm. The encapsulated solvent is known to be an excellent solvent for polystyrene and has a Hansen solubility sphere radius smaller than the solubility sphere radii of the polymer. [Hansen 1999] Additional, the o-dichlorobenzene has a relative low vapour pressure at room temperature preventing a fast evaporation when the solvent is released from the capsules. A low vapour pressure allows for an extensive action of the solvent inside the polymer matrix, providing better healing. Using solvents with a too low vapour pressure however leads to a weakened interface although the crack looks sealed, since it will not escape from the material in time and acts as a plasticizer.

While the mechanical healing efficiencies of this system are yet to be reported, very elegant proof of the healing process was provided studying the healed fracture surface of such a system using a special version of SEM-based X-ray microtomography yielding a spatial resolution of approximately 10 μm. A typical reconstructed image of the volume around the fracture surface shows the depletion of the capsules as well as the solid contact between the former fracture surfaces (see figure 1).   While the route of liquid based thermoplastic polymers is yet in its very infancy, it seems a very interesting and attractive route as the use of a solvent as the healing agent has many advantages over the use of liquid resins used for healing of thermosets and because the total market for thermoplastic polymers is much larger than that of thermosets.
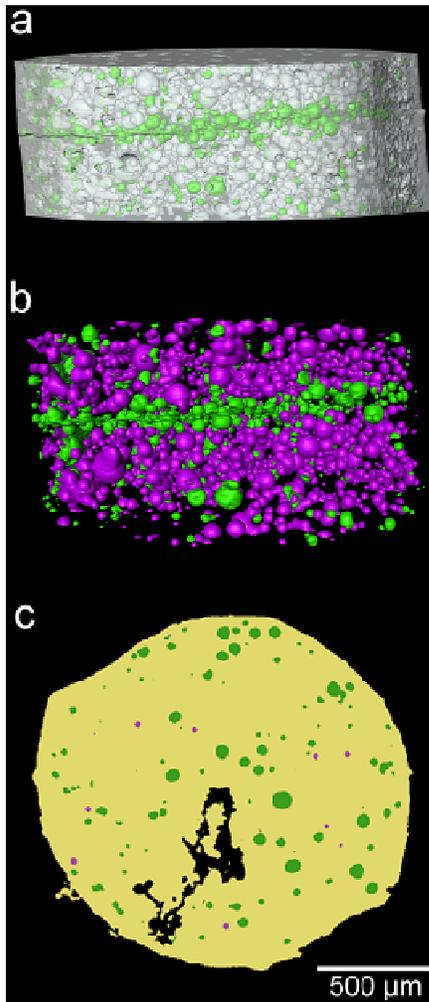
Figure 1.
Reconstructed tomographic views of the segmented data showing full capsules (purple) and empty capsules (green) in the vicinity of the crack; (a) displaying the 3D rendered dataset of 200 slices including the healed crack and the segmented empty capsules, (b) showing only the segmented microcapsules, omitting the matrix material. (c) showing a 2D segmented slice of the data at the healed crack. The dark area in the lower image corresponds to a fraction of the crack area which did not heal completely. The indicated scale-bar applies for all three images.

2.3 Geometrical aspects in encapsulation

As indicated in the introduction, a requirement for adequate healing via the liquid encapsulation route is the necessity to fill the crack gap more or less completely with the healing agent, preferably without the occurrence of massive bleeding [Pang 2005]. It is intuitively clear that the amount of healing agent entering the crack is determined by product of the average volume of healing agent stored per capsule and the areal probability of the crack intersecting a capsule. This product depends on the particle size (nanosized capsules inherently contain very small volumes of healing agent indeed), their volume fraction and in the case of non-spherical particles, their aspect ratio and average orientation of their director.

As a first step in the geometrical optimisation of liquid encapsulated self healing materials we define a representative volume element (RVE) in which spherical and cylindrical 3D geometrical elements are spatially dispersed (Figure 2a and 2b respectively).
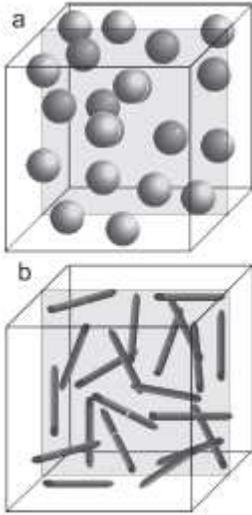

Figure 2: Schematic of capsule distribution in RVE with intersecting fracture-plane: a) spherical and b) cylindrical capsules

The matrix/capsule system can be adjusted by varying the volume of the embedded micro particles (Vcaps), their volume concentration (φ) and the aspect ratio (AR). The theoretical ratio of the volumes of healing agent released for both geometries, i.e. the ratio of released volume for cylindrical and spherical capsules, is denoted as the release improve factor (RIF) and is a function of the cylindrical capsule aspect ratio and is independent of capsule size and capsule volume concentration. The RIF as function of AR is given in Figure 3. The RIF shows a non-linear behaviour with increasing aspect ratio. The increase of RIF as function of AR demonstrates the ability to enhance the liquid-based healing mechanism by applying cylindrical shaped microcapsules in stead of spherical ones.
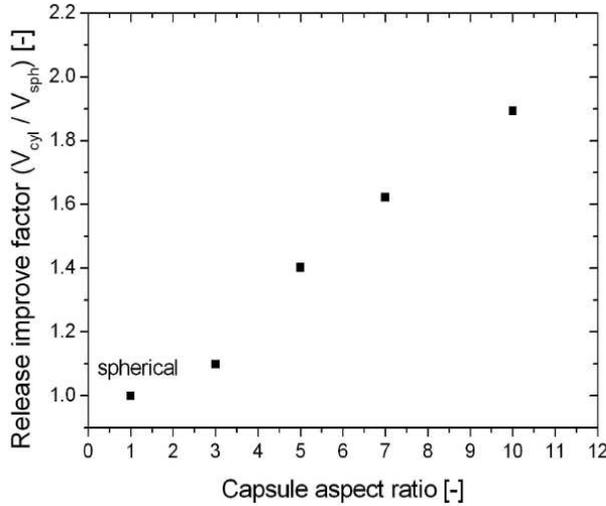
Fig 3: RIF as function of capsule aspect ratio

To illustrate the beneficial effect of the elongated character of the capsules, Figure 4 shows the average released liquid volume as function of the capsule volume concentration for the different aspect ratios, assuming a random orientation of the elongated particles. In this graph the effect of changing the capsule aspect ratio on the capsule concentration is made visible. From the graph it can be concluded easily that the same amount of healing fluid per fracture plane area can be obtained at a lower volume fraction for elongated particles than for spherical particles. The lower volume fraction of liquid present will have a positive effect on the other mechanical properties of the system.
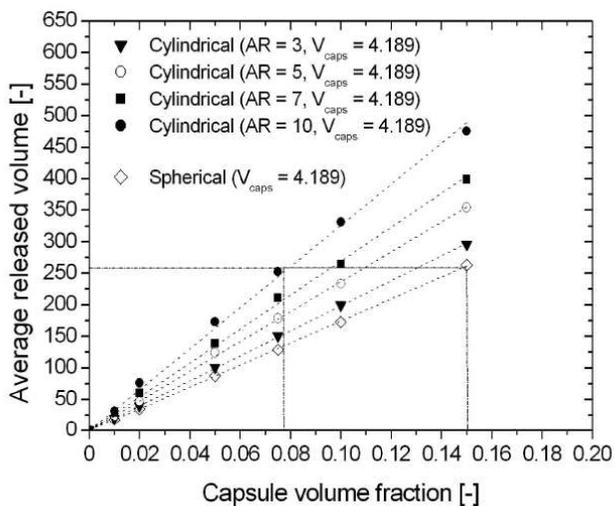
Figure 4: Average release liquid volume as function of capsule loading for different capsule aspect ratios

 Finally, the average orientation of the cylindrically shaped capsules inside the material is also of influence on the healing agent release. The orientational order parameter <P_2> for dispersed cylindrical rod-like structures is given by:

$$\langle P_2 \rangle = \frac{\langle 3\cos^2 \theta \rangle - 1}{2} \qquad \text{eq.1}$$

in which θ is the angle between the cylinder axis and the normal axis (X), perpendicular to the fracture orientation, as shown in Figure 1. Now by varying <P_2> from -0.5 (parallel to fracture plane) to 0 (random) and 1 (perpendicular to fracture plane) the effect of capsule orientational order can be determined. The results of these calculations are presented in Figure 5. The figure shows the release improve factor (RIF) as function of the orientational order parameter. The RIF was determined at a given capsule aspect ratio AR = 5. The positive effect of preferred orientation of the cylinders perpendicular to the fracture plane also offers the possibility to lower the capsule loading even further with respect to a system based on spherical capsules.
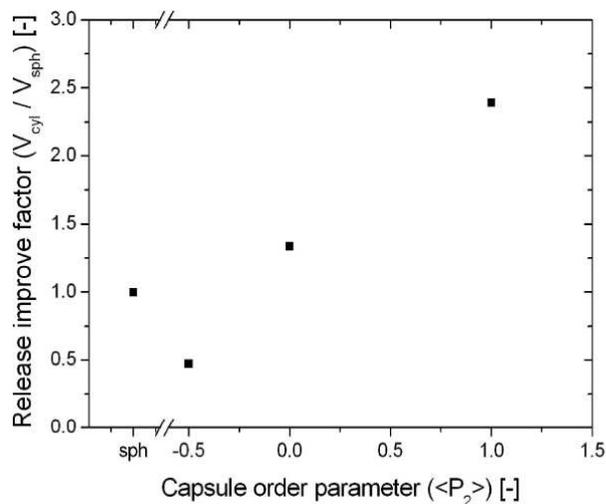

Figure 5 : RIF as function of capsule orientation

To illustrate the magnitude of the effect caused by the orientational order in combination with the aspect ratio, the average released volume as function of the capsule concentration is plotted in Figure 6 for the different $<P_2>$ values for dispersed cylinders with AR = 5 taking the case of homogeneously dispersed spheres as the reference state.
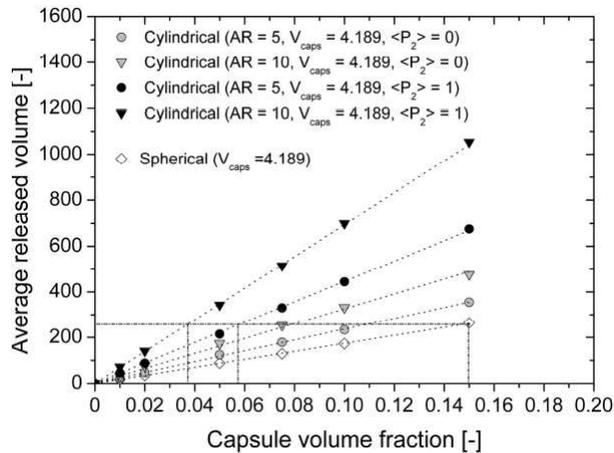

Fig 6: Average released liquid volume as function of capsule loading for different orientational parameters

In conclusion, irrespective of the nature of the matrix, healing efficiencies in liquid based self healing materials can be increased significantly over current levels by using elongated rather than spherical capsules. A decrease in capsule size to dimensions of about 1 micron is possible without loosing the self-healing properties [Blaiszik 2008], however a further decrease to nanoscale dimensions limits the healing potential due to an increase in capillary action of the capsules themselves, as well as the minimal amount of healing agent released per capsule.

3. Nanoparticle reinforced self healing polymer systems

3.1 Modelling the modulus of nanoparticle filled polymers

There are a variety of possible approaches to start assessing the mechanical properties of polymer nanocomposites. One of the aspects that is still unclear at present is to what extent the presence of nanoparticles gives rise to a change in the local polymer dynamics. For instance if there is a strong polymer-particle interaction one may anticipate a local decrease in dynamics and a corresponding increase of the local glass transition temperature. Similarly a poor interaction may give rise to a faster polymer mobility and local T_g decrease. At present we prefer not to address these issues directly and primarily deal with what should happen to the mechanical properties purely on the basis of the particle aspect ratio and concentration. So the question is: what should happen without considering any change in the matrix polymer dynamics? It will become clear that already in this case interesting phenomena may occur especially at higher particle aspect ratios.

To understand the mechanical properties of our nanocomposites have chosen to use the Halpin–Tsai model (Equation 2), which was originally developed to describe the mechanical properties of semi-crystalline polymers [Halpin 1976, Halpin 1969], using the shape factors derived by Van Es [VanEs 2001].

$$\frac{E_c}{E_m} = \frac{1 + \varsigma \eta \phi_f}{1 - \eta \phi_f} \text{ in which } \eta = \frac{(E_f / E_m) - 1}{(E_f / E_m) + \varsigma} \qquad \text{eq. 2}$$

Here: E_c composite Young's modulus; E_f Filler modulus, E_m matrix modulus; ς shape factor - depending on geometry, aspect ratio and orientation; ϕ_f filler volume fraction. Similar expressions can be derived for the other moduli like G.

It should be noted that in the literature often the Halpin-Tsai equations are described as a semi-empirical approach. This however does not do justice to their original derivation as they are the result of closely examining the works of Kerner, Hill and Hermans [Halpin 1976] that analysed composite stiffness in terms of self-consistent mechanical models,

where the particles, of certain aspect ratio, are embedded in a polymer matrix and this is embedded in a continuum (consisting of polymer and particles). The self-consistency constraint then gives rise to equations for the various moduli that under certain assumptions can be reduced to the form proposed by Halpin and Tsai. This means that the Halpin-Tsai equations should be considered as a mechanical mean-field model and not as an arbitrary choice.

With the appropriate shape factors for different particles shapes and orientations this model can successfully describe Young's and shear moduli. The specific shape factors can be determined by comparing the model with experimental results or with more fundamental theories i.e. the Eshelby theory, the Mori–Tanaka theory and 3D finite element modelling [Sheng 2004, VanEs 2001, VanEs 2001b].

The shape factors for the tensile moduli of platelet-reinforced composites (*a* width; *b* thickness) are [Van Es 2001]:

E11 or E22 $\varsigma = \dfrac{2}{3}\left(\dfrac{a}{b}\right)$ (in the radial direction of the platelets)

E33 $\varsigma = 2$ (perpendicular to the platelets)

The shape factors for fibres (*a* length; *b* width) are [Van Es 2001]:

E11 or E22 $\varsigma = 2$ (perpendicular to the fibre direction)

E33 $\varsigma = 2\left(\dfrac{a}{b}\right)$ (in the fibre direction)

When the stiffness of the composite, matrix and filler are known, the Halpin–Tsai model can also be used to back-calculate the aspect ratio of the reinforcing particles.
This will be an effective aspect ratio, because the particles can have different shapes, sizes and thickness, as has been pointed out in various articles [Fornes 2003, Kuelpmann 2005, Wu 2004, Sheng 2004]. Instead of using image analysis of TEM images to estimate

the aspect ratio distribution [Fornes 2003, Kuelpmann 2005, Sheng 2004], we simply use the effective aspect ratio that the model gives based on the experimental data. This effective aspect ratio is at least a reasonable estimate of the average aspect ratio [Vlasveld 2005b, Vlasveld 2005c] and provides a useful parameter to compare different nanocomposite compositions. The Halpin–Tsai equations predict that platelet-shaped particles are hardly effective at very low aspect ratios (<10). The maximum stiffening effect is reached only at aspect ratios above 1000 for platelets and 100 for fibres [VanEs 2001b], see figure 7.
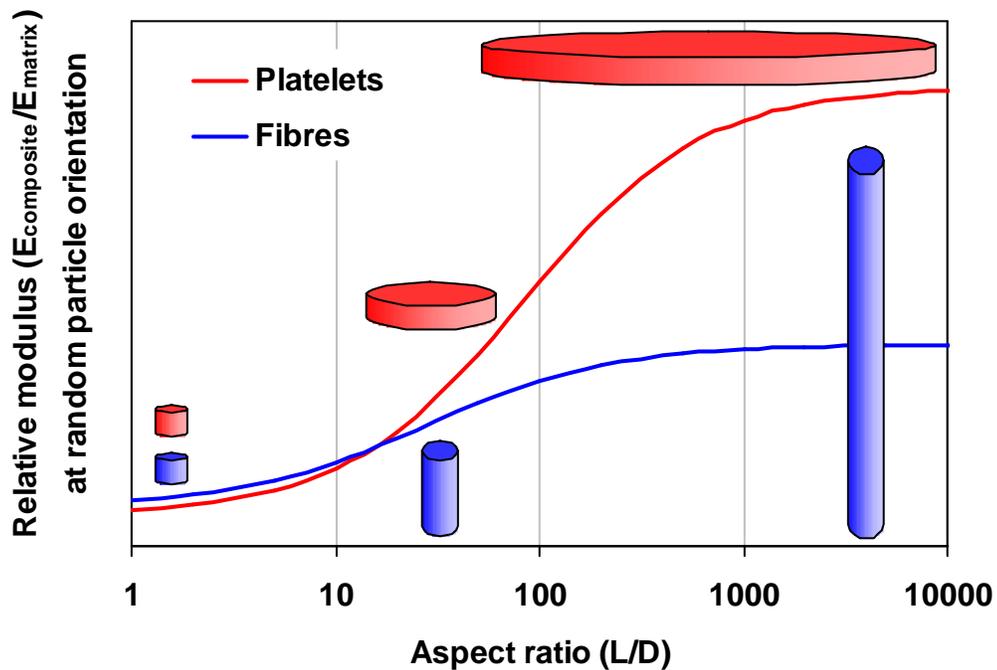

Figure 7: Influence of the aspect ratio on the modulus for platelets and fibres [VanEs 2001-2]

When Eq. (2) is rewritten in one equation as is shown in Eq. (3), the physical nature of the Halpin–Tsai model becomes more transparent:

16

$$E_c = \zeta E_m \frac{(\phi_f + 1/\zeta)E_f + (1-\phi_f)E_m}{(1-\phi_f)E_f + (\phi_f + \zeta)E_m}$$
<div align="right">eq.3</div>

When the aspect ratios are much smaller than the ratio of filler and matrix modulus ($\zeta <<$ E_f/E_m) the Halpin–Tsai model gives results close to a series model:

$$E_c = \frac{E_m E_f}{E_f(1-\phi_f)+E_m\phi_f} = \left(\frac{\phi_f}{E_f} + \frac{1-\phi_f}{E_m}\right)^{-1}$$
<div align="right">eq.4</div>

When the aspect ratios are much larger than the ratio of filler and matrix modulus ($\zeta >>$ E_f/E_m) the Halpin–Tsai model gives results close to a parallel model:

$$E_c = E_f\phi_f + E_m(1-\phi_f)$$
<div align="right">eq 5</div>

For nanocomposites the series model underestimates the modulus. Because the volume fraction of filler is low the first term in Eq. (4) dominates giving values close to the matrix modulus. Similarly the parallel model, Eq. 5, overestimates the composite modulus at low matrix moduli, since it assumes a continuous reinforcing phase.

Further insight in the Halpin-Tsai model can be obtained if eq.3 is approximated for large aspect ratios and low filler fractions as shown in equation 6:

$$E_c = \frac{E_m\zeta}{E_f + E_m\zeta}\left(E_f\phi_f + E_m\left(1-\phi_f\right)\right)$$
<div align="right">eq.6</div>

Here we observe that if the matrix modulus remains sufficiently high the pre-factor will reduce to a value close to 1 and the parallel model is obtained. When the matrix modulus times the ζ factor get below E_f the pre-factor will start forcing the composite modulus to lower values and ultimately the soft matrix will dominate the behaviour of the material.

This explains why a nanocomposite with large aspect ratio particles can perform so well at elevated temperatures using a semi-crystalline polymer matrix. Above the T_g the Young's modulus of a semi-crystalline polymer is normally too low for any useful application. But for nanocomposites the physical network (from the crystalline regions) allows the large aspect nanoparticle to contribute to the modulus roughly in accordance with the parallel model. This means that the filler contribution is additive to the modulus of the soft semi-crystalline matrix and a useful stiffness results. Note that this does not work for an amorphous polymer, as the modulus in the rubber plateau of amorphous polymers is far too low for the pre-factor be useful.

3.2 Experimental validation for non-self healing systems

To validate the model nanoparticle reinforced composites using silicate clays as reinforcement and Nylon6 as the matrix material were produced and their mechanical properties were determined. Special attention was paid to the influence of moisture on the modulus of the composite, as moisture level variations allow the variation of the modulus of the matrix, while keeping all other parameters of the composite exactly constant. Figure 8 shows some representative data for a variety of dry and humidified PA6 samples. In all cases the stiffness increase is comparable however the humid samples start at a much lower initial modulus value. If the mechanical model is correct then the calculated aspect ratio of the nanoparticles should be independent of the value of the matrix modulus. That this is the case is demonstrated in figure 9, which shows a systematic decrease of the effective particle aspect ratio with increasing weight fraction of silicate nanoparticles, irrespective of the moisture level in the matrix.
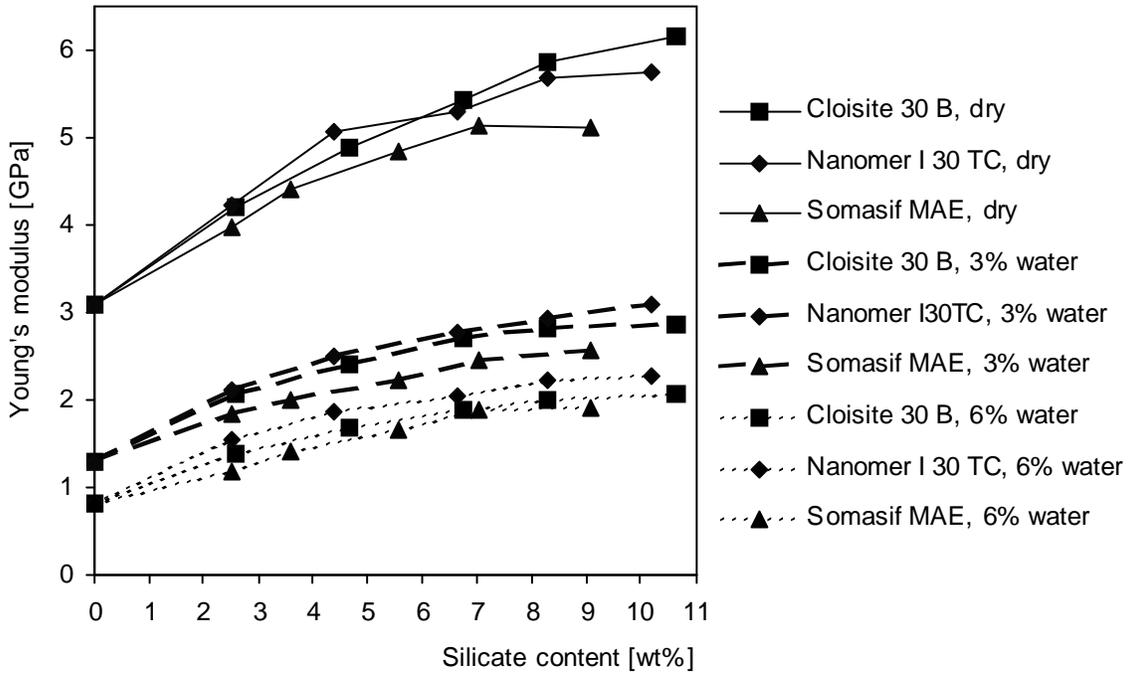
Figure 8: Modulus as a function of silicate content for three different moisture contents.
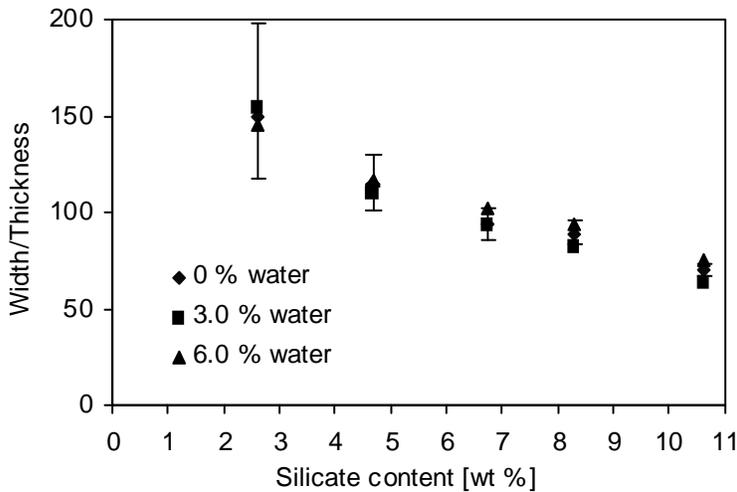

Figure 9: Aspect ratios calculated from the moduli as a function of silicate content for three different moisture contents (Cloisite 30B nanocomposites).

The most important result in figure 9 is the fact that the data for three different moisture contents do overlap indeed. This shows that the modulus of a nanocomposite can be

explained by the combination of a very stiff filler particle with a high aspect ratio and the regular matrix modulus, which in this case is varied by changing the moisture content. Apparently, the Halpin-Tsai composite theory can be used to describe the modulus of nanocomposites for a wide variety of matrix moduli, both below and above Tg of the matrix polymer, with the same aspect ratio for all matrix moduli. The fact that the modulus of nanocomposites can be explained by the Halpin-Tsai theory, independent of the modulus of the matrix, proves that the reinforcing mechanism in nanocomposites is similar to traditional composites. No additional stiffening of the matrix due to confinement of the polymer has to be assumed to explain the high modulus of nanocomposites.

3.3 Design of a self healing nanoparticle composite

From the results obtained on PA6 based PNCs we can conclude that the Halpin-Tsai model is able to describe the enhancement of the mechanical properties rather successfully. In addition we find that the interaction between the polymer and the nano-particles can give rise to a (small) yield stress. Using this insight that nanoparticles can give a modulus increase as well as a yield stress enhancement allows us to design a self-healing PNC with acceptable mechanical properties.

For this we need to return to equation 6:

$$E_c = \frac{E_m \zeta}{E_f + E_m \zeta} \left(E_f \phi_f + E_m \left(1 - \phi_f \right) \right)$$
eq. 7

From this expression it is observed that if the pre-factor is in the order of 1 the modulus will be dominated by the linear (parallel) addition term $E_f\phi_f$. In the case of PA6 this leads to the good enhancement of the properties above Tg as the semicrystalline network still provides sufficient stiffness to meet the requirement for the pre-factor to remain close to 1, i.e. $E_m\zeta > E_f$.

By extending this argument it is possible in principle to use a soft dynamic matrix polymer (E_m = small) if the shape factor is sufficiently large to prepare materials that combine mechanical stiffness (via the $E_f \phi_f$ term) and local mobility by using a matrix polymer that contains a dynamic network. This class of polymers is known generically as "reversible supramolecular polymers". Examples are the dynamic hydrogen bonded materials of Sijbesma [Sijbesma 1997], metal-organic coordination polymers by Schmatloch [Schmatloch 2004], and boric-acid modified PDMS also known as "Silly-Putty" (see materials section). In this class of materials the polymer chains, or crosslinking networks, are only present in a dynamic sense. The polymer chains are continuously breaking and forming over time, while the level of interaction is sufficient to have a high large dynamic degree of polymerisation.

To demonstrate the principle of this idea we have prepared Silly-Putty nanocomposites by mechanical blending of standard Silly-Putty with about 5 and 10% MAE nanoparticles.

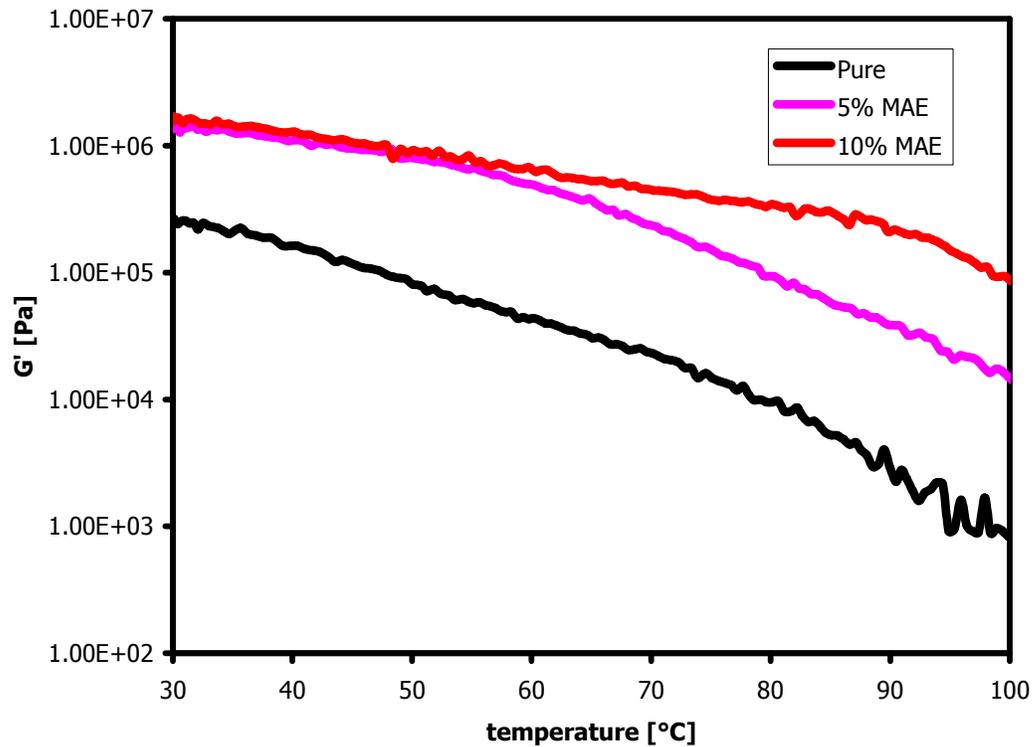The resulting properties are shown in figure 10

Figure 10: dynamic modulus of Silly Putty and nanoparticle reinforced grades as a function of temperature.

From these results we conclude that although the mechanical stiffness of the matrix living polymer network is still relatively low, the adding of nanoparticles can enhance the dynamics stiffness by a factor 100 or more. Furthermore, at clay loading levels of approximately 5% the material keeps its shape over extended time periods (months), unlike the unfilled sample, so that the particles also cause a yield stress preventing flow under low stress conditions.

Additional experiments were performed using Dow Corning 3179 dilatant compound (the professional variant of Silly Putty) with and without nanofiller as the matrix for a glass fibre reinforce composite [Jansen, 2009]. Without the nano-particles the resulting material did not show any useful properties, while adding the nano-particles to the matrix

dramatically improved the energy absorption using a falling weight test. The results obtained are summarised in table 2.

Material	MM	Glass fabric	B-PDMS	Failure/J
Reference	0	57	43	3
10%	5	57	38	8
20%	10	57	33	8

Table 2: Failure energy versus composition of the matrix of glass-fibre reinforced B-PDMS (Dow Corning 3179 dilatant compound) nanocomposites.

The impact energy absorption capability of this system is still not very high, but by embedding two layers of glass fabric in the polymer sheet the absorbed impact energy increased to 55 Joules per impact. After the impact test the samples were left for several days to recover their integrity. The mobility of the nanofilled matrix remained sufficient for rebonding of the impact damaged part, although obviously the broken glass fibres could not heal together again. The unfilled reference samples allowed imaging by C-scan clearly demonstrating the self healing of a damaged zone, see figure 11.
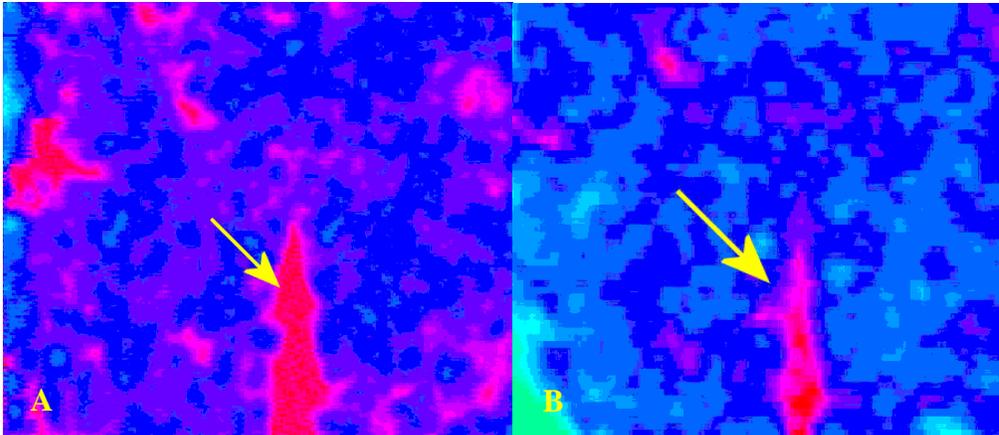

Figure 11: Self healing in (non-nano)B-PDMS/glass fibre panels (A) after impact damage, (B) after 1 week of recovery, red zones are delaminated.

The observation, mentioned in passing above, that the glass fibres failed under impact is in fact highly relevant to demonstrate the utility of this physical self healing concept. The occurrence of fibre fracture demonstrates that the limiting properties are obtained from the properties of the fibre reinforcement, and that the matrix has sufficient dynamic stiffness to efficiently transfer the stress to he reinforcement fibres.

It is of course clear that a substantial amount of further development and fine tuning may be required to fully realise the potential of the physical self healing of living polymer nanocomposites. Nevertheless the current experimental results clearly show that a combination of dynamics and stiffness on the one hand and repetitive self healing on the other is indeed possible under the appropriate conditions and with a judicious design of the material.

4. Concluding remarks

While the development of liquid based self healing polymers has been going on for some time and the simultaneous control and optimisation of mechanical and self healing properties can now be addressed properly, the development of self healing nanoparticle reinforced composites is still in its infancy. We however believe that this concept has a lot of potential. The development of the material should be combined with the development of new techniques to quantify the degree of healing, both for single damage events and for multiple healing. The development of the material is clearly made easier by the existence of validated mechanical models. While it is somewhat outside the scope of the current chapter it is worth mentioning that while the analysis of polymer dynamics in confined and hybrid systems has been a topic of considerable scientific interest, to our knowledge the concept of self-healing polymer nanocomposites is one of the first practical applications resulting from the fundamental insight that has been gained over the years in how to deal with the properties of polymers in complex hybrid systems. In terms of potential applications of such dynamically self healing materials one can envisage personal protection for sports and other outdoor activities, protective clothing e.g. for motorcyclists, and indeed military applications.

Acknowledgements

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