

FIREPROOF SILICONE SEALANTS FOR SHIPBUILDING

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Abstract

Enhancement of fire behavior indeed represents a challenging issue for many materials and particularly for polymers. In this work, the fire performance of a commercial silicone sealant commonly used in shipbuilding industry was investigated. The effects of inorganic fillers were studied by thermo-gravimetry analysis (TGA) and micro-calorimetry (MCC).

The use of these techniques, TGA and MCC, allowed for the creation of small batch of materials and corresponding formulation as compared to the kilogram sample needed for cone calorimeter testing.

Results shown slightly variation of the total heat released rate and corresponding peak temperature, while a significant change in specific heat release capacity measured for the highest sepiolite percentage, degradation and flammability behavior due to the inorganic content.

1 Introduction

A fire could be a devastating event on a ship, particularly on a passenger vehicle, where large numbers of people have to be evacuated.

Fire Protection Regulations by The International Convention for the Safety of Life at Sea (SOLAS), are designed to ensure that fire scenario could be :

1. prevented from occurring;
2. rapidly detected;
3. contained and extinguished.

“A” class firedoor systems - considered in the present work - are one of the most widely adopted passive safety devices to contain fire or smoke up to 60 minutes according to the Resolution A.754 of the Fire Test Procedure Code (IMO). In particular, firedoors must withstand the direct exposure of a furnace in which temperature reaches 945°C at the end of the test. Moreover, to avoid production and structural problems related to conventional welded joints between the ship bulkheads and the firedoors frame, adhesive joints are widely used.

Among the polymeric materials used as adhesives/sealants, silicones have an inherent stability at high temperature in an oxidizing environment due to the high energy associated with the siloxane bond (Si-O). This feature makes these materials particularly interesting for such

applications where the versatility must be associated with a good fire resistance. Unlike organic polymers, silicones do not burn completely, but form a layer of silica particulate ash, on the polymer surface, acting as an “insulating blanket”. This layer reduces the contact between the flammable pyrolysis by-products and oxidizing atmosphere. Since this residual silica is in a powder-like form, after the action of fire, the sealant materials become useless for its original functionality in the assembly structure. For this reason, researchers are paying much attention to enhance coherence and strength of the material at microstructural level, by modifying their morphology in order to ensure both maintenance of a continuous structure and polymer shrinkage attenuation.

To investigate such application, completely innovative in the shipbuilding industry, a commercial one-part silicone sealant, with good resistance to flame spread, has been considered and investigated.

Among the different parameters required to determine hazard in fire and mainly in enclosed room scenario (i.e. building, aircraft or ship), the rate at which heat is released by burning material, indeed may represent the most important. The reasons are strictly connected with the thermal balance with surrounding space which may cause the firing of other system and at the same time feed the existing flame scenario.

Across, different industrial sector, several different bench scale methods have been developed for measuring the heat release rate, however, these experimental testing require replicate samples on the order of several hundred grams each with final results highly dependent on specific feature (i.e. ignition source) [1], sample geometry and location [2,3], edge and boundary condition of the fluidodynamic scenario [4]. Correlation of fire behavior and “constituents” materials property is driving the attention of many research to relate thermogravimetric analyses to flammability [5,6].

Single parameters have been used generally to assess the degradation or thermal resistance of materials such as, char yield or degradation temperature, however description of flammability of material based on these parameter has failed. Direct measurement of heat release rate of milligram-sized samples of materials is possible by using pyrolysis combustion flow calorimeter, developed by R. Lyon [7]

The aim of the present work is to evaluate the performance of the commercial silicone sealant and to improve its fire resistance behaviour, by introducing inorganic fillers, basically by acting in accordance with the follow mechanisms:

- to oppose a physical barrier to the diffusion, within the material, of flammable volatiles towards the flame front and the oxygen.

2 Materials and testing methods

The matrix silicone sealant Sika Firesil N used in this research, is a commercially available from Sika Group. Natural fillosilicate Sepiolite were supplied by Mi.Mac. Srl. It is a family of fibrous hydrated magnesium silicate with the theoretical half unit-cell formula $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{OH}_2)_{4\cdot8}\text{H}_2\text{O}$ [8].

The nanocomposites investigated were prepared mixing by sonication, sepiolite at different percentage (1%; 3,5%; 5%) in silicone sealant. The high energy sonicator used, in this work, is a Misonix S3000, characterized by a generator with 600 W output, a 20 kHz converter and a temperature controller.

Thermogravimetric analysis (TGA) was performed with a TA Instrument TGA – 2950 (TA Instrument, New Castle, US) to analyze the thermal stabilities of samples from 30° to 700°C at 10°C/min under nitrogen flow. Thermogravimetric analysis (TGA) and derivative signal (DTG) represent a quantitative methodology useful to analyze the stability of materials. TGA scans were performed on all composite samples for each concentration.

Microcombustion calorimetry (MCC) measurements were carried out by using a FAA microcalorimeter instrument supplied by Fire Testing and Technology Ltd (UK). Each measurement (sample weight was 5 ± 0.5 mg) was repeated on three different samples for repeatability purposes and then results averaged. This technique allows to pyrolyse the milligrammed sample before a mixture of O_2/N_2 can convey the evolved gas into a combustion furnace. The furnace stage, held at isothermal temperature of $900^\circ C$, bring to complete combustion the evolved gas leading to a consumption of the oxygen measured by an end-line positioned sensor. All sample were weighted before and after the experiment to evaluate also char yield. The unique, patented MCC allows for the rapid evaluation of extremely small samples in a quantitative and highly reproducible manner.

3 Result and discussion

Microscale combustion calorimeter (MCC), developed by FAA researchers, represents a valid scientific technique to measure flammability propriety of material by separating the solid state and gaseous phase evolving from a flaming combustion by controlled pyrolysis followed by a completely combust in excess of oxygen. In the last few year, also thanks to the excellent work of Prof. Lyon from FAA have been shown that parameters derived from MCC can help to predict the burning behavior of materials evaluated by standard flammability tests with the strong advantage of using only few milligram of material compared with kilogram samples of standard technique.

The MCC measurements were performed on samples cut from a bigger plate with nominal dimensions 100mm X 100mm which will be later tested by cone calorimetry.

The silicon system and corresponding silicon compounds were cast in aluminum mould and allowed to react according to the procedure reported above.

Each sample, approximately 5 mg, was heated to a specified temperature using a linear heating rate of $1^\circ C/sec$ in a stream of nitrogen flowing at $80\text{ cm}^3/min$ flow rate. The thermal degradation products (fuel gases) were mixed with a $20\text{ cm}^3/min$ stream of oxygen prior to entering the combustion furnace where the complete combustion of the effluent products takes place. Each sample was run in three replicates and the data presented here are the averages of the three measurements.

The flammability parameters which can be extracted from MCC data are:

- heat released rate (HRR), i.e. the rate of released heat due to the degradation of the materials;
- peak heat released rate (PHRR) which identifies the temperature at which the maximum rate of released heat is measured;
- total heat released (THR) is the time integral of the released heat over the whole flammability test;
- the char yield gives a measure of the degradation residual content;
- the heat release capacity (HRC) is a time and rate-independent material flammability property which defies the capability of a material system to release heat under controlled degradation conditions.

The total heat of combustion of the volatiles after the complete pyrolysis process under controlled temperature conditions is simply the time integral of the material degradation or mass loss function with oxygen rate consumption returned to zero.

Considering that the fuel generation process of a combustible material in a fire is anaerobic [9] and assuming that the material under investigation follows a single-step degradation process with a residual fraction μ , then specific maximum mass loss is given by the expression:

$$-\frac{1}{m_0} \frac{dm}{dt}_{MAX} = (1-\delta) \frac{\beta E_a}{eRT_p^2}$$

where E_a is the activation energy for pyrolysis, T_p , is the temperature of maximum mass loss rate, and e , R , are the natural number and gas constant, respectively. Normalizing the maximum heat release rate of the solid mass loss and dividing by the only test parameter left, i.e. the temperature rate, β , the specific heat release capacity of the solid polymer can be written as:

$$HRC = \frac{\dot{Q}_C^{MAX}}{m_0} \cdot \frac{1}{\beta} = \frac{h_{cs}^0 E_a}{eRT_p^2}$$

The above defined capacity property of the system depends only on chemical composition of the initial solid mass therefore can be related to the initial system undergoing a degradation pyrolysis followed by complete combustion of the evolved gas. This parameter, having the unit of hear capacity represent the release heat of the initial polymer system under controlled temperature rate.

Figure 1 reports the curve of hear released rate for neat and sepiolite loaded silicon systems for the three different considered percentages (1%; 3,5%; 5%).

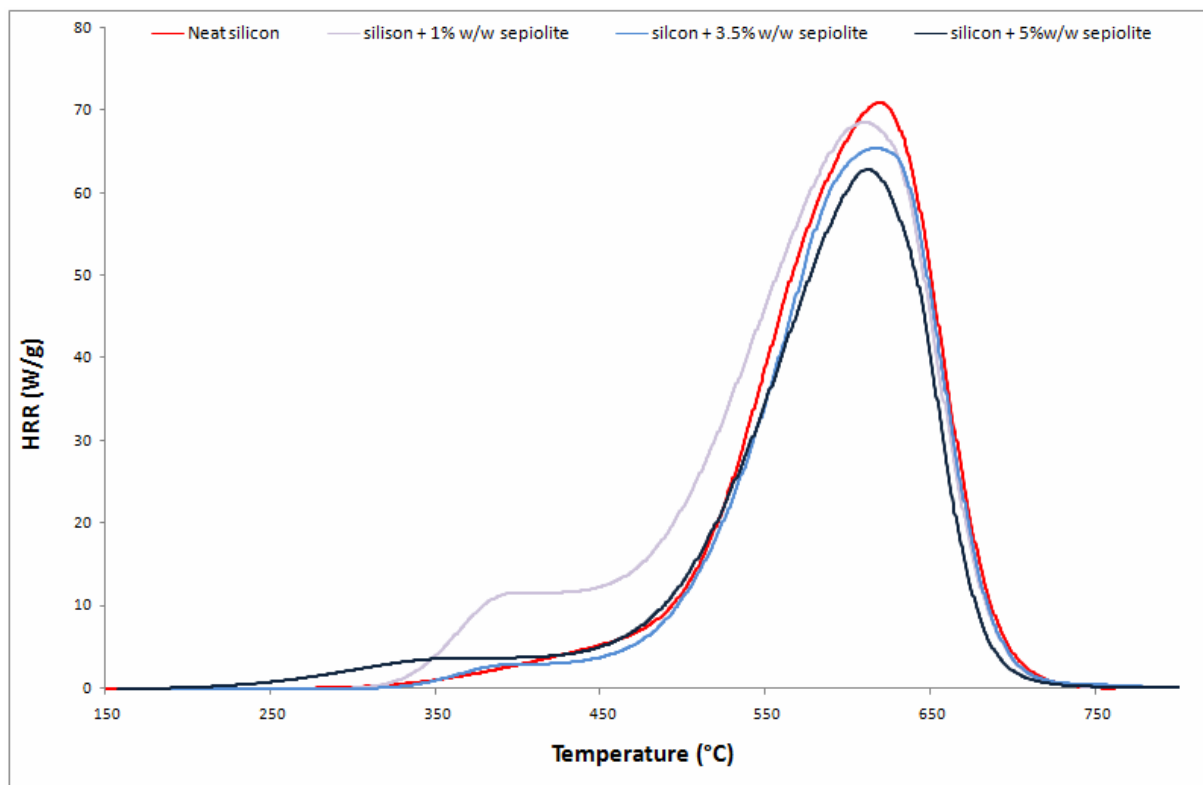


Figure 1. HRR curves for neat and sepiolite loading silicon at different w/w contents

The neat silicon curve can be suitably fitted by a single stage reaction whereas the curves corresponding to the loaded system report a earlier peak which not only is attenuated by increasing the sepiolite content but it is also spread over a longer temperature range as clearly shown for the highest sepiolite percentage.

The shape of the HHR curve for the neat system identifies an initial mass loss temperature for the controlled condition at 300°C. Negligible variation of the flaming temperature is recorded by adding 1% and 3.5% of nanofiller, however for the highest percentage a significant variation of about 100°C is measured (~200°C). The faster degradation of the highest loaded system, assuming that no chemical reaction has occurred between the bulk system and the nanofiller may be due to the reduced permeability of the forming char and therefore it could be related with an early degradation of the nanoporous final structure.

The net heat of complete combustion calculated from oxygen consumption as the total area under the heat release rate curves are reported in figure 2. The reduced value of THR for the neat silicon system confirms, as expected, that the system has a limited flaming behaviour, only 8.9 J/g. The addition of sepiolite at different w/w percentage does not change significantly the total heat released by the conditioned degradation of the silicon system, in fact at low content (1% w/w) the measured THR values are within the repeatability error, whereas for the higher percentage (3.5% and 5% w/w) the variation results more relevant, of about 10% respect to the neat system.

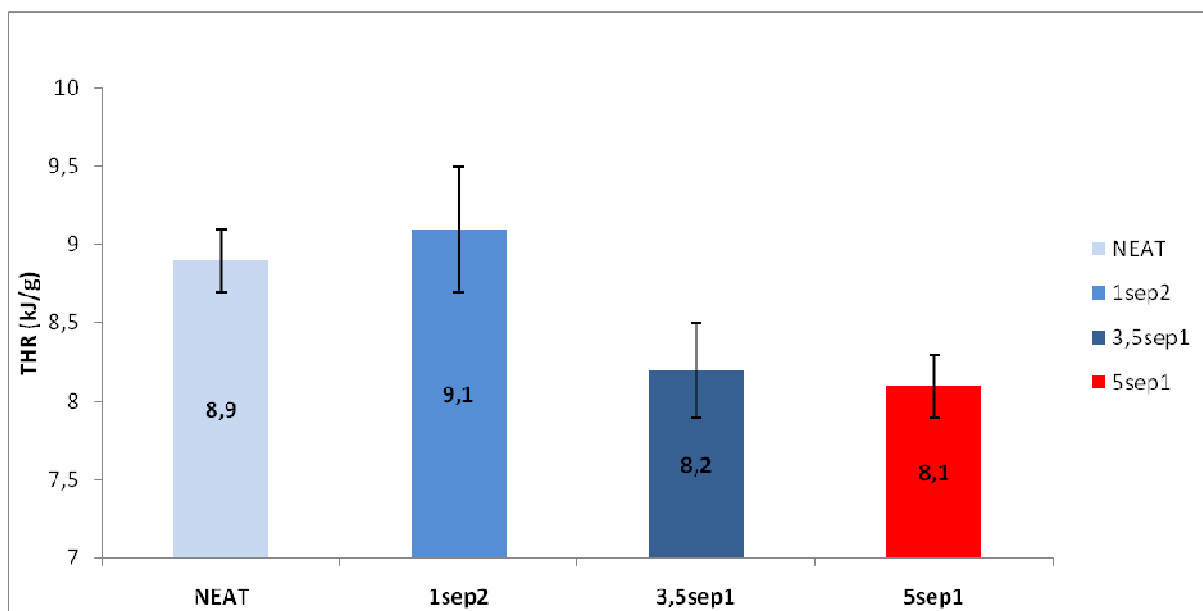


Figure 2. THR values for neat and sepiolite loading silicon at different w/w contents

The effect of sepiolite on specific heat released capacity (HRC) is significant with a total reduction of more than 20% compared with neat silicon system (figure 3). This result indicated that the addition of sepiolite limit the flaming behaviour of the overall silicon modified compound.

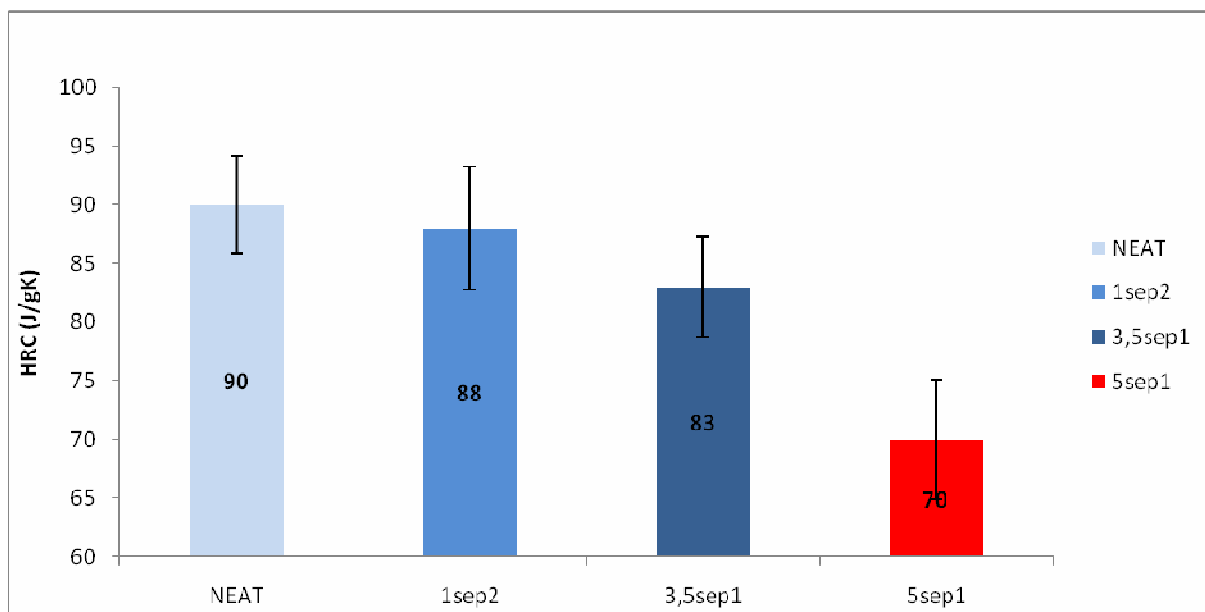


Figure 3. HRC values for neat and sepiolite loading silicon at different w/w contents

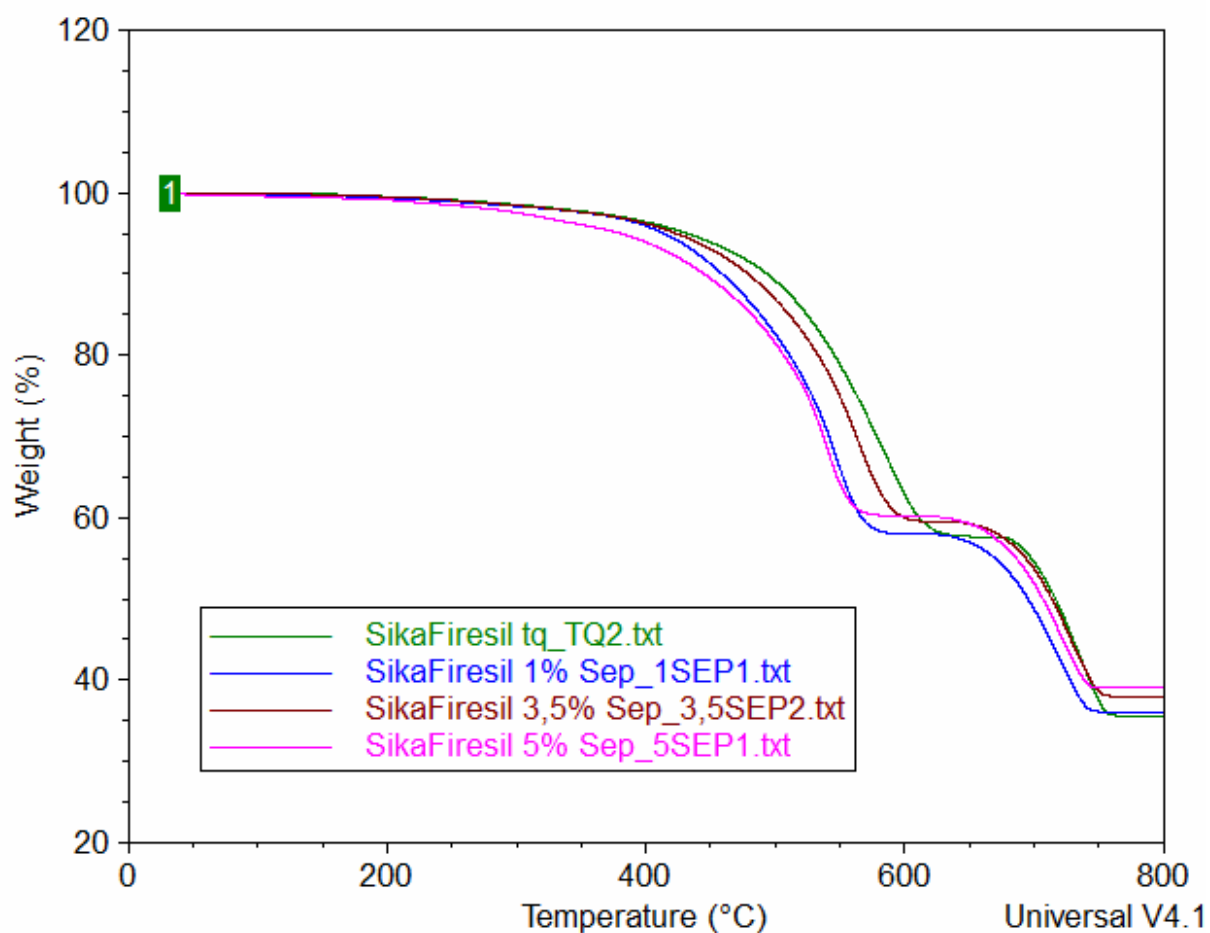


Figure 4. TGA curves of the three different systems and corresponding neat material

TGA curves of the three different systems and corresponding neat material (figure 4) substantially confirm that the addition of sepiolite anticipates the degradation of the solid

polymer, as clearly shown by the 5%w/w sepiolite loaded compound, in fact the initial mass loss temperature is around 250°C compared with the 320°C of the neat silicon. However, the flammability behavior of the modified system results significantly reduced due to the lessened “fuel” stream heat released capacity as recorded by the MCC data.

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