Incorporation of Medetomidine (Selektope®) into Silicones ®

Key findings

R&D work undertaken by I-Tech has confirmed that medetomidine can be incorporated silicones.

It has been shown that medetomidine can be covalently attached to PDMS by forming isocyanate adducts, which is a method for incorporation of medetomidine into silicone coatings.

The next step will be to study in detail the incorporation of the medetomidine-PDMS adduct into silicone coatings.

Abstract

To-date, the marine biocide, Selektope (Medetomidine) has been successfully commercialised in multiple self-polishing biocidal coating products for the function of repelling barnacle larvae from the hull to prevent settling behaviour. The barnacle repelling effect is obtained when medetomidine leaches out from the coating surface when it is continuously polished by seawater.

The leach rate of medetomidine at the coating surface can differ depending on the characteristics of the coating. The main challenge is to control the release rate of medetomidine – this is the case for both self-polishing coatings and foul release coatings.

Currently, the use of medetomidine in foul release coating types has not been commercialised.

However, extensive R&D work undertaken by I-Tech has confirmed that medetomidine can be incorporated silicones, by the reaction between a functional isocyanate group attached on silicones.

This technical paper is based on the incorporation if medetomidine into silicones using the isocyanates adduct. The silicone could act as carrier for medetomidine with potential of decreasing the leaching rate and to significantly improve the protection against barnacle fouling.

Previous method: medetomidine-containing polymer

I-Tech and the Research Institutes of Sweden (RISE) have previously created a synthesis method where medetomidine was reacted with a monomer, 2-(Methacryloyloxy)ethyl isocyanate, with a functional isocyanate group.

These results were presented September 2023 at the International Antifouling Conference in Gothenburg. A technical paper was published with the method and results, which can be accessed from: https://selektope.com/blog/whitepapers-and-brochures/

The resulting medetomidine-containing monomer was then reacted with other acrylic monomers, creating a co-polymer. The polymer containing that monomer was developed as a means to control the release rate of the medetomidine in marine antifouling coatings. The theory of creating a hydrolysable carrier polymer with covalently attached medetomidine is to try and mimic the function and control of release as was achieved with the old TBT-polymer/binder systems.

In Figure 1, the reaction of the monomer with medetomidine is shown as well as the hydrolysis of medetomidine containing monomer.

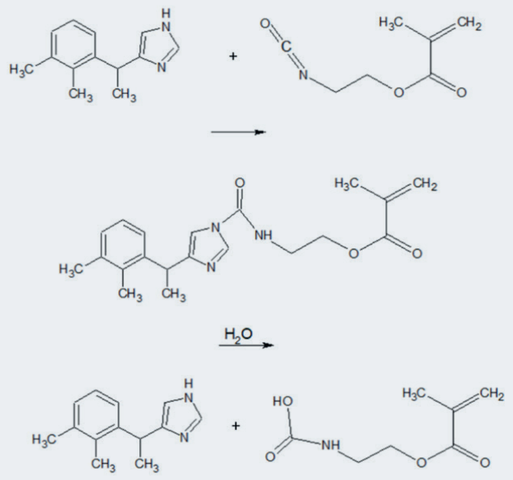

Figure 1. *In the first step of the reaction, 2-(Methacryloyloxy)ethyl isocyanate reacts with medetomidine causing them to covalently attach. In the second step, if treated with water, the 2-(Methacryloyloxy)ethyl isocyanate with medetomidine is hydrolysed and the medetomidine is released.*

I-Tech and RISE have shown that, in contact with water, this medetomidine-containing polymer can provide a stable and controlled leach rate over time as the medetomidine gradually gets released upon hydrolyzation of the urea bond. Good antifouling efficacy of the formulation containing polymer-bound medetomidine in static field test were achieved over a ten-month period.

Alternative method

More recently, I-Tech has investigated the same concept which was used for the acrylic polymers to as a method for incorporating medetomidine into silicone coatings. This concept presents an alternative possibility to use medetomidine in non-polishing, FRC systems.

Previously, it has been demonstrated and reported in literature that medetomidine can react with (trialkoxysilyl)alkyl isocyanate, see Figure 2. (trialkoxysilyl)alkyl isocyanate was used as a reactant for creating an adduct between medetomidine and the silicone network through the isocyanate and alkoxy groups in the (trialkoxysilyl)alkyl isocyanate.

The reaction product can then be used to incorporate medetomidine into fouling release coatings through the reaction between the alkoxy groups and free silanols in the paint.

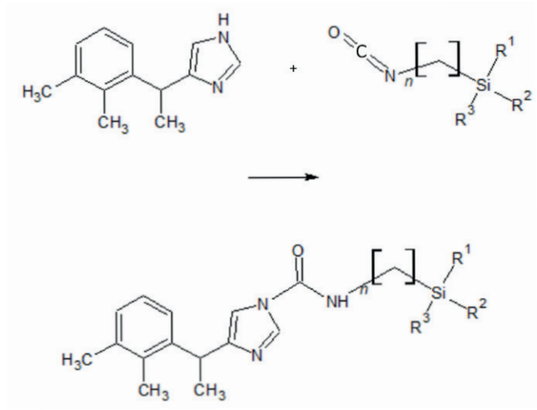

Figure 2. *Medetomidine attached at the ends of a (trialkoxysilyl)alkyl isocyanate through the reaction with the isocyanate group. The hydrolysis of the formed urea bond results in the release of medetomidine. R1, R2 and R3 are any alkoxy group.*

I-Tech has worked on an alternative polymer for the incorporation into silicones. Here, a linear di-functional isocyanate silicone pre-polymer, polydimethylsiloxane (PDMS), was reacted with medetomidine in an inert solvent (Dowanol PMA) to incorporate medetomidine at the end of the PDMS chain, see figure 3.

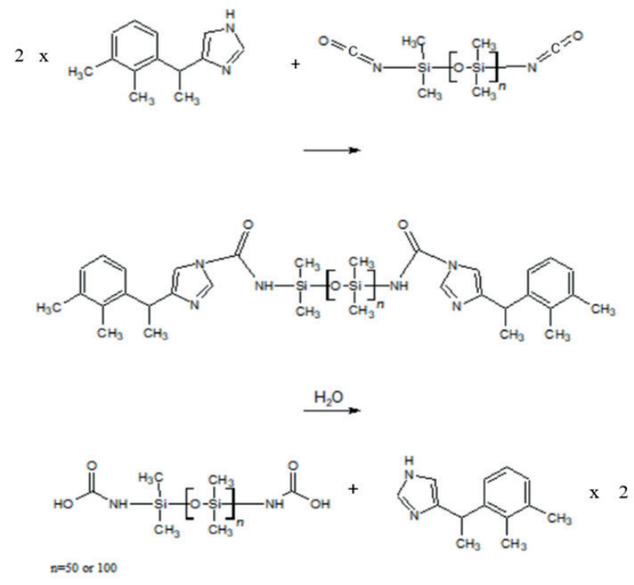

Figure 3. *In the first step of the reaction, PDMS with isocyanate at the ends reacts with medetomidine causing them to covalently attach. In the second step, the medetomidine terminated PDMS is hydrolysed and the medetomidine is released.*

ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared) spectroscopy was used to study the reaction of isocyanates attached to the PDMS, by analyzing the absorption peak of the isocyanate-stretching vibration that is around 2275-2250 cm−1. Three different samples were examined in this study. Sample #1 contained the isocyanate functional PDMS, medetomidine and Dowanol PMA, with a 1:1 molar ratio between isocyanate and medetomidine. Sample #2 contained the isocyanate functional PDMS, medetomidine and Dowanol PMA with a 2:1 molar ratio between isocyanate and medetomidine. Sample #3 contained the isocyanate functional PDMS and Dowanol PMA and was used as a reference.

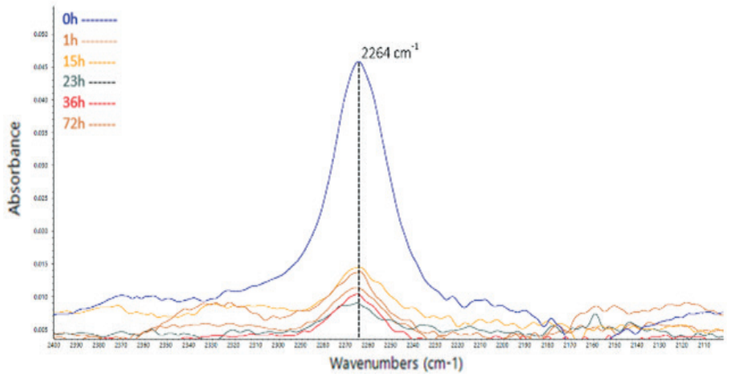

Figure 4. *Sample #1. IR spectra of the absorption of isocyanate bound to a linear di-functional isocyanate terminated silicone pre-polymer in solvent together with medetomidine. Isocyanate and medetomidine with a molar ratio of 1:1. The sample was measured at different time points. IR spectra in the wavenumber region 2400-2200.*

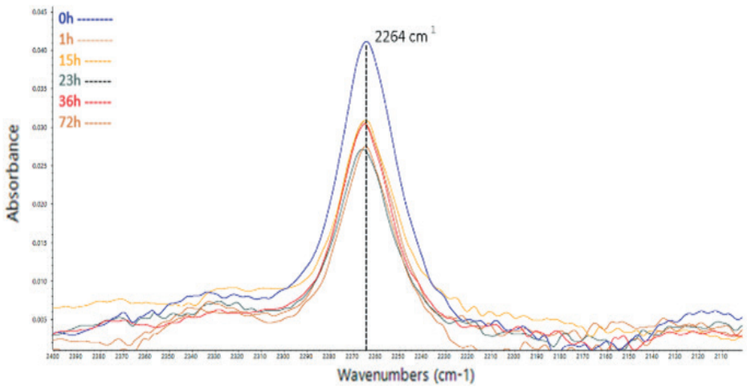

Figure 5. *Sample #2. IR spectra of the absorption of isocyanate bound to a linear di-functional isocyanate terminated silicone pre-polymer in solvent together with medetomidine. Isocyanate and medetomidine had a molar ratio of 2:1. The sample was measured at different time points. IR spectra in the wavenumber region 2400-2200 cm−1.*

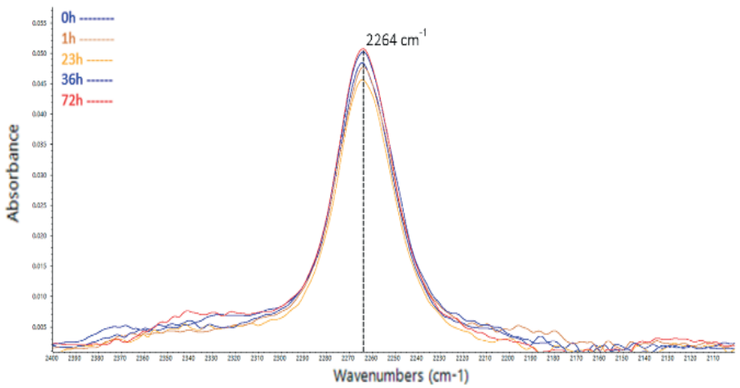

Figure 6. *Sample #3. IR spectra of the absorption of isocyanate bound to a linear di-functional isocyanate terminated silicone pre-polymer in solvent. The sample was measured at different time points. No medetomidine was added. IR spectra in the wavenumber region 2400-2200 cm−1.*

In Figure 4, sample #1 is examined, the absorption peak for the isocyanate drastically drops within the first hour. It appears that most of the isocyanate in sample #1 has reacted. Because of the 1:1 molar ratio between isocyanate and medetomidine, it is believed that most of the medetomidine has reacted with the isocyanate.
In Figure 5, sample #2 is examined, the absorbance of the isocyanate peak drops from 0.045 to around 0.030 within the first hour. The remaining isocyanate stays intact during the rest of the experiment (3 days), which indicates that all, or most, of the medetomidine and around half of the isocyanates are consumed. This is expected because of the 2:1 molar ratio between medetomidine and isocyanate.

In Figure 5, sample #3 is examined. The absorption peak for the for the isocyanate stays intact for the whole experiment, which indicates that no isocyanate has reacted. The conclusion that can be drawn from these graphs is that the isocyanate functional PDMS reacts with medetomidine to form an adduct.

Conclusion

This paper present two approaches of integrating medetomidine into silicones; the first approach is by reacting medetomidine with (trialkoxysilyl)alkyl isocyanates which thereafter can be integrated in silicone coatings based on the alkoxysilane-silanol cross-linking chemistry.

The second approach is by reacting medetomidine with isocyanate functional PDMS. It has been shown that medetomidine can be covalently attached to PDMS by forming isocyanate adducts, which is a method for incorporation of medetomidine into silicone coatings. Alternatively, it can also be released from silicone oils. The medetomidine can thereafter be released from the silicone network through hydrolyzation upon contact with sea water. There is still work to be done in this field, which is needed and ongoing.

Next steps

The next step will be to study in detail the incorporation of the medetomidine-PDMS adduct into silicone coatings. This can be done either by adding a fully reacted medetomidine terminated PDMS oil, free from reactive isocyanate groups, or by adding an isocyanate functional PDMS oil where parts of the isocyanates have been reacted with medetomidine and the remaining isocyanate groups can react with, for instance, free silanols in the silicone paint.

The medetomidine-containing silicone paint will then be applied onto panels and thereafter immersed in the seawater, to test the release and antifouling performance of medetomidine-containing silicone-based coatings prepared with the novel method described herein.

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selektope®

Selektope is an organic, metal-free active agent added to marine antifouling paints to prevent barnacles from settling on coated surfaces by temporarily activating the swimming behaviour of barnacle larvae. This bio-repellent effect makes Selektope the only type of technology of its kind available to the marine paint manufacturers.

i-tech

I-Tech is a global biotechnology company operating in the marine paint industry. The company has developed and commercialised the product, Selektope. With Selektope, I-Tech is uniquely the first company to ever apply principles from biotechnology research in the marine paint industry to keep ship hulls free from marine fouling.