DOI: 10.1002/masy.200650304

Some Properties of Nanomaterials prepared through the Encapsulation within Polymer Fibrils of 1-D Filaments of a Self-assembled Bicopper Complex

Jean-Michel Guenet,[*1] Sandrine Poux,[2] Annette Thierry[1]*

Summary: A new type of nanomaterial prepared from ternary systems *polymer/bicopper organic complex/solvent* is presented. Each binary system displays differing types of behaviour: The *polymer solutions* produce thermoreversible gels while the *bicopper organic complex* forms randomly-dispersed, self-assembled threads in organic solvents The nanomaterial results from the encapsulation of the bicopper complex threads into the polymer fibrils through *heterogeneous nucleation*. The magnetic behaviour and the rheological properties of these materials will be briefly outlined and discussed.

Keywords: nanomaterial; polymer fibrils; self-assembling system; magnetic properties; rheological properties

Introduction

Organic solutions of copper (II) tetra-2-ethylhexanoate, designated as CuS8 (see Figure 1) form viscous jellies consisting of long, rigid 1-D filaments by a self-assembling process[1,2].

These systems are referred to as *supermolecular polymers*. Unlike covalent polymers the threads of supermolecular polymers continuously break up while new ones are formed with a typical lifetime of less than 1s [2]. In order to stabilize these filaments, that is to obtain an infinite lifetime, we have used physical methods that allow one to encapsulate them within the fibrils of thermoreversible gels from isotactic polystyrene[3].

These gels possess a network morphology made up of interconnected fibrils[3] with a mesh size in the μm range while the fibrils possess cross-section radii in the nanometer range. A composite material is produced wherein filaments of the bicopper complex are encapsulated into *nanosized* polymer fibrils[4,5] as is portrayed in Figure 3.

The encapsulation process is the heterogeneous nucleation of the growth of the gel fibrils by the bicopper complex threads that appear at higher temperature than the gelation threshold. Details on the encapsulation process can be found in previous publications [5,6].

One salient result which shows the involvement of heretogeneous nucleation in the encapsulation process is the increase of the gelation temperature when increasing the fraction of bicopper complex as is shown in Figure 4.

The presence of copper atoms make these materials liable to exhibit unusual magnetic properties. In this paper we shall therefore present and discuss the magnetic properties of these materials, and in a second part, we will focus our attention on the mechanical properties of these new nanomaterial composite.

Magnetic Properties

The bicopper complex threads form hexagonal mesophases in the solid state. The

---

[1] Institut Charles Sadron, CNRS UPR22, BP 40016, 6 rue Boussingault, F-67083 STRASBOURG Cedex, France
Fax: +33(0) 388 41 40 99
E-mail: guenet@ics.u-strasbg.fr

[2] Present address: Basel University, Department of Chemistry, Klingelbergstrasse, 80, CH-4056 Basel, Switzerland

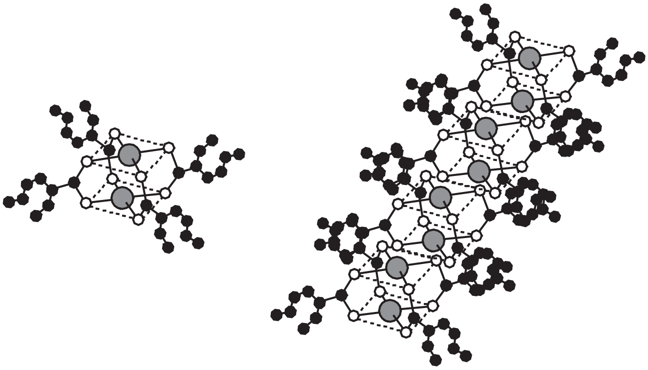

Figure 1.
Chemical structure of the bicopper complex (*left*) and the way these molecules pile up to form 1-D threads in the solid state (*right*). In this state, the piling occurs in such a way that a copper atom interact with the oxygen atom of the adjacent molecule. Grey circles = **Cu**, white circles = **O**, black circles = **C**, hydrogen atoms are not drawn.

magnetic susceptibility varies as shown in Figure 5[7].

This variation can be reproduced theoretically by means of the theoretical expression derived by Bleaney and Bowers [8], which is written:

$$\chi_M = \frac{N_A g^2 \mu_B^2}{kT} \frac{2\exp(2x)}{1+3\exp(2x)} \quad \text{with } x = \frac{J}{kT} \tag{1}$$

in which N_A is Avogadro's number, g is the number of unpaired electrons in the molecule and μ_B Bohr's magneton. Here $-2J = 202\ \mathrm{cm}^{-1}$, and $g \approx 2$.

This means that, despite the fact the bicopper complex molecules are piled up onto one another, they behave as if they were randomly-dispersed, with no mutual interactions. This is so because the piling in the solid state occurs sideways through the interaction of the copper atom with the oxygen atom of the adjacent molecule as shown in Figure 6 *left*. As a result, coupling between copper atoms is only possible within the bicopper complex, hence the behaviour obeying Bleaney-Bowers theory. In particular, as the system is antiferromagnetic, the magnetic susceptibility must be zero at $T = 0$ because the spin of the copper atoms in the complex have opposite

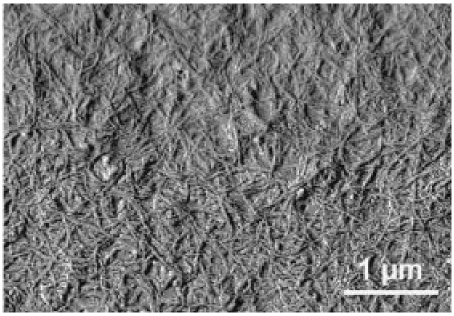

Figure 2.
Fibrillar morphology of xerogel from an iPS/trans-decalin gel as revealed by AFM.

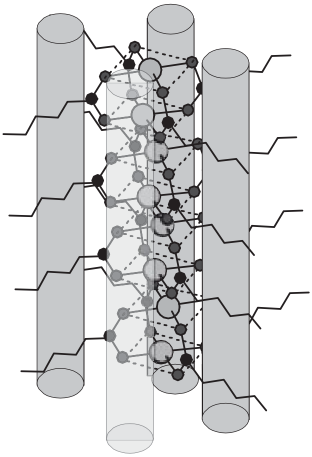

Figure 3.
Schematic representation of the encapsulation of bicopper complex filaments within polymer fibrils. The grey cylinders stand for iPS chains under the usual 3_1 helical conformation [4].

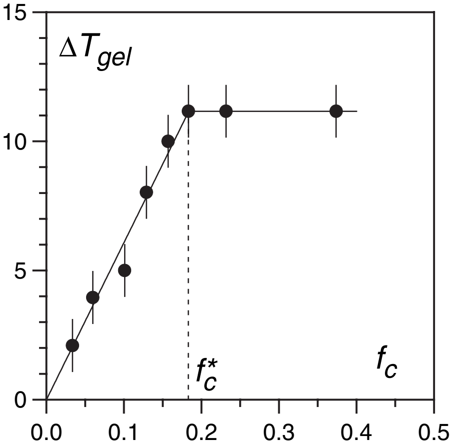

Figure 4.
Variation of the gelation temperature as a function of the bicopper complex fraction (with respect to the total amount of polymer and bicopper complex). At a given bicopper complex fraction f_c^* there is a leveling-off. This indicates that further addition of bicopper complex to the system is no longer efficient for nucleating the growth of the gel fibrils [4,5].

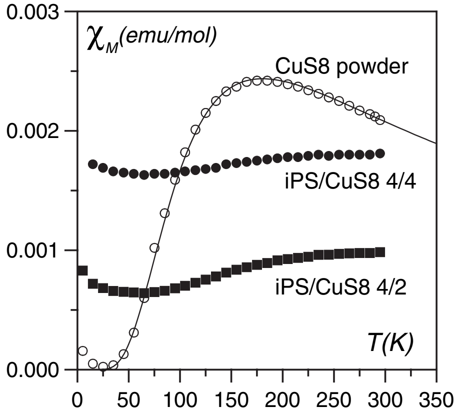

Figure 5.
Magnetic susceptibility per mol of copper atoms measured as a function of temperature with a SQUID device. Systems as indicated (numbers indicate the w/w fraction). For the encapsulated state the concentration of the polymer solution in *trans*-decalin is $C_{iPS} = 0.04$ g/cm^3. The systems are dried prior to any measurement. The full line is a best fit with relation 6.

directions (the slight upturn seen in Figure 5 at low temperature is due to diamagnetic impurities)

In the encapsulated state, the magnetic susceptibility never goes to zero as opposed to what was observed in the case of the solid state. Interestingly, χ_M, which is a value per mole of copper, is roughly a constant within the explored temperature range, yet its magnitude depends upon the fraction of copper. Typically, χ_M is directly proportional to the copper fraction. This therefore suggest that χ_M is not only related to the copper fraction but also to another parameter. It is known that the average length of the threads depend upon the bicopper complex concentration following a scaling law of the type[9]:

$$\langle L \rangle \propto C^{\alpha} \qquad (2)$$

where α depends on the thread conformation. The value $\alpha = 0.5$ corresponds to flexible threads taking on a gaussian conformation while $\alpha = 1$ corresponds to very rigid, straight filaments, which is most probably the case here.

That the average length of the encapsulated filaments increase with bicopper complex concentration is therefore expected. This may suggest that the increase of

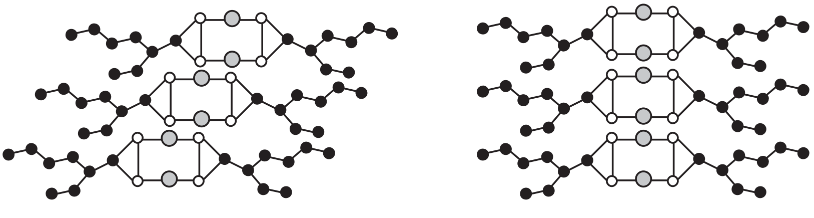

Figure 6.
Schematic representation of the piling of bicopper complex molecules as seen perpendicular to the thread. ◍ = **Cu**, ○ = **O**, ● = **C**; *left* = copper-oxygen interaction as in the solid state; *right* = supposed interaction in the encapsulated state where a "copper ladder" is formed.

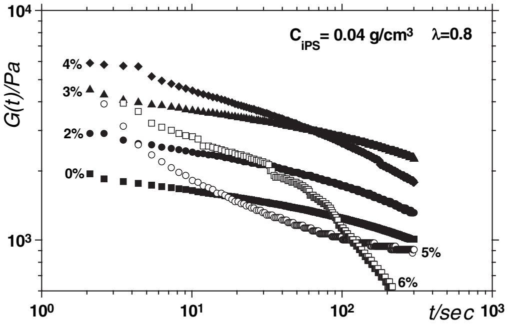

Figure 7.
Relaxation of the reduced stress $G(t)$ as a function of time for a deformation $\lambda = 0.8$. Constant polymer concentration $C_{iPS} = 0.04$ g/cm^3 with various bicopper complex concentrations from 0 to 0.06 g/cm^3 (labeled 0% to 6%). ■, $C_{CuS8} = 0\%$; ●, 2%; ▲, 3%; ◆, 4%; ○, 5%; □, 6%. At this polymer concentration f_c^* corresponds to $C_{CuS8} = 0.04$ g/cm^3.

χ_M observed for the encapsulated filaments is directly related to their average length. In an attempt to account for the magnetic behaviour, we propose the model of piling for the bicopper complex molecules shown in Figure 6 right. Here, a ''copper ladder'' is formed through the interaction of copper atoms of adjacent molecules. This implies the existence of a coupling over several copper atoms thus breaking the basic assumptions used for establishing Bleaney-Bowers relation. This may constitute what is designated as a ''spin ladder''[10].

These assumptions will be tested by means of other techniques such as RPE or RMN.

Rheological Properties

It is know that thermoreversible gels from isotactic polystyrene (iPS) display considerable relaxation when submitted to a constant compression deformation. The variation is approximately described, in the early stage of the relaxation process, by a relation of the type:

$$Log(\sigma) \propto \beta Log(t) \tag{3}$$

where σ is the stress and t the time, and for which $\beta \approx 0.15$–0.2 for iPS gels in *cis*-decalin or *trans*-decalin [11]. The behaviour is neo-hookean as the reduced stress $G(t)$:

$$G(t) = \frac{\sigma(t)}{\lambda^2 - (1/\lambda)} \tag{4}$$

does not depend significantly upon the deformation λ ($\lambda = l/l_o$, where l_o is the initial height of the gel cylinder and l the height after deformation).

In the case of the gel/bicopper complex system, two main observations are worth commenting: i) for bicopper fraction lower than the critical bicopper fraction f_c^* the relaxation behaviour is basically the same, yet the value of the reduced stress increases with increasing the bicopper content; ii) for bicopper fraction larger than the critical bicopper fraction f_c^*, the relaxation behaviour differs significantly with a rate much larger (at the early stage $\beta \approx 0.29$ to 0.83 at the late stage for $C_{CuS8} = 0.06$ g/cm^3).

Clearly, the encapsulation of bicopper complex filaments within the polymer fibrils produces a reinforcement of the gel mechanical properties as the isochronal modulus is seen to increase significantly with bicopper complex fraction below f_c^* (see Figure 8). iPS thermoreversible gels are of the ''rigid gels'' type [12], their modulus is theoretically written [13]:

$$G_r \propto e \times r_\sigma^{(6-6D_f)/(3-D_f)} \times \varphi_{net}^{(3+D_f)/(3-D_f)} \tag{5}$$

in which e is the intrinsic modulus of the material, r_σ the fibril cross-section, φ_{net} the network fraction, and D_f the fractal dimension of the fibril long-axis. In the case of iPS gels the value of D_f is about 1.18 due to the

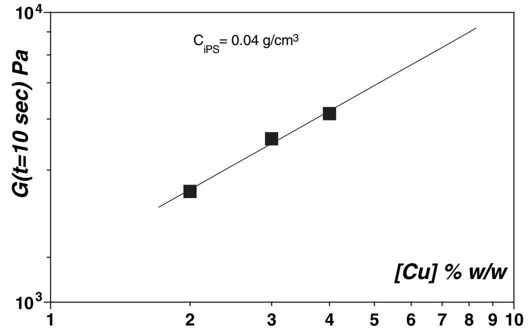

Figure 8.
Variation of the isochronal modulus *G*(*t*) for $t = 10$s of the iPS thermoreversible gels upon addition of bicopper complex. The polymer concentration is constant, $C_{iPS} = 0.04$ g/cm^3.

fact that the fibrils are not strictly straight [12] (if they were straight D_f would be equal to unity). This eventually implies that:

$$G_r \propto e \times r_\sigma^{-0.59} \times \varphi_{net}^{(3+D_f)/(3-D_f)} \qquad (6)$$

As has been observed by neutron scattering and AFM [4,6], the fibril cross-section decreases upon addition of bicopper complex (an effect consistent with a heterogeneous nucleation process). Consequently, the increase of the isochronal modulus is probably essentially due to the decrease in fibril cross-section without any reinforcement effect due to the encapsulated bicopper complex filaments.

As deduced from Figure 8 the increase of isochronal modulus $G(t = 10s)$ as a function of bicopper fraction f_c for $f_c < f_c^*$ is:

$$G(t = 10s) \propto C_{CuS8}^{0.9\pm0.05} \qquad (7)$$

This suggests that

$$\frac{1}{r_\sigma} \propto C_{CuS8}^{1.5} \qquad (8)$$

which is qualitatively consistent with what has been observed so far [4,6].

Above f_c^* excess of bicopper complex filaments, that are not encapsulated, has a negative impact on the mechanical properties as the reduced stress $G(t)$ drops rapidly, which a much higher rate than what is observed for $f_c < f_c^*$. This suggests that physical junctions between fibrils are still more labile than in the only gel. Note that for $f_c > f_c^*$ an additional phase is created, which essentially contains non-encapsulated filaments [4].

Concluding Remarks

The encapsulation of the self-assembled filaments of a bicopper complex in polymer fibrils produces interesting properties. Most significant is the change of the magnetic behaviour of the bicopper complex as the magnetic susceptibility does not vanish at absolute zero. Yet, additional experiments are needed to throw some light on the mechanisms involved, especially to test the hypothesis of a piling that would differ from that reported in the solid state. Conversely, the rheological properties are satisfactorily accounted for on the basis of the structure that has been determined by neutron scattering and AFM.

[1] Terech , P.; Maldivi , P.; Guenet , J.M.*Europhys. Lett.* **1992**, *17*, 515
[2] Dammer , C.; Terech , P.; Maldivi , P.; Guenet , J.M.*Langmuir*, **1995**, *11*, 1500
[3] J.M. Guenet*Thermoreversible Gelation of Polymers and Biopolymers* 1992*Academic Press London*
[4] D. Lopez and J.-M. Guenet*Eur. Phys. J.*, **1999**, *B12*, 405
[5] Lopez , D.; Guenet , J.M.*J. Phys. Chem. B* **2002**, *106*, 2160
[6] J.M. Guenet, S. Poux, D. Lopez, A. Thierry, A. Mathis, M.M. Green, W. Liu *Macromol. Symp.* **2003** *2009*

[7] Maldivi , P. Thesis Université J. Fourier, **1989** Grenoble, France.

[8] Bleaney , B.; Bowers , K.*Proc. R. Soc. Lond*, **1952**, *A214*, 451

[9] Cates , M.E.*Macromolecules* **1987**, *20*, 2289, and *J. Phys. France* **1988**, *49*, 1593

[10] J. Sagi and I. Affleck, *Phys. Rev. B* **1996**, *53*, 9188

[11] McKenna , G.B., Guenet , J.M.*J. Polym. Sci. Polym. Phys. Ed.* **1988**, *26*, 267

[12] Guenet , J.M.*J. Rheol.* **2000**, *44*, 947

[13] Jones , J.L. and Marqués , C.M.*J. Phys. (les Ulis)*, **1990**, *51*, 1113