The use of comb-type copolymers to sustain the surface bactericidal effect of highly water-soluble cationic biocides

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Summaries
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A series of free radical comb-type acrylic copolymers was prepared in a solution incorporating charged and/or neutral stabilising species on the backbone. The polymer solutions were formulated with cationic biocides to give physically stable formulations with a long shelf life. Furthermore, through the control of polymer architecture of both the side-chain and the backbone, hydrophobicity a controlled release of a biocide could be achieved. This technology has resulted in the design of temporary coatings demonstrating a sustained surface disinfecting effect. In laboratory trials, coated surfaces with polymeric/biocidal formulations continued to show a disinfection effect after several washes.

L’usage des copolymères en peigne pour préserver les effets bactériocides sur-faciques des biocides cationiques très hydrosolubles

Une série de copolymères acryliques en peigne à radical libre a été préparée dans une solution qui incorporait sur la chaîne principale des espèces stabilisantes chargées et/ou neutres. Les solutions polymériques étaient formulées en utilisant des biocides cationiques pour donner des formulations qui étaient physiquement stables et qui jouissaient d’une longue durée de conservation avant vente. D’autres, grâce au contrôle de l’architecture polymérique et de la chaîne latérale et de la chaîne principale en pourraient attérdir Hydrophobité, une libération contrôlée d’un biocide. Cette technologie a abouti à la conception de revêtements temporaires qui font preuve d’un effet soutenu qui concerne la désinfection de surfaces. Au cours des essais de laboratoire, des surfaces revêtus de formulations polymeric/biocides ont continué à faire preuve d’un effet désinfectant même après plusieurs lavages.

Kammartige Kopolymeren heilen, die antibakterielle Wirkung von stark wasser-löslichen kationischen Bioziden an der Oberfläche zu erhalten

Eine Serie von kammartigen, frei-radikalen Acryl-Kopolymeren wurde in einer Lösung mit geladenen und/oder neutralen Stabilisatoren im Rückgrat hergestellt. Die Polymerlösungen wurden mit kationischen Biociden hergestellt, die sie lange haltbar machten. Die Hydrophobität sowohl des Polymerrückgrats als auch der Nebenkettlen wurde genau kontrolliert, damit das Biocid zielgerichtet freigesetzt werden konnte. Diese Technologie hat es ermöglicht, den Teststücken eine nachhaltige Oberflächensterilisationswirkung zu verleihen. Laborversuche zeigten, dass die antimikrobielle Wirkung trotz mehrerer Waschvorgänge bestehen bleibt.
Introduction

By definition, a disinfectant should achieve a 99.999% reduction in viable bacteria. Whilst such contact disinfection performance is common in today's antimicrobial products, there is a drive to the development of products that can impart a hygienic effect on a range of substrates. The effect should last for anything between a few hours and several months, as required.

There has also been an increase in public awareness due to recent outbreaks of diseases such as SARS (severe acute respiratory syndrome), MRSA (methicillin resistant Staphylococcus aureus) and E coli. It has been reported that the SARS virus can survive on a surface for at least 24 hours.2,3 Similarly, harmful bacteria such as Staphylococcus sp4 and Salmonella sp5,6 are known to have resilience when on a surface. The ease with which these diseases can survive and be transmitted from a surface is further reason to provide a sustained hygienic effect.

Such a sustained disinfection effect, as shown against standard laboratory organisms, can be achieved by using controlled delivery of a highly water-soluble biocide such as polyhexamethylene biguanide hydrochloride (PHMB).7

PHMB is a broad spectrum and fast-acting bactericide that has already found regional commercial applications (Japan, Europe and North America) in areas such as hospitals, food preparation, rest rooms, and restaurants, as well as in the home. Common surfaces that may benefit from a sustained effect include poly(propylene), stainless steel, ceramic, glass, cloth and fibre. By varying both the polymer backbone architecture and the side-chain hydrophilicity/hydrophobicity, it is possible to achieve the desired adsorption to the surface whilst maintaining good hygienic properties under repeated microbial challenges.

Comb copolymers (a copolymer that has a polymer backbone with grafted pendant side chains) with similar architecture have already found regional commercial applications (Japan, Europe and North America) in areas such as hospitals, food preparation, rest rooms, and restaurants, as well as in the home. Common surfaces that may benefit from a sustained effect include poly(propylene), stainless steel, ceramic, glass, cloth and fibre. By varying both the polymer backbone architecture and the side-chain hydrophilicity/hydrophobicity, it is possible to achieve the desired adsorption to the surface whilst maintaining good hygienic properties under repeated microbial challenges.

Comb copolymers were prepared with varying backbone charges and hydrophobicity; in total, over 70 differing polymers were prepared.

Significantly during this research, it has been found that comb copolymer technology has allowed stable solutions to be achieved when negative charges in the backbone are in the presence of cationic species such as quaternary ammonium compounds or PHMB.

Standard test procedures used to measure surface hygiene/disinfection effects, such as the Japanese JIS Z 2801 (2000), have proved inadequate to show differences and hence differentiate between the varying comb copolymers. Therefore, test methods have been developed in-house based on variations of JIS Z 2801 (2000).

The aim of this paper is to show how the controlled release of the biocide PHMB, using comb copolymer technology, gives desirable log reductions through repeated challenge cycles when exposed to water and microbial inoculations.

Experimental

Preparation of comb copolymers

Four main types of comb copolymers were synthesised using a free radical solution polymerisation process. The comb copolymers were prepared with varying backbone charges and hydrophobicity; in total, over 70 differing polymers were prepared of the various types listed below:

1. anionic (ie containing acid-functional acrylic monomers);
2. basic (ie containing amino-functional acrylic monomers);
3. non-ionic (ie containing non-functional acrylic monomers);
4. ampholytic (ie containing both acid and amino-functional acrylic monomers).

Synthesis of comb copolymers

A jacketed glass reactor fitted with a stirrer, nitrogen bleed, thermocouple and condenser, was cleaned and dried prior to use.

An initiator solution was prepared using dimethyl 2',2'azobisisobutyrate (WAKO Pure Chemical Industries 98%) dissolved in a (ethanol/water) solvent (1% on moles of total monomer at 2.5% solution concentration).

A monomer solution containing the acrylic monomers (backbone) and polyethylene (propylene) glycol methyl ether methacrylate (side-chains) in the solvent (ethanol/water) was prepared.

Into the reactor was added the solvent (ethanol/water) followed by the monomer solution (line washed through) with more of the solvent mixture. The reactor was heated to 75°C using a circulating heated water bath and stirred at 180rpm under a nitrogen blanket. On reaching the correct temperature, time zero, 25% of the initiator solution was added to the reactor and left for 30 minutes before adding the second aliquot of 50% of the initiator solution. The polymerisation was maintained at 75°C for a further three and a half hours before increasing the temperature to 80°C. On reaching the required temperature, a third aliquot 12.5% of initiator solution was added to the reactor and allowed to polymerise for a further two hours, after which time the final aliquot 12.5% of initiator solution was added. After two hours, the comb copolymer solution was cooled and removed from the reactor. The total time of the polymerisation was eight hours. The final solution was generally colourless and free of particulate matter.

When possible, characterisation of the comb copolymers was performed, typically the molecular weight using GPC (gel permeation chromatography), the glass-transition temperature using DMTA (dynamic mechanical thermal analysis) or DSC (differential scanning calorimetry), the film hardness using the Konig pendulum hardness, the solution viscosity using a Brookfield viscometer, the surface tension using a Du Nouy ring, the cloud point temperature of the aqueous solution, the solubility of the comb copolymer in water of a dried film, and the free monomer content analysis using HPLC (high-performance liquid chromatography).

Formulation of comb copolymers with bactericide PHMB

All four types of comb copolymers were formulated with PHMB to form stable solutions.

Figure 1: Poly(hexamethylenebiguanide)hydrochloride (PHMB)
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This stability had been expected for both the basic and the non-ionic comb copolymers but not those containing acid functionality in the acid and amphoteric cases. Normally, gross flocculation of polymers containing these species should occur. This flocculation was demonstrated with the addition of either PHMB or quaternary ammonium biocide to commercial acrylic emulsion polymers containing acid functionality and also with a homopolymer of methacrylic acid.

The stability gained in these polymer systems has been attributed to a shielding of the charged species in the acid and amphoteric comb copolymers due to aggregates or micelle structures which formed with an enhanced steric hindrance being gained from the pendant polyethylene (propylene) glycol side chains.

Figure 2: Acid comb copolymer aggregates/micelles in aqueous media

Tentative micellar structure of acid comb copolymer in water

Test protocols

Acid Red 52 dye test (test protocol 1)

This test method was developed to measure the amount of free or unbound PHMB that remained upon the addition of the comb copolymers.

CI Acid Red 52 is an anionic dye that reacts with the cationic PHMB. When solutions of the two are mixed and allowed to react, a precipitate forms decreasing the total amount of dye in the solution. The total amount of PHMB available determines the total amount of precipitate; any CI Acid Red 52 that remains in the solution can be measured using an ultraviolet (UV) spectrometer.

Figure 3: Structure of CI Acid Red 52

Initially the four types of comb copolymers were tested by formulating with and without PHMB and the activated dye CI Acid Red 52.

It was expected that the acid-functional comb copolymers would have the greatest interactions, which could lead to reduced biocidal activity against some micro-organisms. This was confirmed, although some sustained activity was shown for all four cases via microbial testing.

Preparation of comb copolymers and PHMB formulations (test protocol 2)

It was possible to prepare the ‘formulations’ of the comb copolymer and the PHMB in either (a) a mixed solvent (ethanol/water) or (b) an aqueous solution. The PHMB was used as a 20% aqueous solution and added to the comb copolymer solution at varying concentrations, with loadings of 0.5% up to 80% PHMB on comb copolymer weight.

On the whole, the formulations were made at 5, 10, 16.7 and 50% loadings of PHMB and the nomenclature used in the later examples was as follows:

1-16 (a) 50.0% PHMB loading on dry polymer film
1-16 (b) 16.7% PHMB loading on dry polymer film
1-16 (c) 5.00% PHMB loading on dry polymer film
1-16 (d) 10.0% PHMB loading on dry polymer film

Coating of formulations (test protocol 3)

Several techniques were used to apply a coating to a substrate such as cotton wool, cellulose wipe or trigger spray, but for consistency, the testing of the release rate and the sustained effect on the formulations were applied using a ‘Sheen’ wire applicator bar.

The first surface that the formulations were coated (to form a dried film) onto for testing was glass. Coated films are currently being tested on other surfaces such as polypropylene, stainless steel, aluminium and ceramic, but these results will be reported separately.

Release of PHMB from a dried coated formulation (test protocol 4)

The panels (150mm x 100mm) were weighed prior to coating and after drying to ascertain the film weight from which the total level of PHMB could be calculated.

Approximately ten dried panels per test were used to measure the release rate of the PHMB from the film (carried out in duplicate).

The coated glass panel was immersed separately (film side up) in distilled water (1 litre) in a two-litre beaker being stirred at a constant speed using a magnetic follower.

After a known time, two water samples were taken for analysis and the experiment was stopped. This was repeated for all panels at various time intervals. A similar experiment was performed with the duplicates.

The water samples were analysed using an ultraviolet (UV) spectrometer and the absorbance of each sample measured at the specific peak corresponding to the λmax of the PHMB molecule (236nm).
Calibration of PHMB using Lambda 900 UV/VIS/NIR spectrometer (test protocol 5)
The spectrometer was calibrated using known concentrations of PHMB diluted in distilled water. The λ max for the system was measured at 236nm. The comb copolymer solutions, with several known concentrations of PHMB, were also measured from which a calibration graph was produced by plotting UV absorbance against PHMB concentration.

Measurements were taken at 1, 2, 5, 10, 15, 30, 45 and 60 minutes.

Calculation of minimum inhibitory concentrations (test protocol 6)
The intrinsic bacteriostatic activity of the formulations was evaluated by measuring the minimum inhibitory concentrations (MICs).

Bacteria (Pseudomonas aeruginosa ATCC 15442) were grown in nutrient broth for 16 to 20 hours at 37°C (to give approximately 109 cells per ml).

A 0.1% (v/v) inoculum was used to seed fresh medium and 100μl was then added to each well of a microtitre plate, except for the first well that contained 200μl.

Using double dilutions, the concentration of the formulations being investigated was varied in each well along the ordinate axis.

The presence or absence of growth was determined by visual inspection after 24 hours of incubation at 37°C. The MIC is the lowest concentration of the sample required to inhibit bacterial growth.

Residual bactericidal activity (test protocol 7)
The residual antibacterial activity of the samples was determined by the following methodology:

1. All formulations were diluted to a 0.5% active ingredient (AI) PHMB. A 50μl aliquot of each formulation was placed in a ceramic tile well and allowed to dry for approximately one hour.

2. Bacteria (Ps aeruginosa ATCC 15442) were grown in nutrient broth at 37°C for 16 to 20 hours.

3. An inoculum of approximately 108 organisms per ml was prepared in a physiological saline (0.85% NaCl).

4. A 150μl aliquot of bacterial inoculum was pipetted into the ceramic tile well previously coated by the formulation, and incubated at room temperature.

5. After five minutes of contact time, the inoculum was removed by pipette and the number of viable organisms enumerated (samples were serially diluted in a CEN neutraliser by 10², a 1ml aliquot was added to 9ml of impedance broth, and RABIT [rapid automated bacterial impedance technique] technology was used to enumerate bacterial cells).

6. The coated formulations in the ceramic wells were then washed up to five times with 5ml aliquots of sterile water.

7. Following the washing steps, the coatings were re-inoculated with a 150μl aliquot of bacterial inoculum.

8. As above, the inoculum was removed after five minutes and the number of viable organisms enumerated by the method described above.

Repeat inoculation test (test protocol 8)
This was a similar test to that described in the residual bactericidal methodology with a modification as follows:

Removal of the washing procedure steps (6) and (7) and replacing this with an inoculum challenge over a varied and longer timescale.

The first inoculation was at time T = 0, the removal of the inoculum as in the previous test after five minutes, and the number of viable organisms enumerated using RABIT technology. The second inoculation was at time T = 2 hours, following the protocol and enumerating viable organisms as before. These inocu-
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Results and Discussion

Release of PHMB from formulations using test protocol no 4

The calibration graph (see Figure 4) of PHMB standards was used to calculate the total PHMB released from the formulations that were measured using test protocol no 4.

Optimisation of PHMB loading

The copolymer (see no 1, Table 1) was formulated with various loadings of PHMB and coated on to glass panels, allowed to dry, and then immersed in aqueous media.

Table 1: % molar compositions of prepared comb copolymers

| Comb copolymer | % MAA | % DMAEMA | % MeOPEG 350MA | % MeOPEG 550MA | % MMA | % EMA | % BMA |
|----------------|-------|----------|----------------|----------------|-------|-------|-------|
| 1              | 33    | 33       | 33             |                |       |       |       |
| 2              | 20    | 20       | 20             | 20             |       |       | 40    |
| 3              | 14.29 | 14.29    | 14.29          |                |       |       | 57.14 |
| 4              | 33    | 33       |                | 20             |       | 20    | 40    |
| 5              | 20    | 20       | 20             | 20             |       | 20    | 40    |
| 6              | 20    | 20       | 20             | 20             |       | 20    | 40    |
| 7              | 20    | 20       | 20             | 20             |       | 20    | 40    |
| 8              | 14.29 | 14.29    | 14.29          | 14.29          |       |       | 57.14 |
| 9              | 9.52  | 9.52     |                | 9.52           |       |       | 71.4  |
| 10             | 20    |          | 20             |                |       |       | 80    |
| 11             | 80    |          |                |                |       |       | 20    |
| 12             | 80    |          |                |                |       |       | 20    |
| 13             | 16.67 | 33       | 16.67          | 33             |       |       |       |
| 14             | 25    | 50       | 25             |                |       |       |       |
| 15             | 25    | 50       | 25             |                |       |       |       |
| 16             | 37.5  | 37.5     | 25             |                |       |       |       |

Key: MAA = methacrylic acid (Sigma Aldrich 99%)
DMAEMA = dimethylaminoethyl methacrylate (Sigma Aldrich 99%)
MeOPEG350MA = polyethylene (350) glycol methyl ether methacrylate (Cognis Performance Chemicals UK 99%)
MeOPEG550MA = polyethylene (550) glycol methyl ether methacrylate (Cognis Performance Chemicals UK 99%)
MMA = methyl methacrylate (Sigma Aldrich 99%)
EMA = ethyl methacrylate (Sigma Aldrich 99%)
BMA = butyl methacrylate (Sigma-Aldrich 99%)

Table 2: Characterisation properties of comb copolymer Table 1

| Comb copolymer | DMTA Tg °C | Viscosity cps (20%wt/wt) | Konig hardness | Cloud point °C | Surface tension dyne/cm | Mol Wt | GPC MW |
|----------------|------------|--------------------------|----------------|----------------|------------------------|--------|--------|
| 1              | 24.2       | 25400 **                  | 14             | >97            | 56.0                   |        |        |
| 2              | 29.4       | 1350                     | 26             | 71             | 46.9                   |        |        |
| 3              | 35.3       | 787                      | 67             | 50             | 45.8                   |        |        |
| 4              | <0         | 2830                     | 6              | >97            | 55.5                   |        |        |
| 5              | 22.7       | 13,400 **                | 23             | 67             | 48.0                   |        |        |
| 6              | 11.8       | 1330                     | 22             | 57             | 40.7                   |        |        |
| 7              | 7.9        | 1120                     | 6              | >97            | 48.8                   |        |        |
| 8              | 19.6       | 1330                     | 16             | 70.5           | 54.8                   |        |        |
| 9              | 34.8       | 2400                     | 59             | 51             | 55.2                   |        |        |
| 10             | 18.2       | 850                      | 2              | n/m            | 53.9                   | 48,000 |        |
| 11             | 38.5       | 1050                     | 16             | 33             | 50                     | 56,200 |        |
| 12             | <0         | 950                      | 3              | 66             |                        |        |        |
| 13             | 25.6       | 1320                     | 43             | 83             | 53.6                   |        |        |
| 14             | 2          | n/m                      | 14             | >97            | 51.9                   |        |        |
| 15             | <0         | 972                      | 4              | >97            |                        |        |        |
| 16             | 27.3       | n/m                      | 32             | >97            |                        |        |        |

Key: Tg = Rheometric Scientific. Onset of storage modulus E1, measured at the frequency 1Hz and at a 3°C/min temperature ramp.
Viscosity measured on a Brookfield RVT/DTV11 viscometer.
The solution viscosities were measured at 23% concentration in a 50/50 aqueous ethanol at 25°C using RV spindle 31 at 100rpm.
** Solution measurement made using spindle 31 at 20rpm
Konig hardness = Erichsen Model 289/500 using a pendulum swing on dried coated film.
Cloud point = measured at 1% polymer concentration in water.
Surface tension = 1% polymer concentration in water using Du Nouy ring.
Molecular weight = Waters Alliance GPC using Phenomenex styragel columns with PMMA standards; acid-functional polymer was methylated prior to analysis.
The amphoteric polymers could not be measured using GPC.
n/m = not measured.
under water. Samples of the water were taken and analysed for PHMB (see Table 3).

Figure 6 shows that the coated film with a 50% loading of PHMB was unable to maintain a sustainable controlled release of PHMB. This can be attributed to the high water solubility of the PHMB which was the dominating factor in controlling the solubility of the coated system, whereas the coated films containing 5 and 10% PHMB were able to control the release as the major influence on the solubility of the formulation was due to the comb copolymer.

Therefore, the loading of PHMB in to the coated film is an important factor in determining the release profile of formulated comb copolymers.

Figure 7 shows formulations with added methyl methacrylate in the backbone and the effect demonstrated on the release of PHMB from a film that had been coated on to glass. All three formulations gave good controlled release of PHMB. Increasing the methyl methacrylate in the backbone gave a controlled reduction in the release of PHMB from the coated formulations after one hour.

Therefore, the loading of monomer in the backbone is another important factor in determining the release profile of PHMB from similar formulated comb copolymers.

Figure 8 shows that the coated formulations with similar loadings of PHMB but varying the hydrophilicity by increasing side-chain length, results in higher solubility of the formulations, giving rise to an increase in the release of PHMB.

Hydrophilicity variability due to the side-chain is another factor in determining the release profile from similarly formulated comb copolymers.

Figure 9 shows that coated films with similar loadings of PHMB but modifying the hydrophobicity of copolymerised monomers in the backbone gave a varied controlled release of PHMB. Increasing the hydrophobicity in the backbone gave a reduced release of PHMB from the coated formulation.

The variability of hydrophobicity in the backbone is another important factor in determining the release profile from similarly formulated comb copolymers.

The MICs of comb copolymer formulations at varying PHMB loadings versus Pseudomonas aeruginosa
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Figure 8: Release of PHMB from coated films varying side-chain molecular weight at PHMB loading 5%

| Formulation | %wt/wt | %wt/wt | %wt/wt | %wt/wt |
|-------------|--------|--------|--------|--------|
| MA          | 9.80   | 17.90  | 49.43  | 22.77  |
| DMA         | 9.21   | 16.82  | 46.57  | 27.40  |
| DMAEMA      | 8.94   | 16.33  | 45.21  | 29.51  |
| MeOPEG350MA |        |        |        |        |

Figure 9: Release of PHMB from coated films varying hydrophobicity in the backbone at 10% PHMB loading

Figure 10: Intrinsic activity of comb copolymers with PHMB (all formulations were tested using protocol number 6 at 0.5% AI of PHMB)

Figure 10 shows that in all four types when no PHMB is present, bacteria proliferate. However, when PHMB is formulated with non-ionic, cationic and amphoteric comb copolymers, the intrinsic bacteriostatic activity is maintained (with these three copolymer formulations, the points as shown in Figure 10 to overlap one and other). Some loss of bacteriostatic activity is seen when the acidic comb copolymers are formulated with PHMB. The activity, however, returns when the weight of PHMB to polymer in the formulation is increased to 50%.

Residual bactericidal activity using test protocol no 7

Figure 11 shows that all three formulations give good antimicrobial efficacy after two washes unlike the PHMB blank.

With further washing, increasing the level of methyl methacrylate in the backbone prolonged the activity of the coated film, extending the coating lifetime and its sustainable effect.

Figure 12 shows the added sustained effect after two washings by increasing the hydrophobicity in the backbone of the comb copolymer.

Repeat inoculum challenge using test protocol 8

Figure 13 shows that under severe microbial challenges, it was possible to sustain a good antimicrobial efficacy. In the cases of the formulated comb copolymers 13c, increasing the functionality in the backbone gave an excellent antimicrobial effect with a 6-log reduction after four repeat inoculations.

Figure 14 shows that increasing the PEG side-chain length increased the solubility of the comb copolymer, releasing the PHMB from the formulations more quickly. The formulation containing (MeO-PLC 350MA) was more sustainable to repeated microbial inoculations of the Ps aeruginosa.

Conclusions

For each polymer type, it has been possible to design stable comb copolymer/PHMB formulations that could give both an immediate and sustained biocidal effect.

There are several factors that have been shown to be key in maintaining a sustained effect through controlling the release of PHMB from a coated formulation:
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Table 7: Repeated washing to test the antimicrobial effect from coated films formulated from comb copolymers (7, 8 and 9) with increasing level of MMA in the backbone at 5% PHMB loading

| Formulation | %wt/wt MAA | %wt/wt DMAEMA | %wt/wt MeOPEG350MA | %wt/wt MMA |
|-------------|------------|---------------|--------------------|------------|
| 7c          | 7.98       | 14.58         | 58.89              | 18.55      |
| 8c          | 6.74       | 12.29         | 49.68              | 31.29      |
| 9c          | 5.28       | 9.65          | 39.00              | 46.07      |

Table 8: Comparing formulated compositions with varying hydrophobicity in the backbone and its effect on antimicrobial sustainabilty

| Formulation | %wt/wt MAA | %wt/wt DMAEMA | %wt/wt MeOPEG350MA | %wt/wt monomer |
|-------------|------------|---------------|--------------------|----------------|
| 1c          | 12.68      | 23.18         | 64.14              | 0              |
| 2c          | 9.81       | 17.90         | 49.54              | 22.75          |
| 6c          | 8.95       | 16.34         | 45.20              | 29.51          |

Figure 13: Log reduction versus *Ps aeruginosa* at five-minute contact time with repeated inoculations at 0.5% AI varying functionality in the backbone

Figure 12: Antimicrobial effect from coated film (1c, 2c and 6c) varying hydrophobicity in the backbone at 5% PHMB loading versus *Ps aeruginosa* at 0.5% AI PHMB

1. the loading of PHMB in the formulation: too much leads to a loss of controlled release;
2. the molecular weight of the MeOPEG side chain which controls part of the hydrophilic behaviour of the formulation and steric stability;
3. the hydrophobic characteristic of the acrylic monomers in the polymer backbone control film solubility and hence the release of the biocide; and
4. the charge functionality within the polymer backbone and how it controls the interactions with PHMB and its release from a coated film.

Formulations prepared from a range of comb copolymers, as described in this paper, have been tested using a test protocol based on JIS Z 2801 (2000). This protocol was developed in-house and has shown when tested varied sustained surface efficacy. The result of this has allowed better predictions of comb polymer compositions that give both an immediate kill and a sustained surface disinfecting effect.

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Table 9: The effects of varying functionality in the backbone at 5% PHMB loading

| Formulation | % wt/wt MAA | % wt/wt DMAEMA | % wt/wt MeO PEG350MA | % wt/wt MeO PEG550MA | % wt/wt MMA |
|-------------|--------------|----------------|-----------------------|-----------------------|-------------|
| 2c          | 9.90         | 17.89          | 49.53                 | 0                     | 22.74       |
| 13c         | 8.31         | 30.37          | 42.01                 | 0                     | 19.31       |

0.5% wt/wt solution of PHMB used as the blank.

Table 10: Repeat inoculation of Ps aeruginosa on formulations varying side chain at 5% PHMB loading

| Formulation | % wt/wt MAA | % wt/wt DMAEMA | % wt/wt MeO PEG350MA | % wt/wt MeO PEG550MA | % wt/wt MMA |
|-------------|--------------|----------------|-----------------------|-----------------------|-------------|
| 14c         | 10.31        | 37.63          | 52.06                 | 0                     | 0           |
| 15c         | 8.31         | 30.37          | 0                     | 61.32                 | 0           |

0.5% wt/wt solution of PHMB was used as the blank.

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