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Polymethylolacrylamide films for antibacterial and biowaste management applications

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A novel electrosynthesis method is quicker and safer than conventional approaches, and allows the practical uses of the products to be broadened.

The extensive application of polymer materials in various fields of science and technology necessitates a deep understanding of their properties. Indeed, it is important to conduct extended preliminary tests to reveal the full characteristics of novel polymers. For example, it is crucial to prevent the emission of harmful substances to the environment. In some cases, however, the toxicity of polymers may play a positive role. It is thus necessary to obtain a full understanding of the toxic properties of novel polymers, as well as the products of their decomposition.[1–4]

It has previously been shown, for instance, that biocidal properties of polymer materials could be useful in the development of antiseptic films and glues (i.e., for medical applications).[5] They may also provide protection—from biofouling and corrosion—for equipment that is used in natural or sea waters.[6,7] Alternatively, the biocidal properties could be harnessed in baromembrane processes to increase the lifetime of polymer membranes.[8] In general, these biocidal protective coatings and materials are produced by introducing antiseptic additives to a polymer.[4] These standard methods, however, tend to have slow rates of film formation. In addition, it is often impossible to change the composition, molecular weight, crosslinking degree, and polymer structure of the resultant polymer layers.

In our work,[9] we have thus demonstrated the feasibility of using other approaches to produce novel polymer materials with biocidal properties. In particular, we use the electropolymerization synthesis method—with acrylic monomers and formaldehyde—to build crosslinked polymethylolacrylamide polymer films on the surface of various metals (e.g., platinum, stainless steel, iron, zinc, chromium, cadmium, nickel, copper, lead, titanium, and aluminum).[10–21] Our methodology presents several advantages over the conventional polymer film production approaches. For example, the films can be created on an electroconducting surface within 5–30 minutes. Moreover, the use of water as a solvent means that our technique is inexpensive, nontoxic, fire- and explosion-proof, as well as ecologically safe.

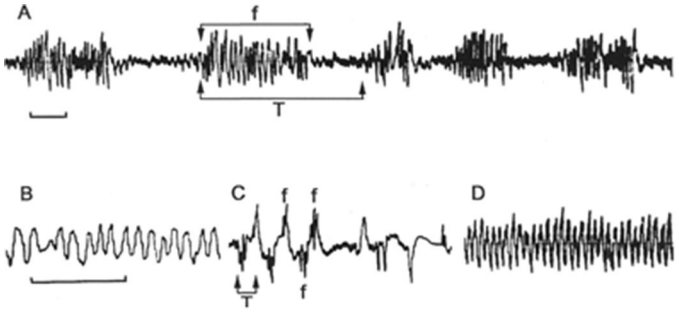

Figure 1. *Results of real-time micro-organism-induced biodegradation experiments. The oscillogram shows the motion (i.e., feeding behavior) of the bacteria during the 'attack' on the electrosynthesized polymethylolacrylamide membranes. The results illustrate that the bacteria attached to the membrane—at the attachment point (A) surface by using special organelles (flagella) and slow rotation. The sinusoidal nature of the throbbing organelles can be seen in B, where the flagellar vibrations occurred at different rates. To unattach from the substrate (C), the bacteria began to rotate faster, and their flagellar apparatus operated at a higher frequency (f). At the start of the nutrition process (D) the bacteria stopped moving, but the flagellar vibrations continued. T: Rotation period.*

To assess the biocidal properties of our electrosynthesized polymers, we used finely ground powders of the polymers to suppress growth of *Staphylococcus* bacteria. The toxicity results for our polymer coatings (see Table 1) show that the antibacterial effect of the films persisted for 2–45 days. Furthermore, with increasing exposure to water, we observe a decrease in the bacterial growth suppression of the polymer films. That is, we achieved the maximum suppression of bacterial growth with the polymer films that had not undergone sample rinsing and the biocidal effect of the polymers gradually

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Table 1. *Toxicity measurements of nine electrosynthesized polymethylolacrylamide films (1–9), as well as for acrylamide (AA), N,N′-methylene-bis-acrylamide (MBAA), and zinc (Zn). S_s: Area of bacterial growth suppression. S_{total}: Total bacterial growth area.*

Sample	Length of water polymer film treatment (days)	S_s (cm^2)	S_s / S_{total}	Antibacterial duration (days)
1	–	4.46	0.98	45
2	–	2.5	0.31	45
3	1	1.70	0.14	45
4	5	1.50	0.11	45
5	7	1.30	0.08	2
6	9	1.30	0.08	2
7	14	1.30	0.08	20
8	40	0	0	0
9	53	0	0	
AA	–	0	0	45
MBAA	–	0	0	45
Zn	–	0	0	45

decreased with sequential rinsing. In addition, after the water treatment exceeded seven days, we found that the area of bacterial growth suppression (as a proportion of the total bacterial growth area) became constant. We ascribe this rinsing-induced reduction in the biocidal properties of the polymers to decreased formaldehyde concentrations in the porous films. In other words, after seven days, practically full elution of formaldehyde from the film had occurred, and the antibacterial action had slowed down and stabilized (but did not stop). This effect is the result of the hydrolysis of methylolamide groups that occurred with formaldehyde formation.

The disposal of polymer waste is a major problem that arises because of their ubiquitous presence in modern life. In another part of our study we therefore directly observed—in real time—the biodegradation characteristics of our polymer membranes by examining the use of micro-organisms for the biodegradation of our electrosynthesized polyacrylamide–formaldehyde materials. Our results—shown in Figure 1—indicate that the polymethylolacrylamide polymer (after the solution containing toxic formaldehyde had been washed away) induced specific bacterial behavior, i.e., a complex set of reactions in which the bacteria searched, captured, and consumed the available nutrients. We find that the bacteria attack the side of the polymer film that is directed toward the electrode during the synthesis less intensively than the opposite (smooth matrix) layer, which is more accessible to the micro-organisms.

The results of our experiments demonstrate that our samples successfully suppressed the growth of *Staphylococcus*. Our work is therefore of practical importance because the microbiological purity of polymer products is often rigorously mandated. Our polymethylolacrylamide films thus have the potential to be used in the production of medical implants and as antiseptic materials. In addition, the microbiological stability and sterilizing nature of our films mean that the operation times of the ultrafiltration membranes can be prolonged and they can be used to provide partial sterilization of organic solutions. Indeed, we have previously shown that our membranes—after ultrafiltration purification—can prevent mold formation and fermentation in phytic acid extracts.[8, 22] Moreover, because of the membranes' sterilizing effect, it may be possible to use them in some industrial applications to accumulate (and store for long periods) large volumes of filtrates. We have also shown that our polymethylolacrylamide polymers have a similar biocidal effect on marine biological organisms (i.e., where the films act as a nutritional substrate for bacterial species that cause biocorrosion).[23]

In summary, we have successfully demonstrated the antibacterial properties of electrosynthesized polymethylolacrylamide polymer films. The inherent antibacterial nature of the materials that we produce with our novel synthesis technique (arising from the presence of formaldehyde in the macromolecular chain) means that we eliminate an additional stage in conventional approaches, i.e., in which biocidal substances are introduced into the polymer matrix. Our synthesis method thus represents a quicker and safer option than the standard techniques. Furthermore, our resultant polymethylolacrylamide films have a broader range of applications, and can be used in a number of practical situations. For instance, our membranes can be used in medicine for implants or antiseptic materials, or for equipment to protect against biopollution and biocorrosion. Our future research will be focused on the creation of new, modified polymeric materials. These additional substances will allow us to expand the range of antiseptic actions.

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