Development of Low-Biofouling Polypropylene Feedspacers for Reverse Osmosis

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ABSTRACT: Microbial fouling, or biofouling, is the accumulation of microorganisms onto material surfaces. The goal of this project was to develop low-biofouling polypropylene (PP) films through the functionalization of PP by a spacer arm with metal chelating ligands charged with copper ions. Virgin and modified PP films were put in contact with 3.0×10^5 *Escherichia coli* cells/mL solutions for periods of time varying from 24 to 168 h. Fourier transform infrared spectroscopy (FTIR) and x-ray energy dispersive spectroscopy (EDS) were used to verify the functionalization reactions and monitor copper leaching. Direct counts of cells stained with dsDNA showed, invariably, that the microbial attachment to the modified PP films was an order of magnitune lower than on the virgin PP. Further, over a period of time of 2 weeks, no significant amounts of copper leached from the low-biofouling PP films. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3068–3073, 2009

Key words: polypropylene; low-biofouling; copper chelation; graft-polymerization

INTRODUCTION

Polypropylene (PP) is a commercial polymer that is ubiquitous in many fields such as textiles, medical devices, automobiles, food packaging, membrane filtration, etc.[1–3] Chemical resistance, low cost, and versatile properties have made PP an attractive polymer in many applications.[2,3] Although PP is known for its inherent chemical stability, surface modifications can be performed to make this polymer more attractive. In the many industries where sanitation is of great significance, such modifications that could increase the anti-biofouling properties of PP would be of great interest. Grafting of unsaturated vinyl monomers onto PP is a convenient route to develop new polymeric materials with synergistic properties.[4] Polymer-metal complexes have been extensively studied and successfully employed in several fields.[5] As in low-molecular-weight compounds, a polymer ligand must donate unshared electrons to the metal ion to form metal-ligand bonds. Among the multidentate ligands, iminodiacetic acid (IDA) possesses one aminopolycarboxylate and provides a reactive secondary amine hydrogen to react with alternate functional groups.[5] Hence, IDA can be more easily introduced to the side chain of a polymer or vinyl monomer via an epoxy group reaction of glycidyl methacrylate (GMA) and IDA. This reaction has two advantages: (1) GMA is a commercial industrial material that is cheaper than any other vinyl monomers that possess an epoxy ring in the side chain; and (2) it produces a vinyl monomer that can be polymerized by the addition of initiators or copolymerized with other vinyl groups.

The goal of this project was to develop low-biofouling PP, which can used for numerous applications such as food packaging, medical devices, and reverse osmosis feed spacers, through the functionalization of PP. The functionalized PP contained a spacer arm (GMA) with metal chelating ligands (IDA). Many studies have been conducted on the use of copper ions to disinfect water against microbial biofilms.[6] These ions are believed to interfere with enzymes involved in cellular respiration and bind DNA at specific sites.[7] For this reason, the metal chelating ligands were charged with copper ions, as shown in Figure 1. *Escherichia coli* was then used as a model to measure the low-biofouling properties of the modified PP.

EXPERIMENTAL

Materials

PP was obtained from Professional Plastics, Houston TX. GMA was purchased from Fisher Scientific and vacuum distilled before use. Sodium iminodiacetate disbasic (IDA) hydrate 98% was purchased from

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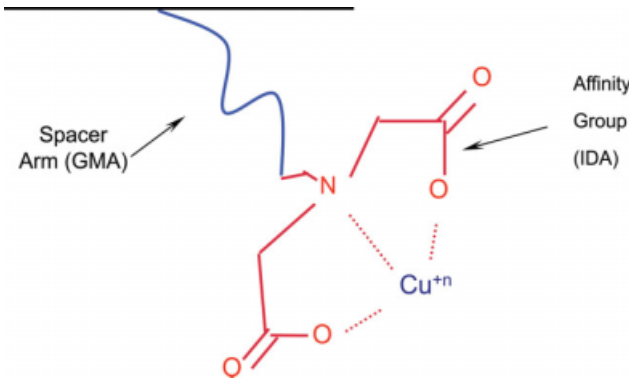


Figure 1 Schematic showing the graft polymerized spacer arm to the PP surface (blue); the covalently bound affinity group to the spacer arm epoxy group (red); and the copper chelated to the affinity group. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Aldrich Chemistry and used as received. Benzoyl peroxide, toluene, acetone, and copper sulfate were also used as received.

Preparation and characterization of Cu(II) charged PP-graft-GMA-IDA

PP sheets were cut into squares with and area ranging from 2 cm^2 to 4 cm^2 and sonicated in ethanol to clean and remove anything on their surfaces. The small sample sizes were used because this study was a proof-of-concept, and currently larger samples ($\sim$ 150 cm^2) are being tested to determine their biocidal abilities, leaching properties, and copper-coverage variability. The sheets were then vacuum-dried at 60°C for 24 h. A schematic of the reaction apparatus is shown in Figure 2. The initial weights (W_o) of the sheets were determined before they were placed in a round-bottom flask containing toluene as a solvent/interfacial agent, the radical initiator benzyol peroxide, and GMA. GMA and benzoyl peroxide (BPO) have been used as grafting initiators for PP. According to the literature,[8] polymerization occurs via C—C double bond cleavage and results in a graft material with the original reactivity of the epoxy ring. Thus, the epoxy group can be effectively used to anchor the desired species. After the sheets soaked in solution, the reaction vessel was purged with nitrogen and the temperature was increased to 80°C and the grafting of GMA to PP was allowed to occur. The sheets were then taken out and washed with acetone to remove all GMA homopolymer. To confirm the grafting of GMA to the PP, the sheets were dried at 60°C for 24 h and were analyzed by an attenuated total reflection FTIR (ATR-FTIR, Digilab UMA 600 FT-IT microscope with a Pike HATR adapter and an Excalibur FTS 400 spectrometer). The weights of the sheets were also determined at this time (W_f). The grafting level (GL%) of GMA onto PP was determined by using the following relation:

$$\text{GL } \% = \frac{W_f - W_o}{W_o} \times 100$$

The sheets were then placed into an IDA solution. After the reaction with IDA, DI water was used to rinse the sheets before they were vacuum dried and again analyzed by an ATR-FTIR spectrometer. The PP-graft-GMA-IDA sheets were placed into a Copper Sulfate solution to allow IDA to chelate Cu(II) ions. The presence of copper was detected using x-ray energy dispersive spectrometry (XEDS, UTW Si-Li Solid State X-ray detector with integrated EDAX Phoenix XEDS system, located at the University of Michigan, Ann Arbor).

Low-biofouling analysis of Cu(II) charged PP-graft-GMA-IDA

Two 150 mL Erlenmeyer flasks of LB Broth (Difco/Becton, Dickinson and Company, Sparks, MD) containing *E. coli* bacterium cells at a concentration of 3.0 $\times 10^5$ cells/mL were prepared. Three sheets of both virgin PP and Cu(II) charged PP-graft-GMA-IDA were added to the each flask, and they were then incubated at 35°C. At 24 h, 96 h, and 168 h sheets were taken from each flask. Cells were detached from the sheets using a Stomacher 400 Circulator (Seward, London, England). Detached cells were stained with Quant-iT PicoGreen dsDNA stain and counted using an Olympus BX51 fluorescent

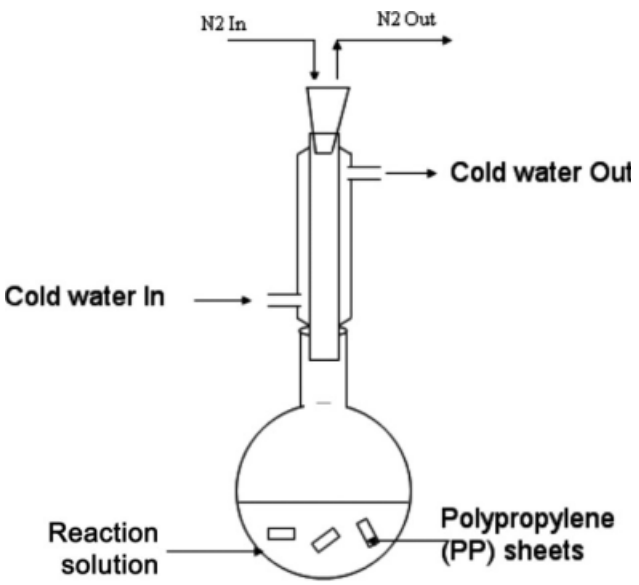


Figure 2 The reaction apparatus consisted of a round-bottom flask, a condenser, and heating the reaction mixture, under a nitrogen atmosphere.

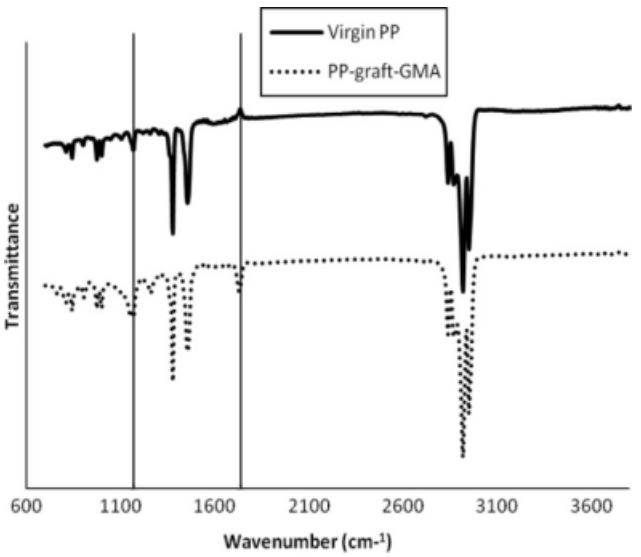


Figure 3 FTIR of virgin (—) and GMA-grafted PP (·····) films with peaks indicate the addition of the GMA to the PP by presence of carbonyl stretching (1724 cm^{-1}) and ester vibrations (1253 cm^{-1}) from the epoxy of GMA.

microscope and an Olympus DP-70 digital camera. Triplets of each sample were taken, counting 10 fields each time.

Release of copper ions from chelating ligand

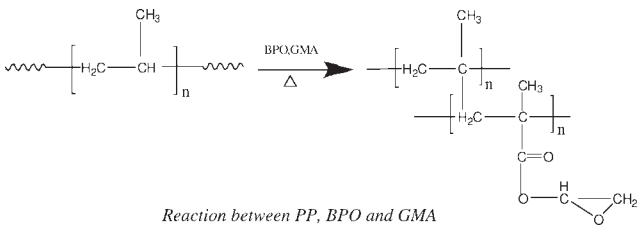
One hundred milliliters of DI water was added to three 150 mL Erlenmeyer flasks. To one flask, 2.67 g of NaCl, 0.267 g of MgCl, and 0.267 g of $CaCl_2$ were added. Another flask was prepared to contain 5 m*M* EDTA at a pH of 11 (adjusted with NaOH). The final flask had its pH adjusted to 3.5 with HCl. Three modified sheets were added to each flask and they were placed on a shaker table. After 1 week and 2 weeks, a sheet was removed from each solution, washed with DI water, vacuum dried overnight and analyzed using XEDS. Four areas were analyzed per sheet and compared to a modified sheet that was not placed in any solution after its initial modification.

RESULTS AND DISCUSSION

Preparation and characterization of Cu(II) charged PP-graft-GMA-IDA

The work proposed focused on the functionalization of model PP sheets via a spacer arm with metal chelating ligands because these groups are (i) quite stable and easily synthesized, (ii) operate over a diverse range of conditions, (iii) have easily controlled binding affinities, and (iv) are well suited for model studies.[8,9] For immobilized metal affinity (IMA) based separations, a chelate group is used to fix a copper ion to the PP backbone via a spacer arm. Chelate groups are strong Lewis acids that form several coordinate bonds with the metal ion through the sharing of three or more pairs of electrons. The chelating ligands (IDA) are bound to the polymer via a spacer arm (GMA) to make the chelating group more accessible. The over-reaching goal of this study, however, is the attachment of copper to PP, so the results presented here focus on the polymer properties incurred by the addition of copper.

In this study, BPO was used as a radical initiator for the graft polymerization of GMA to the PP surface at a temperature of 80°C, or nearly half of temperatures outlined in the literature.[1,10] Figure 3 displays the ATR-FTIR spectrum of a PP-graft-GMA sheet. The adsorption bands present at 1724 and 1253 cm^{-1} were caused by carbonyl stretching and ester vibrations of the epoxy group, respectively, indicating the attachment of GMA. This chemical reaction is the following:



Reaction between PP, BPO and GMA

Then, via an SN2 reaction, IDA was added to the PP-graft-GMA. The mean grafting level (GL%) for all of the sheets was approximately 40%; i.e., over 3–4 times higher than those associated with other studies.[1,8] Previous studies have shown that the use of

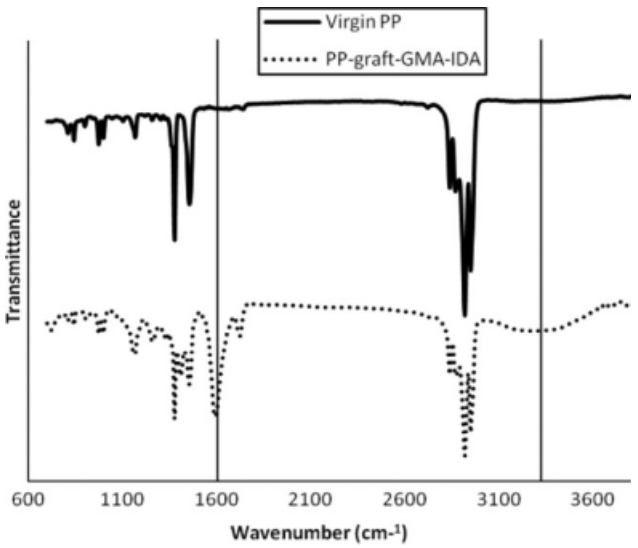


Figure 4 FTIR of virgin PP (—) and PP-graft-GMA-IDA (·····) films with peaks indicate the addition of the IDA to the PP-graft-GMA by presence of carbonyl stretching (1589 cm^{-1}) from a carboxylic acid and hydroxyl group stretches (3321 cm^{-1}) from the carboxylic acids present in IDA.

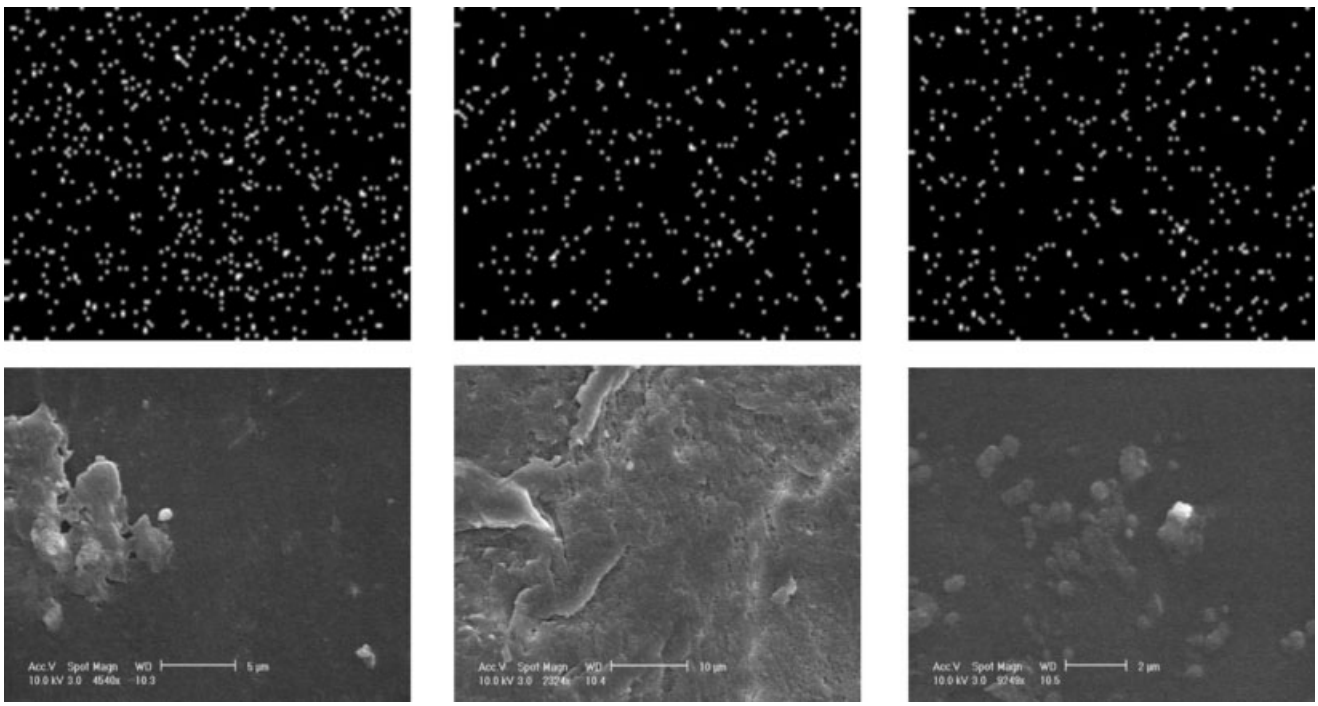
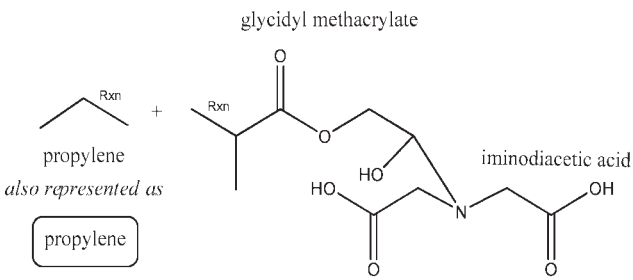


Figure 5 SEM imaging and EDS analysis showing even chelation of copper over the PP surface. Each copper map (above) was taken for the area captured by the SEM image (below). The white dots indicate the presence of a uniform distribution of copper.

PP powder or granules with a reaction temperature of 100–140°C yielded ~ 7% grafting.[1] Another study showed that for radical development, soaking of PP films with GMA and BPO in supercritical CO_2 for 10 h and 130 bar at 70°C followed by thermal-induced grafting at 120°C yielded only 13.8% grafting.[10] The hypothesis for the high level of grafting observed in this study is proposed to be due to uncontrolled radically initiated polymerization with high concentration of GMA monomer, which agrees with other studies.[11,12] Figure 4 displays the ATR-FTIR spectrum of PP-graft-GMA-IDA. Adsorptions at 1589 and 3371 cm^{-1} were caused by carbonyl stretching from carboxylic acids and OH stretching from carboxylic acids present in IDA, respectively. The chemical reaction involved is shown below



Reaction between PP and GMA-IDA.

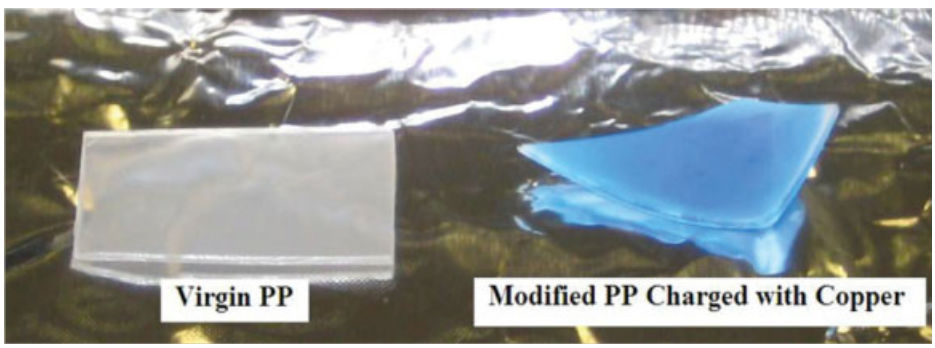


Figure 6 A virgin PP sheet (left, opaque in color) and a PP-graft-GMA-IDA sheet (right, blue in color) were placed in a 0.2 *M* copper sulfate solution for 8 h. At the end of the 8-hour period, the sheets were repeatedly rinsed with DI water. The PP-graft-GMA-IDA sheets turned blue due to the chelation of the copper ions, whereas the virgin PP remained its original color. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

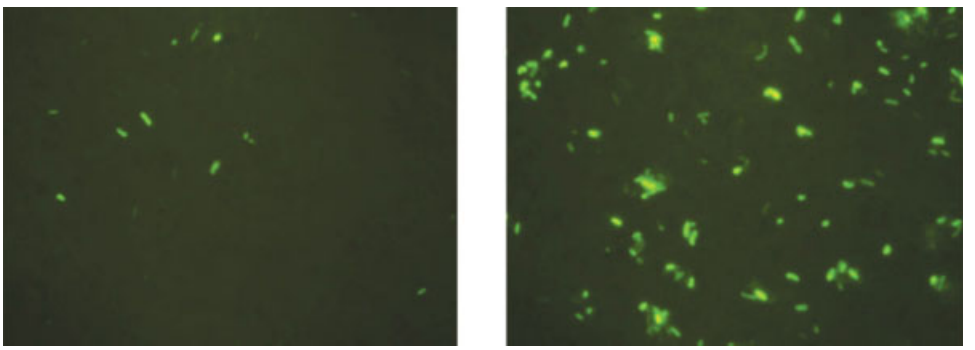
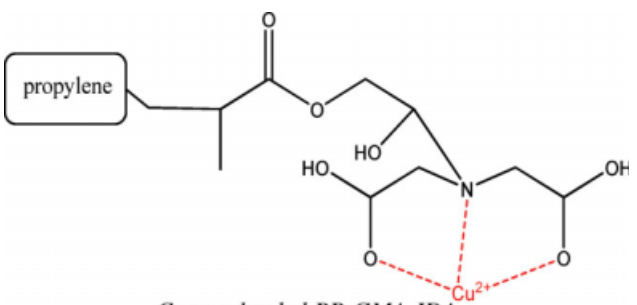


Figure 7 The above images were taken after 24 h of incubation in the *E. coli* broth, and they represent the biofilm growth on one modified (left) and one unmodified (right) PP film. The virgin PP sheet had ~ 14 times more cells attached to it than the modified PP sheet. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Finally, after exposure to copper sulfate (reaction shown below), XEDS analysis was performed on the sheets, and it showed that there was 3.27 ± 0.74% by weight copper loading on the surface. Also, as Figure 5 shows, mapping of the copper indicated uniform distribution over the surface of the sheets despite visual physical abnormalities present in SEM images. A simple visual inspection of the sheets gives a clear indication that copper was chelated to the PP-graft-GMA-IDA. As seen in Figure 6, the PP-graft-GMA-IDA sheet turned blue when exposed to the copper sulfate solution while a virgin PP sheet exposed to the same solution retains its original color (slightly opaque/white).



Copper loaded PP-GMA-IDA.

Biofouling analysis of Cu(II) charged PP-graft-GMA-IDA

Figure 7 shows two of the fluorescence microscope photographs taken after 24 h of incubation from each *E. coli* containing flask. For each sheet removed at the different time intervals, 30 of these images were taken. The number of cells attached to the PP-graft-GMA-IDA sheet after 24 h was significantly less than those attached to the virgin sheets. Figure 8 shows the data collected over the entire 168 h. After 24 h, attachment was $2.9 \times 10^6 \pm 2.9 \times 10^5$ cells/cm^2 on the modified sheet versus $4.0 \times 10^7 \pm 2.1 \times 10^6$ cells/cm^2 on the unmodified sheet. Similar results were obtained at 96 h, $3.1 \times 10^7 \pm 2.2 \times 10^5$ cells/cm^2 on the modified and $9.1 \times 10^8 \pm 3.9 \times 10^6$ on the unmodified, and at 168 h, $4.5 \times 10^7 \pm 4.9 \times 10^4$ on the modified and $3.7 \times 10^8 \pm 1.1 \times 10^5$ on the unmodified. Therefore, the number of cells attached to the PP-graft-GMA-IDA sheets was consistently approximately an order of magnitude lower than those attached to the virgin sheets.

Release of copper ions from chelating ligand

Figure 9 shows that the release of copper after 2 weeks in concentrated common cleaning solutions was not drastic. The only two instances where a significantly different weight percentage of copper was observed was after 2 weeks in the 5 m*M* EDTA

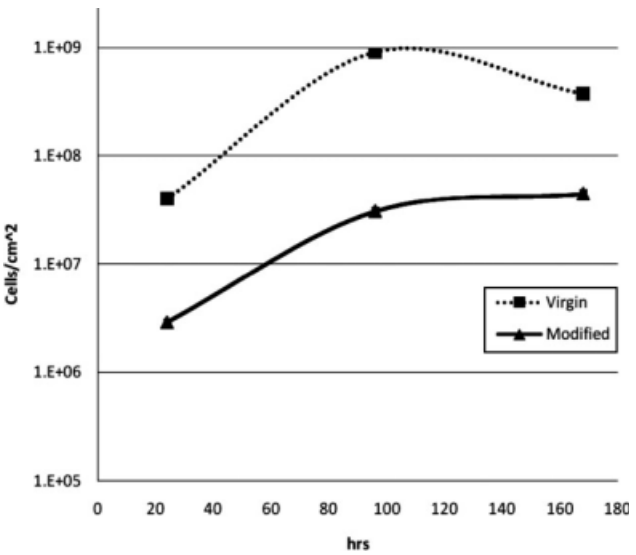


Figure 8 Over the 168-h period of incubation in the *E. coli* broth, the copper containing PP-graft-GMA-IDA sheets (solid line with triangles) maintained a cell attachment about an order of magnitude lower than on the virgin sheets (dotted line with squares).

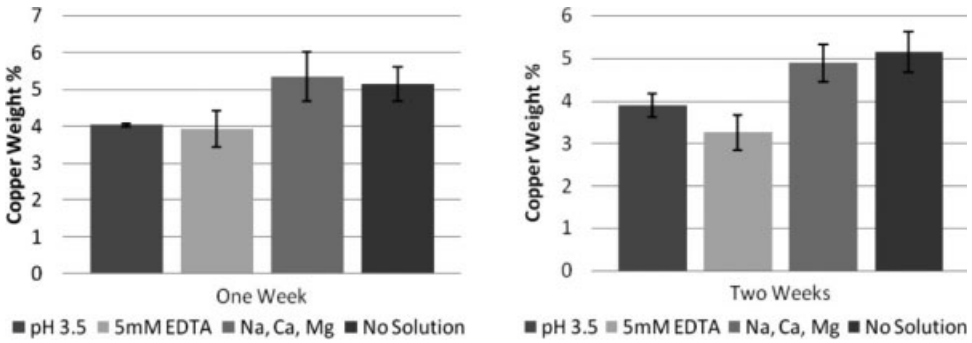


Figure 9 The copper charged PP-graft-GMA-IDA sheets were placed into three solutions, representing both cleaning solutions and sources of metal salts that might displace the chelated copper. From left to right, the columns represent a solution of pH = 3.5; a 5 m*M* EDTA solution; a solution with Na, Ca, and Mg; and no solution.

solution at pH 11, and the HCl solution at pH 3.5 after both 1 and 2 weeks. The data collected indicated that common metal ions such as sodium, calcium, and magnesium do not displace the chelated copper. Although the highly acidic solution and 5 m*M* EDTA did appear to have some affect on the sheets after 2 weeks, the weight percent of copper remaining on the sheets after exposure was 3.26% ± 0.41 and 3.89 ± 0.28 for the HCl and EDTA solutions, respectively. As the experiments in this article show, this weight percent of copper still acts affectively as a biocide.

CONCLUSION

The goal of this project was to develop low-biofouling PP that could be possibly be used in food packing or medical applications and also as feed spacers for reverse osmosis spiral wound elements. To this end, PP was functionalized with metal affinity ligands via a spacer arm. Infrared spectroscopy verified that PP was successfully modified to become PP-graft-GMA-IDA at temperatures of 80°C as opposed to either higher temperatures or harsher conditions proposed in other studies. SEM and elemental analysis were used to show that the PP-graft-GMA-IDA was uniformly charged with copper(II). The modification method utilized simple a reaction apparatus, inexpensive straightforward techniques, and commonly used, readily available chemicals. Biofouling analysis showed that the number of cells attached to virgin PP sheets, over a 168 h time span, was approximately an order of magnitude higher than those attached to the copper(II) charged PP-graft-GMA-IDA sheets.

The modified and charged PP could potentially be used in the above mentioned applications and could increase performance and longevity while ultimately decreasing cost. Although results presented here were based on small sample sizes, larger samples ($\sim$ 150 cm^2) are currently being tested. Research is being conducted to test the efficiency of the biocidial properties of the PP as a membrane feed spacer. Additionally, leaching of the copper during filtration is being monitored and quantified. Future optimization of the process and equipment will likely allow for industrial application of this modification.

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The work presented here has been submitted for a patent (regarding reactant concentrations, reaction time, and reaction temperature), and one is pending (Ser. No. 61/061,099 filed June 12, 2009).

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