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Benjamin Isare, Laurence Petit, Emmanuelle Bugnet, Régis Vincent, Laurence Lapalu, et al.. The weak help the strong: low molar mass organogelators harden bitumen. *Langmuir*, 2009, 25 (15), pp.8400-8403. 10.1021/la804086h . hal-02945326

HAL Id: hal-02945326

<https://hal.science/hal-02945326>

Submitted on 22 Sep 2020

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The weak help the strong: low molar mass organogelators harden bitumen

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Abstract: Low molar mass organogelators (LMOG) can turn liquids into thermoreversible gels, because they self-assemble into a fibrous network. In contrast, using the same kind of low molar mass additives to harden materials, which are already solid-like on their own, has been hardly exploited. We show here that simple dicarboxylic acids are very efficient low molar mass organogelators (LMOG) for bitumen. Indeed, they increase the range of temperatures where the bitumen is a solid. Moreover, the hardness and elastic modulus of bitumen at room temperature are also improved. This concept of improving the mechanical properties of a solid with a LMOG can probably be applied to other materials.

Introduction

Low molar mass organogelators (LMOG) are organic compounds, which are able to turn liquids into gels, when they self-assemble into a fibrous network of anisotropic and usually crystalline fibers.^{1,2} These thermally reversible organogels have been extensively studied during the last decade because of their potential use as sensors, media for electrochemistry, templates for the fabrication of nanostructures, biomaterials, and rheological modifiers, as well as because of their interesting supramolecular assembly patterns. The concept of reversibly hardening a free flowing liquid with a non-polymeric additive is thus well established. In contrast, using the same kind of low molar mass additives to harden materials, which are already solid-like on their own, has been hardly exploited. The only related examples concern the use of LMOG as nucleating agents for semicrystalline polymers,³ or to increase the melt rheology of polymers,⁴ or to improve the impact strength of predrawn polystyrene.⁵ Additionally, low molar mass compounds have been introduced as fillers in thermoplastic elastomers bearing hard blocks with matched hydrogen bonding patterns.⁶ The aim of the present work is to show that very simple LMOGs can be used to improve the mechanical properties, in particular at room temperature, of non-liquid materials such as bitumen.

Experimental Section

Materials: Diacids were purchased from Aldrich or Acros Organics and used as received. Crude oil distillate (Regenis 50) of viscosity 50 to 85 mm² s⁻¹ at 100°C was provided by Total company. The bitumen was a 70/100 grade from Feyzin refinery. Mixing of the diacid with the bitumen was performed in a mechanically stirred closed reactor at 160°C for 30 minutes. Care should be taken to limit sublimation of the shortest diacids.

Characterisations: Infrared spectra of thin films on KBr disks were recorded on a Nicolet Avatar 320 spectrometer. The temperature was controlled with a heating device (P/N21525) from Specac. The softening temperature of bitumen samples was determined by measuring the temperature at which an iron bead flows through the sample, according to the NF normalized procedure number EN 1427. The hardness of bitumen samples was determined by measuring the indentation depth (penetrability) in mm, according to the NF normalized procedure number EN 1426. STEM experiments were performed with a FEI XL30 FEG microscope operated at an accelerating voltage of 20 to 30 kV and a partial water vapor pressure of 0 to 3 Torr. Samples were prepared by extraction of bitumen from a gel sample by washing

with a selective solvent (tetrachloroethylene or xylene). Rheology measurements were carried out using an ARES rheometer from TA Instruments, equipped with an 8mm parallel plate geometry, at 10°C.

Computational Details: In the present work, optimizations of the atomic coordinates for C6-C12 diacid crystals were performed from periodic Density Functional Theory calculations using the PW91 exchange correlation functional⁷ and the implementation of the VASP^{8,9} code (Vienna ab initio simulation program). The electron-ion interactions are described with the projector-augmented wave method (PAW).^{10a,b} This method has been shown to give good results for solids constructed from intermolecular hydrogen bonds.^{10c} The one electron wavefunctions are expanded on a basis set of plane waves until a cutoff of 400 eV. Unit cell parameters and starting geometries for C6-C10 diacids were taken from X-ray data collected at 298 K by Thalladi et al..¹¹ Experimental data for longer C11 and C12 diacids are from ref. 12 and 13. Unit cell parameters were frozen to the X-ray determined values and all atomic coordinates were fully relaxed. DFT energies were corrected for dispersion using the method described in ref. 14.

Results and Discussion

Designing a LMOG for a specific medium is a challenging task and remains mostly an empirical endeavor. However, a few guiding principles are well established, and in particular, it is recommended to incorporate both strong self-complementary intermolecular interactions to enforce one-dimensional self-assembly and solubilizing groups to ensure solubility at high temperature.^{1,15} Bitumen are complex materials obtained from crude oil after distillation of volatile hydrocarbons. Their chemical composition is extremely diverse and includes aliphatic and aromatic hydrocarbons, and molecules with condensed polyaromatic cores and with polar functional groups (asphaltenes).¹⁶ However, on average, bitumen are non polar, hydrophobic materials. Therefore, we selected dicarboxylic acids as a family worth testing for the gelation and hardening of bitumen. Indeed, the acid group is known to form strong hydrogen bonds and the aliphatic spacer can be expected to show some compatibility with the bitumen matrix. Changing the length of the diacid should make it possible to tune the delicate balance required between high temperature solubility and room temperature self-assembly. Moreover, a few diacids have been reported to gel some non polar plant oils.¹⁷

To accelerate screening, preliminary gelation tests were performed with a model liquid: diacids were dissolved in a crude oil distillate with solubility properties approaching those of bitumen. Figure S1

qualitatively shows that diacids of intermediate length (from glutaric acid (C5) to tridecanedioic acid (C13)) form gels at room temperature. In contrast, the shorter diacids are not successful because of their insufficient solubility at high temperature, which prevents the formation of well-dispersed fibers. At the other extreme, the longer diacids are probably too soluble at room temperature, so that crystallization is not efficient.

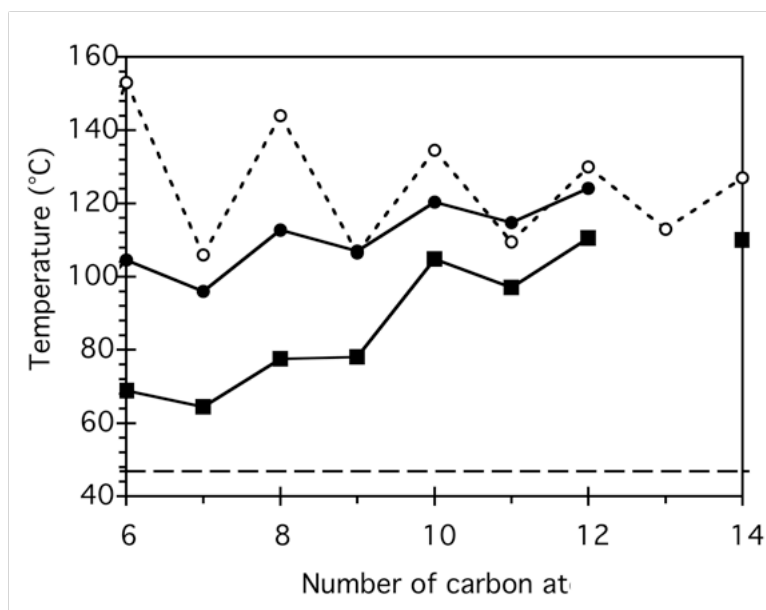


Figure 1. Softening temperature of bitumen with 3% (w/w) of diacid (■), versus number of carbon atoms of the diacids. These values can be compared to the softening temperature of pure bitumen (dashed line), the melting temperature¹¹ (○) and sublimation temperature (at a pressure of 0.5Pa)¹⁸ (●) of pure diacids.

These encouraging results prompted us to test the diacids in bitumen: the mixtures were prepared at 160°C and then cooled down. In this case, simple visual inspection is not informative because all samples are black solids, due to the bitumen nature. The efficiency of the additives was assessed by measuring the softening temperature of the mixtures (Figure 1). The presence of only 3% (w/w) of additive has a tremendous effect: the softening temperature of pure bitumen (47°C) is increased by as much as 60°C in the case of the longest diacids tested. Moreover, the softening temperatures lie below the melting points of the corresponding pure diacids, which is to be expected if the gelation is due to the

formation of crystalline fibers. The fact that the remarkable improvement of bitumen properties is indeed due to the formation of crystalline fibers is confirmed by microscopy and FTIR spectroscopy experiments. First, Figure 2 shows a STEM photograph of a sample after extraction of bitumen with a selective solvent: a percolating network of micrometer long fibers of dodecanedioic acid are observed together with a few more compact particles. Moreover FTIR spectroscopy (Figure S2) shows that the acid groups are hydrogen bonded at room temperature ($\nu_{\text{C=O}}$ at 1697cm^{-1}), and that they dissociate ($\nu_{\text{C=O}}$ at 1713cm^{-1}) in the temperature range corresponding to the softening temperature of the sample.

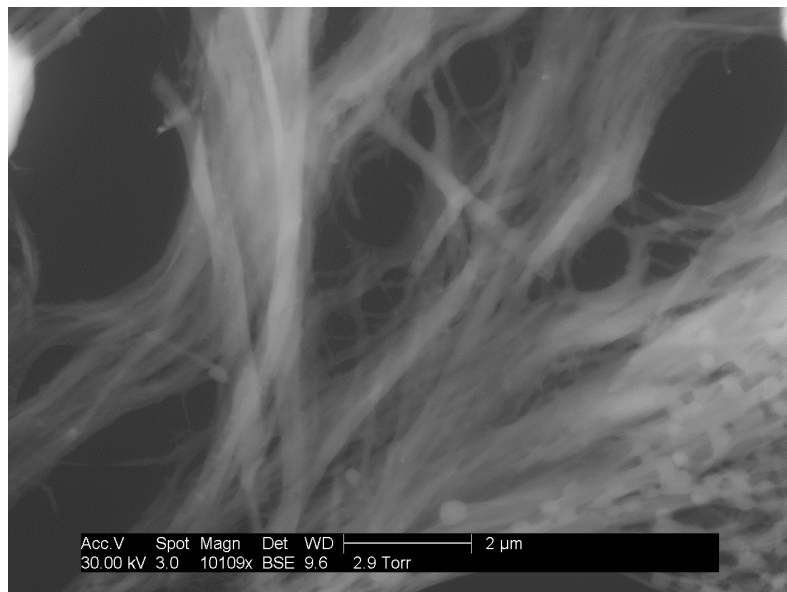


Figure 2. STEM observation of a sample made from bitumen and 6% (w/w) dodecanedioic acid, after selective dissolution of the bitumen.

It is of interest to analyze further the influence of the diacid length on the softening temperature (Figure 1). On the whole, the softening temperature shows a switchback evolution, combining two main patterns: (i) the softening temperature alternates between odd and even diacids while (ii) the best additives are obtained for the longest molecules tested. This behavior of diacids in bitumen can be clarified by DFT calculations (see Computational Details). The cohesion energy (E_{coh}) of diacid crystals was computed and decomposed into the different interactions and constraints involved in the crystal packing:

$$E_{\text{coh}} = E_{\text{distortion}} + E_{\text{int}} = E_{\text{distortion}} + E_{\text{Hbond}} + E_{\text{VDW}}$$

where $E_{\text{distortion}}$ is the energy needed to distort the molecules from their gas phase geometry to their structure in the crystal and E_{int} is the interaction energy between the already distorted molecules. E_{int} can

be further separated in the hydrogen bond (E_{Hbond}) and the van der Waals (E_{VDW}) components. Each of these terms is plotted in Figure 3.

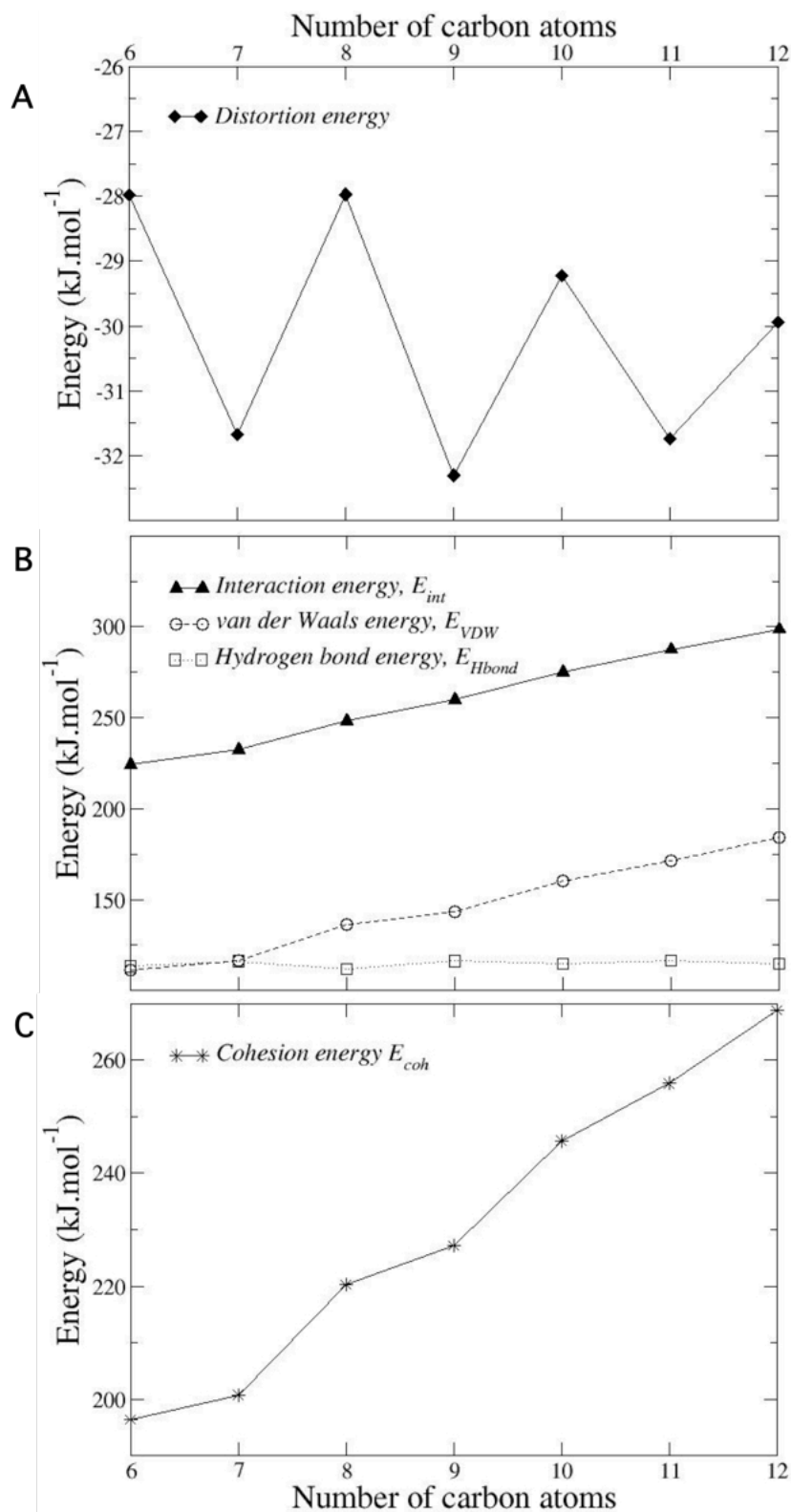


Figure 3. Decomposition of the cohesion energies in C6-C12 diacid crystals: $E_{\text{coh}} = E_{\text{Hbond}} + E_{\text{VDW}} + E_{\text{distorsion}} = E_{\text{int}} + E_{\text{distorsion}}$. Values are expressed per molecule to make comparisons easier.

Alternation is a characteristic trend for all diacid transition phase properties (fusion, solubility, etc.) that are related to the solid-state. As proposed by Thalladi et al.,¹¹ our calculations show that the distortion energy ($E_{\text{distorsion}}$) is responsible for such an alternation, odd diacids being more distorted in the crystal, and thus less stable, than even diacids (Figure 3A). In contrast, liquid state properties (vaporization) do not feature any alternation but steadily increase along with the alkane chain length. In Figure 3B, this is the trend followed by the interaction energies of diacid crystals, and it mainly arises from the van der Waals interactions. As the softening temperature exhibits both trends – alternation and regular increase – it must involve the properties of the solid and the liquid state. Indeed, the softening temperature compares nicely both with the experimental sublimation temperatures¹⁸ (Figure 1) and with our computed cohesion energy E_{coh} (Figure 3C). Therefore, diacids in bitumen must organize within the fibers, more or less as in the crystals, combining torsion constrains, hydrogen bonds and van der Waals interactions.¹⁹ Upon measuring softening temperatures, their fibers in bitumen matrices are fully disrupted, and the diacids molecules are dispersed, as in a sublimation process.

The increase in softening temperature for the bitumen / diacid mixtures is then due to the formation of a network of crystalline diacid fibers. The fibers dissolve at temperatures high enough, so that there is a range of temperatures where pure bitumen is liquid, but the mixture does not flow because of the rigidity of the diacid fibers. Thus, the hardening of bitumen by diacids at intermediate temperatures is conceptually identical to the hardening of usual liquids by LMOG.¹ What is more interesting in the present case, is that the mechanical properties of bitumen are improved even at room temperature where bitumen is a soft solid. Hardness measurements at room temperature (Figure S3) show that the network of crystalline fibers significantly reduces the penetrability of the material.²⁰ Moreover, rheology experiments (Figure 4) show that below room temperature, the elastic modulus (G') of the material is improved by an order of magnitude (at 1Hz) because of the presence of 3% of diacid.²¹ Finally, unlike polymer additives, which are often added to bitumen, these supramolecular LMOG improve bitumen mechanical properties at room temperature without increasing the melt viscosity at typical processing temperatures (Figure S5).

Conclusion

In conclusion, we have shown that dicarboxylic acids are very efficient LMOG for bitumen. They increase the range of temperatures where the bitumen is a solid, without increasing the melt viscosity. Moreover, the hardness and elastic modulus at room temperature are also improved. We believe that this concept of improving the mechanical properties of a solid with a LMOG can be successfully applied to other materials.

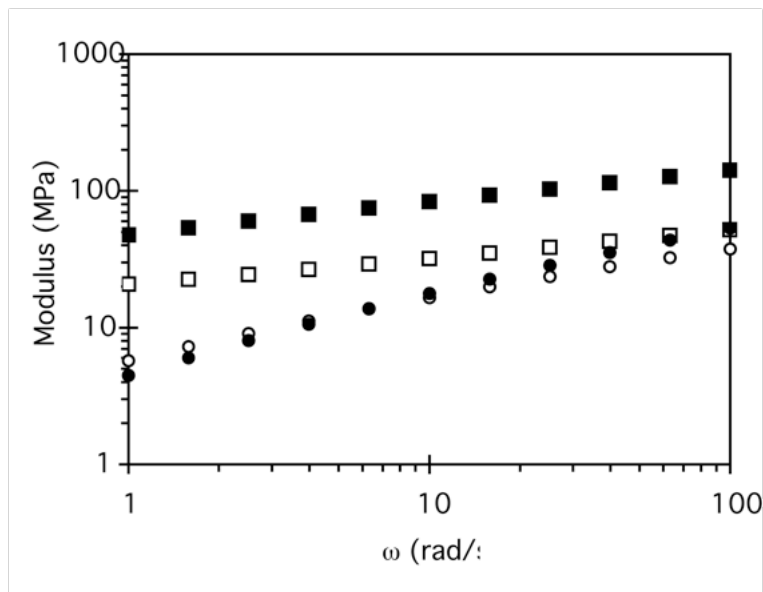


Figure 4. Storage modulus (G' , full symbols) and loss modulus (G'' , hollow symbols) versus frequency for pure bitumen (circles) and bitumen with 3% (w/w) dodecanedioic acid (squares), at 10°C.

Acknowledgment: L.P. and P.S. would like to thank Annick Goursot and Tzonka Mineva for providing them detailed results and structures from ref. 14. Dominique Basset is acknowledged for his participation to STEM experiments.

Supporting Information Available: Additional FTIR, rheology and penetrability data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) The reason why fibers (preferential 1D growth) are formed instead of compact crystals (3D growth) is not known, but is probably related to the directionality imposed by the formation of hydrogen bonds between acid groups.
- (20) Contrary to the softening temperatures, penetrability measurements show no odd-even alternation. From our previous DFT calculations, it means that during hardness measurements, the local structure of diacid monomers remains close to the solid state. Secondly, the downward trend of the penetrabilities with the chain length means that some of the intermolecular interactions (hydrogen bonds and/or van der Waals) between diacid fibers are disrupted upon hardness measurements.
- (21) At temperatures higher than room temperature, but lower than the softening temperature, the relative effect of the diacid is even stronger (see Figure S4).