SUPRAMOLECULAR ADDITIVES FOR BITUMEN MODIFICATION

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ABSTRACT

Supramolecular additives are organic compounds which are able to form gels, when they self-assemble into a three-dimensional network. The aim of the present work is to show how simple low molar mass additives can be used to improve the mechanical properties of bitumen. We selected symmetrical dicarboxylic acids, where the acid group is known to form strong hydrogen bonds and the aliphatic spacer with different lengths is expected to improve compatibility with bitumen. Some additives have a tremendous effect on the softening temperature without increasing the melt viscosity. The ring & ball temperature of bitumen is increased by as much as 60°C in the case of the longest diacid tested and the penetration is significantly reduced at room temperature. In contrast, the shorter diacids are not successful because of their insufficient solubility at high temperature, which prevents the binder structuration. The remarkable improvement of bitumen properties is due to the formation of a network of crystalline fibers, confirmed by electron microscopy. FTIR spectroscopy shows that the acid groups are hydrogen bonded at room temperature and they dissociate in the temperature range corresponding to the softening temperature. Bitumen modification by supramolecular additives is a good solution for Warm Asphalt Mix technologies.

Keywords: Supramolecular, gel, dicarboxylic acid, electron microscopy, FTIR

1. INTRODUCTION

Supramolecular additives are organic compounds of low molar mass which are able to turn liquids into gels, when they self-assemble into a three-dimensional fibrous network of anisotropic and usually crystalline fibers [1]. These thermally reversible organogels have been extensively studied during the last decade because of their potential uses. These additives can be used also as nucleating agents for semicrystalline polymers [2] or to increase the melt rheology of polymers [3]. Chemical composition of bitumen is extremely complex, including aliphatic and aromatic compounds and molecules with condensed polyaromatic and polar functional groups (asphaltenes) [4]. However bitumen is a nonpolar hydrophobic material. The carboxylic acid group is known to form strong hydrogen bonds and aliphatic groups can be expected to show some compatibility with the bitumen matrix. Therefore, we selected a simple symmetrical dicarboxylic acid family of low molar mass for gelation and hardening of the bitumen. The balance required between high-temperature solubility and low temperature self-assembly is controlled by the diacid length.

The present paper shows the mechanical properties improvement of bitumen by addition of only 3% (w/w) of dicarboxylic acids, and some evidences of crystallized network formation which explains this improvement. .

2. MATERIALS AND METHODS

2.1 Materials

Diacids used (from C4 to C13) as received were purchased from Aldrich or Acros Organics. Formula and melting point of diacids studied are indicated in table 1. Bitumen with a 70/100 grade were provided by Total Company. Mixing the diacid with the bitumen was performed in a mechanically stirred closed reactor at 160°C for 30 min. Care should be taken to limit the sublimation of shortest diacids.

Table 1: Formula and melting point of diacids used

Formula	Common name	Synonym	Melting Point (°C)
COOH $(CH_2)_2$ COOH	Succinic acid	1,4-butanedioic acid	187
COOH $(CH_2)_3$ COOH	Glutaric acid	1,5-pentanedioic acid	97
COOH $(CH_2)_4$ COOH	Adipic acid	1,6-hexanedioic acid	152
COOH $(CH_2)_5$ COOH	Pimelic acid	1,7-heptanedioic acid	105
COOH $(CH_2)_6$ COOH	Suberic acid	1,8-octanedioic acid	144
COOH $(CH_2)_7$ COOH	Azelaic acid	1,9-nonanedioic acid	102
COOH $(CH_2)_8$ COOH	Sebacic acid	1,10-décanedioic acid	132
COOH $(CH_2)_9$ COOH		1,11-undecanedioic acid	109.5
COOH $(CH_2)_{10}$ COOH		1,12-dodécanedioic acid	128.5
COOH $(CH_2)_{11}$ COOH	Brassylic acid	1,13-tridecanedioic acid	111

2.2 Methods of characterization

2.2.1 Physical properties

The softening temperature of bitumen samples was determined by the normalized EN 1427 Ring and Ball method.

The hardness of bitumen samples was determined by measuring the indentation depth (in 1/10 mm) of a needle according to the normalized EN 1426 method.

Viscosity measurements were carried out at 140°C using a Brookfield viscosimeter with cone and plate, under a shear rate of 4000 s^{-1}.

Rheology measurements were carried out at 10°C using a dynamic rheometer (ARES from TA Instruments), having 8 mm parallel plate geometry.

2.2.2 Analytical characterizations

Infrared spectra of thin films on KBr disks were recorded on a FTIR spectrometer (Avatar 320 from Nicolet). The temperature was controlled with a heating device (P/N21525 from Specac).

STEM (Scanning Transmission Electron Microscopy) experiments were performed with a High Resolution Environmental Scanning Electron Microscope (XL30 FEG from FEI) with a field emission gun, operated at an accelerating voltage of 20 to 30 KV and a partial water vapor pressure of 0 to 3 Torr. Because of the low difference of contrast between the bitumen matrix and diacids, a specific sample preparation is used, based on the difference of solubility in a selective solvent. Samples were prepared by extracting bitumen from a small piece of gel (10 mm^3) by washing with xylene. The supramolecular additive, which is insoluble in the solvent is collected on a 5 nm thick carbon film, transparent to electrons beam, then the sample is directly observed by STEM without gold deposition and staining. Figure 1 represents the different steps of the sample preparation. In the STEM device, transmitted electrons are collected by the backscattered electrons detector (BSE), located just below the sample [5].

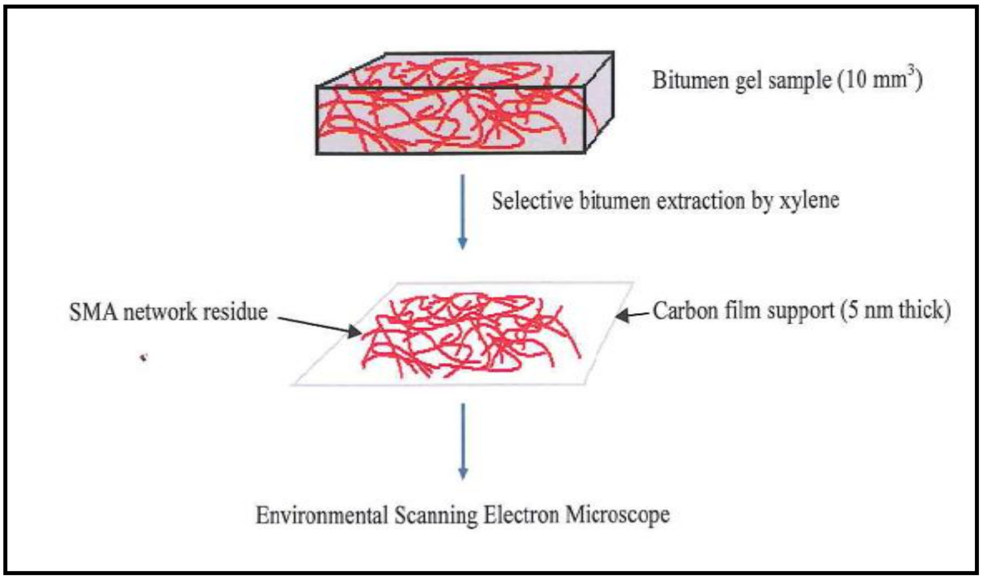

Figure 1: Different steps of the sample preparation for STEM observation

3. RESULTS AND DISCUSSION

3.1 Physical properties

The efficiency of additives in bitumen at the concentration of 3% (w/w) was assessed by measuring the softening temperature (figure 2). The softening temperature exhibits two trends: (i) alternation between odd and even diacids, which is characteristic of the solid state (like sublimation or melting temperatures) and (ii) regular increases in function of the number of carbon atoms of the additives, which is characteristic of the liquid state (like vaporization temperature). The softening temperature of pure bitumen (47°C) is increased by as much as 60°C in the case of the longest diacids tested. However, the shorter diacids (C4 and C5) are not successful because of their insufficient solubility at high temperature, which prevents the formation of well-dispersed fibers. The softening temperatures lie below the melting points of the corresponding pure diacids, which is to be expected if the gelation is only due to the formation of crystalline fibers.

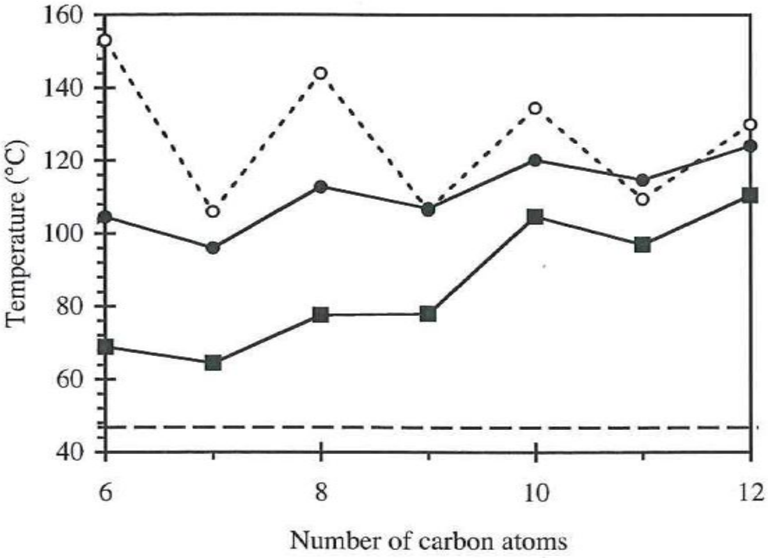

Figure 2: Softening temperature of bitumen with 3% (w/w) diacid versus the number of carbon atoms of the diacids(black square). Comparison with pure bitumen (dashed line), melting point (white circle) and sublimation temperature at a pressure of 0.5 Pa (black circle) of pure diacids.

Alternation is a characteristic trend for all diacid transition-phase properties (solubility, melting point, sublimation.). The first attempts to relate crystal structure of diacids and their melting point alternation appeared around 1940 [6] As demonstrated in previous papers by calculations [7] [8], the distorsion energy in the crystal is responsible for such phenomena: distorsion of odd diacids are more important than even diacids, therefore melting points of odd diacids are lower than even diacids (figure 3). In contrast, liquid-state properties (vaporization) do not feature any alternation but steadily increase with the chain length because the van der Waals interactions increase. Therefore, diacids in bitumen must organize within the fibers, more or less as in crystals, combining torsions constrains, hydrogen bonds, and van der Waals interactions.

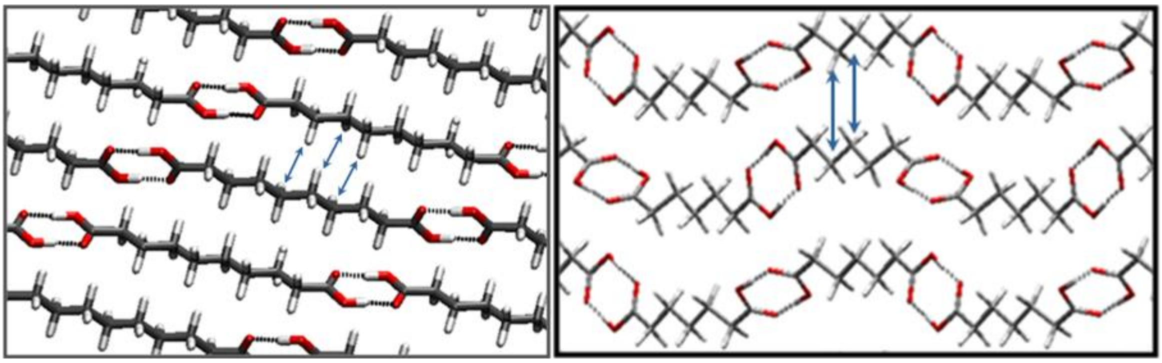

Figure 3: Possible molecular conformations for the packing of even (left) and odd (right) diacids (dashed lines correspond to hydrogen bonds, arrows correspond to van der Waals interactions).

In fact, upon measuring softening temperature, the fibers in bitumen are fully disrupted and the diacid molecules are dispersed, as in sublimation process [8]. Below the softening temperature, the mixture does not flow because of the rigidity of the diacid fibers. The mechanical properties of bitumen are improved even at room temperature. Penetration measurements at 25°C versus number of C atoms show that the network of crystalline fibers significantly increases the hardness of the material (figure 4). Contrary to softening temperature, penetrability measurements show no odd-even alternation.

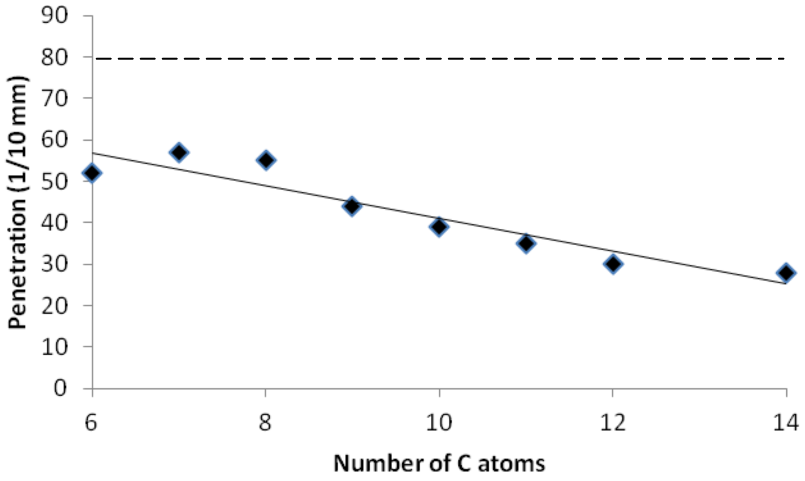

Figure 4: Penetrability at room temperature of bitumen with 3% (w/w) of diacid versus number of carbon atoms of the diacids. The penetrability of pure bitumen is indicated by the dashed line.

Figure 5 shows the viscosity evolution of bitumen with 3% (w/w) diacid, in function of carbon atoms of the additive. The viscosity decreases by 14% comparatively with pure bitumen when the diacid length increases from C7 to C12, without alternation. Surprisingly, with adipic acid (C6), the viscosity of the mixture is more important than the viscosity of pure bitumen.

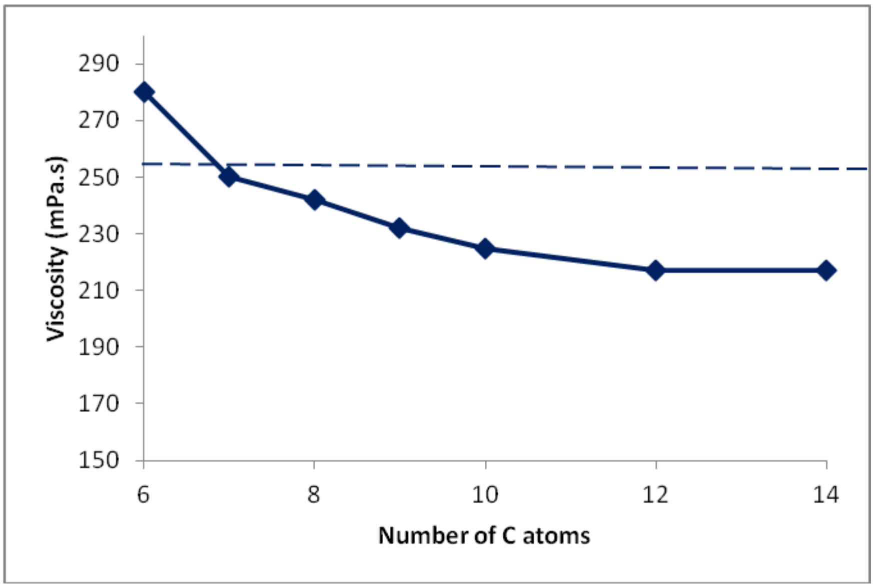

Figure 5: Viscosity at 140°C of bitumen with 3% (w/w) of diacid versus number of carbon atoms of the diacids. The viscosity of pure bitumen is indicated by the dashed line.

Rheology experiments at 10°C show that the elastic modulus (G’) of the material with 3% (w/w) dodecanedioic acid is improved by an order of magnitude comparatively with pure bitumen at 1 Hz (figure 6).

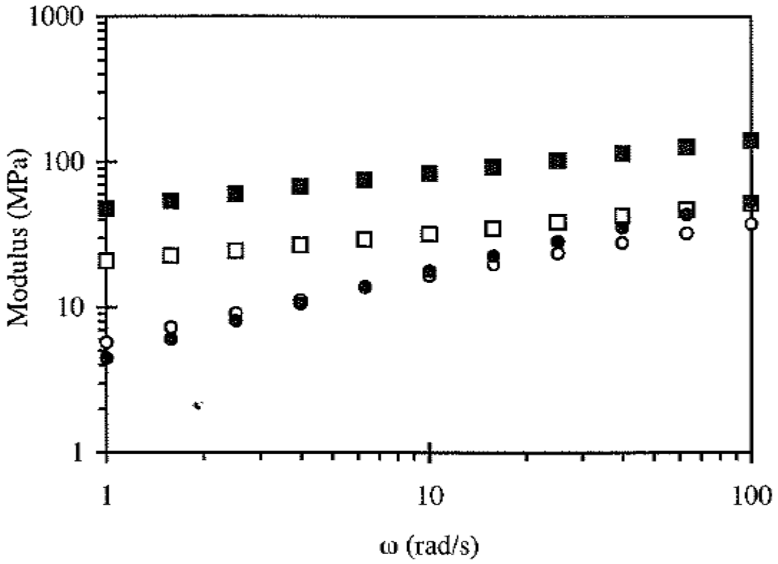

Figure 6: Storage modulus (G’, black) and loss modulus (G”, white) at 10°C versus frequency for pure bitumen (circle) and bitumen with 3% (w/w) dodecadioic acid (square).

3.2 Analytical characterizations

Electron microscopy experiments confirm that the remarkable improvement of bitumen hardening is due to the formation of crystalline fibers. Figures 7 and 8 show STEM micrographies of bitumen + 6% (w/w) dodecanedioic and bitumen + 3% (w/w) sebacic acid respectively, after extraction of the bitumen with xylene. An interconnected diacid network of micrometer-long and few nanometer-thick fibers (figure 7) or ribbon-like threads (figure 8) is observed on these samples.

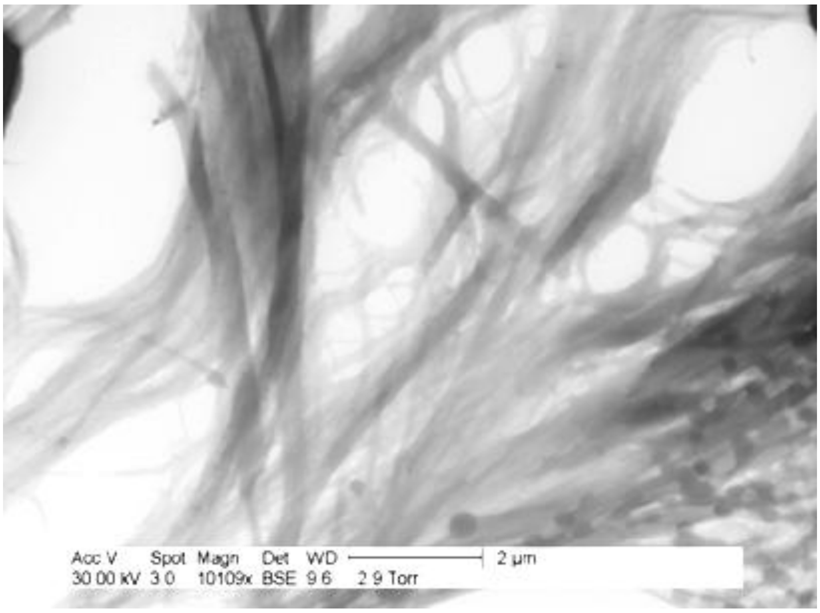

Figure 7: STEM observation of a sample of bitumen modified with 6% (w/w) dodecanedioic acid after selective dissolution of bitumen.

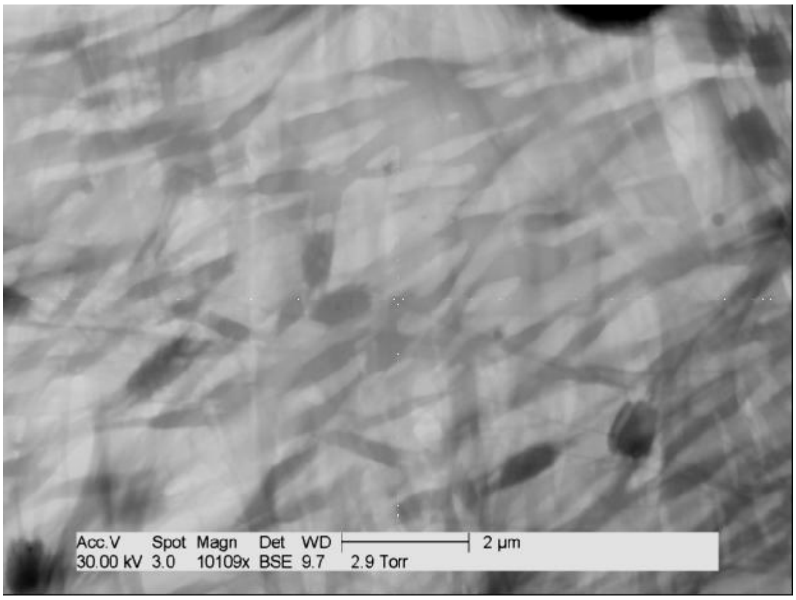

Figure 8: STEM observation of a sample of bitumen modified with 3% (w/w) sebacic acid after selective dissolution of bitumen.

FTIR spectra of bitumen + 3% (w/w) dodecanedioic acid, at temperatures between 20°C and 140°C (figure 9) shows that acid groups are hydrogen bonded at room temperature (ν c=o at 1697 cm^{-1}) and dissociate (ν c=o at 1713 cm^{-1}) in the temperature range corresponding to the softening temperature of the sample (figure 10).

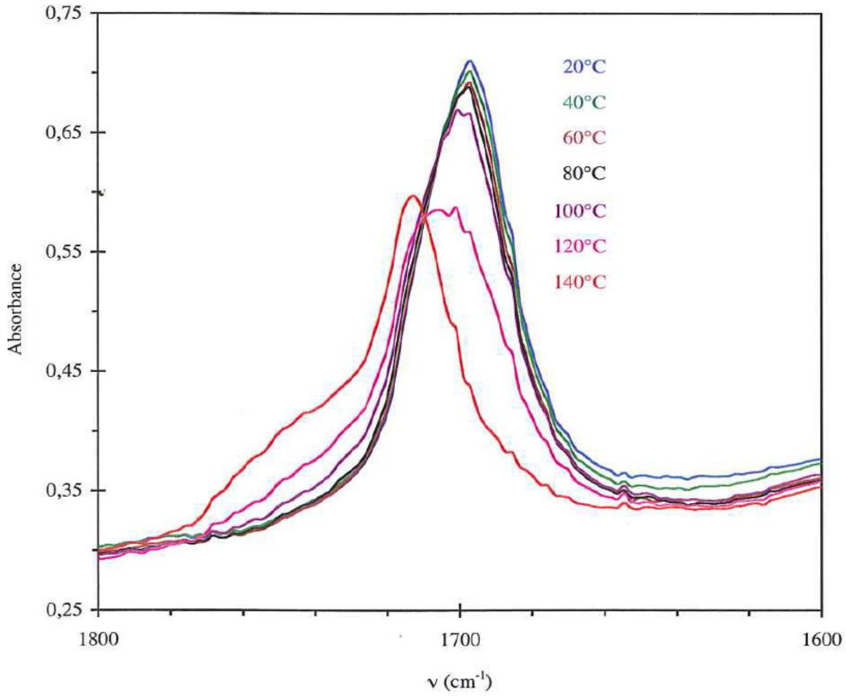

Figure 9: FTIR spectra of a sample of bitumen with 3% (w/w) of dodecanedioic acid at several temperatures.

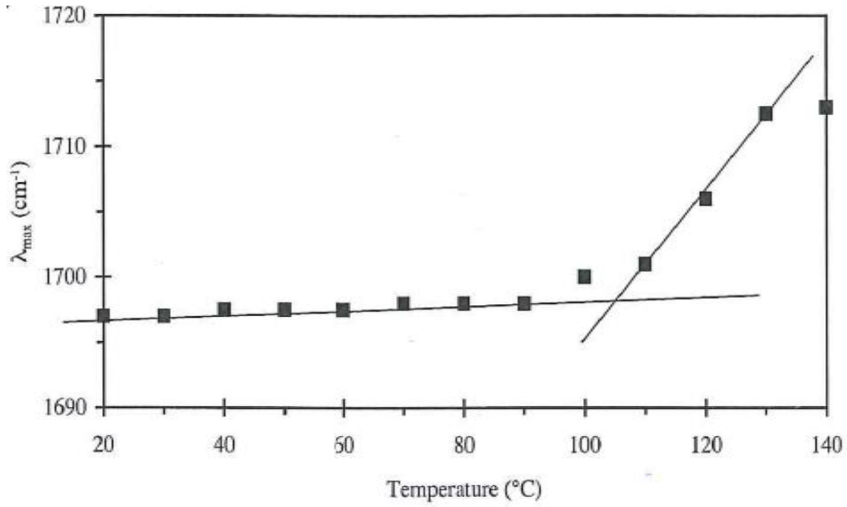

Figure 10: FTIR spectra of a sample of bitumen with 3% (w/w) of dodecanedioic acid at several temperatures. Wavelength of maximum absorption versus temperature.

4. CONCLUSION

Based on testing physical properties, we have shown that simple dicarboxylic acids are very efficient supramolecular additives for bitumen at only 3% (w/w). They increase significantly the softening temperature as much as 60°C and decrease the melt viscosity. The hardness and elastic modulus at room temperature are also improved. The remarkable improvement of bitumen properties is due to the formation of a network of interconnected crystalline fibers, where acid groups are hydrogen bonded at room temperature and dissociate in the temperature range corresponding to the softening temperature. Supramolecular additivation is a new promising way for bitumen improvement for road (WMA) and industrial applications (roofing).

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