Advanced Materials Research Vol. 747 (2013) pp 501-504
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doi:10.4028/www.scientific.net/AMR.747.501

Anti-bacterial Efficacies and Discolorations of Polypropylene doped with HPQM based Water Solution and Neusilin

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Keywords: Magnesium aluminometasilicate, HPQM, Neusilin, Polypropylene, Color change

Abstract. 2–Hydroxypropyl–3–Piperazinyl–Quinoline Carboxylic acid Methacrylate (HPQM), as one of the most effective anti-bacterial agents was introduced into polypropylene (PP) for the aim of anti-bacterial improvement. HPQM based water (HPQM-Solution) and HPQM based magnesium aluminometasilicate or Neusilin (HPQM-Neusilin) were supplied in the forms of liquid and solid powder, respectively. Physical appearances by means of discolorations of PP after introducing the HPQM-Solution or –Neusilin were also investigated. Halo test and the dynamic shake flask methods accompanying with plate count agar technique were used for quantitative anti-bacterial performance analyzes and the results were reported in terms of radius of inhibition zone and percentage of bacteria reduction. HPQM-Neusilin samples showed obvious and better anti-bacterial performance as compared with the HPQM-Solution samples. The results by dynamic method suggested that the anti-bacterial efficacies of the HPQM-Neusilin samples were three times higher than those of the HPQM-Solution. To achieve the 99.9% of bacteria reduction, the optimum concentration of HPQM-Solution and HPQM-Neusilin required were 7,500 and 2,500 ppm, respectively. The addition of HPQM-Neusilin considerably changed the total color difference (ΔE^*), the lightness (L*) and chromatic coordinate values (a* and b* values) of the PP, the effect being less pronounced in the case of HPQM-Solution.

Introduction

Microbial contamination is one of the major concerns for health problems and economic losses in food packaging and sanitary industries. Polypropylene (PP) have been mostly manufactured for many food packaging products, such as, food tray, plastic bags, cup, bucket, and film. Addition of anti-microbial agents into the materials formulations is one of the promising methods for protecting materials form microbial contaminations. Uses of many anti-bacterial agents have been studied extensively in order to enhance anti-bacterial properties of polymeric materials [1-4]. Besides, the recent literatures suggested that the anti-microbial performances of biocide incorporated polymeric materials were dependent on many factors, for example, types and contents of biocide, biocide diffusivity, material incorporating methods, polymer matrix, additives, specimen forms and so on [1, 3-4].

In this present work, 2–Hydroxypropyl–3–Piperazinyl–Quinoline Carboxylic acid Methacrylate (HPQM) were introduced in the PP material for the purposes of improving the anti-bacterial efficacies. Two forms of the HPQM were used, these being HPQM based water solution (HPQM-

Solution) and HPQM based magnesium aluminometasilicate or Neusilin (HPQM-Neusilin). Physical appearances of PP after incorporating with the HPQM substances were also discussed.

Experimental

Materials and chemicals: Polypropylene (PP), grade P403J, supplied by Siam Cement Company (Bangkok, Thailand), was used as polymer matrix. The commercial biocide, 2–Hydroxypropyl–3–Piperazinyl–Quinoline Carboxylic acid Methacrylate (HPQM), regarded as an active bactericidal substance (provided by Micro Science Tech Co., Ltd, South Korea), having two different forms of HPQM based water (HPQM-Solution) and HPQM based Neusilin (HPQM-Neusilin) were used as anti-bacterial agent in this study. Table 1 demonstrates the specifications of the HPQM used.

Table 1 Specific information of anti-bacterial agent

Anti-bacterial agent	Active ingredient (HPQM) content	Physical properties	Thermal properties
HPQM-Solution	10.0 % (based Deionized water)	- Clear liquid, Odourless - Density = 1.05 g/cm^3 (25^{o}C)	Boiling point = 100^{o}C Melting point < 0^{o}C
HPQM-Neusilin	21.0-23.0 % (carried on Magnesium aluminometasilicate, Neusilin)	- White powder (Amorphous, degree of whiteness 95%) - Density ~ 0.21-0.23 g/cm^3 (25^{o}C)	Melting point > 1600^{o}C

Specimen preparation: The procedure was commenced by mixing PP with anti-bacterial agent using twin screw extruder (Haake Polylab-Rheomex CTW 100P, Germany). The mixing conditions used were mixing temperature of 200^{o}C and screw rotating speed of 40 rpm with three die strand having a diameter of 3 mm. The concentration for each type of anti-bacterial agent used was varied between 0 and 10,000 ppm by weight. The obtained PP compound was then transformed into sheet specimen having 1.0 mm thickness using a hydraulic press. The processing conditions in the hydraulic press was carried out by molding temperature, molding pressure and holding time of 200^{o}C, 100 kg·cm^{-2} and 5 min, respectively. After cooling down to room temperature by water coolant for 5 min, the molded sheet specimens were made into the standard testpieces by cutting the specimens as determined by the testing methods selected in this study.

Evaluations of antibacterial performance: To perform quantitative analysis for anti-bacterial properties of polymeric materials in this study, the halo test and dynamic shake flask method were used as anti-bacterial evaluating methods. The details for experimental procedures of the both methods used were described elsewhere [1-3]. The results from the halo test and dynamic shaking method were reported in terms of "Redius of inhibition zone (mm)" and "Reduction of bacteria (%)". *Escherichia coli* (ATCC 25922) was used as a testing bacteria.

Measurement of surface color changes: Measurement of discoloration of materials was carried out by LAB color space system. The total color difference ($\Delta E*$), lightness (L*), magenta/green (a*) and yellow/blue (b*) chromatic coordinate values were measured and calculated under a D65 light source using the UV-Vis spectrophotometer (model UV-3100; Shimadzu, Kyoto, Japan) [3].

Results and discussion

The results of anti-bacterial evaluations by halo test and dynamic shake flask method are demonstrated in Table 2 and Fig. 1, respectively. Generally, higher radius of inhibition zone, and greater percentage reduction of bacteria indicate better anti-bacterial performance. From the results by halo test, it was obviously seen that the PP with HPQM based-Neusilin samples exhibited much greater anti-bacterial performance than that with HPQM based-Solution samples, espeacially when higher dosage of anti-bacterial agents were used.

The results by dynamic shake flask method suggested that uses of both HPQM-Solution and –Neusilin could perform the bactericical behavior of PP material. To achieve 99.9% of bacteria reduction in the PP, 2,500 ppm of HPQM-Neusilin, or 7,500 pp, of HPQM-solution were recommended for the contact time of 3 or 4 h. In this aspect, it might be concluded that the anti-bacterial performance of the HPQM-Neusilin doped PP was approximately three times more effective than that of the HPQM-Solution under the experimental conditions used in this study. The main reason for this result may be due to that the Neusilin or Magnesium aluminometasilicate in amorphous stage is as a porous carrier and has relatively high porousity on the surface, and this would encourage HPQM to release with a controlable rate at the surface of the PP material and subsequently also enhanced the anti-bacterial efficacy in the PP.

Table 2 Inhibition zone radius for HPQM incorporated PP

Anti-bacterial agent	**Radius of inhibition zone (mm)**				
	Anti-bacterial agent content (ppm)				
	0	**2,500**	**5,000**	**7,500**	**10,000**
HPQM-Solution	0.0	0.5	0.5	0.5	1.3
HPQM-Neusilin	0.0	1.0	1.0	2.0	3.6

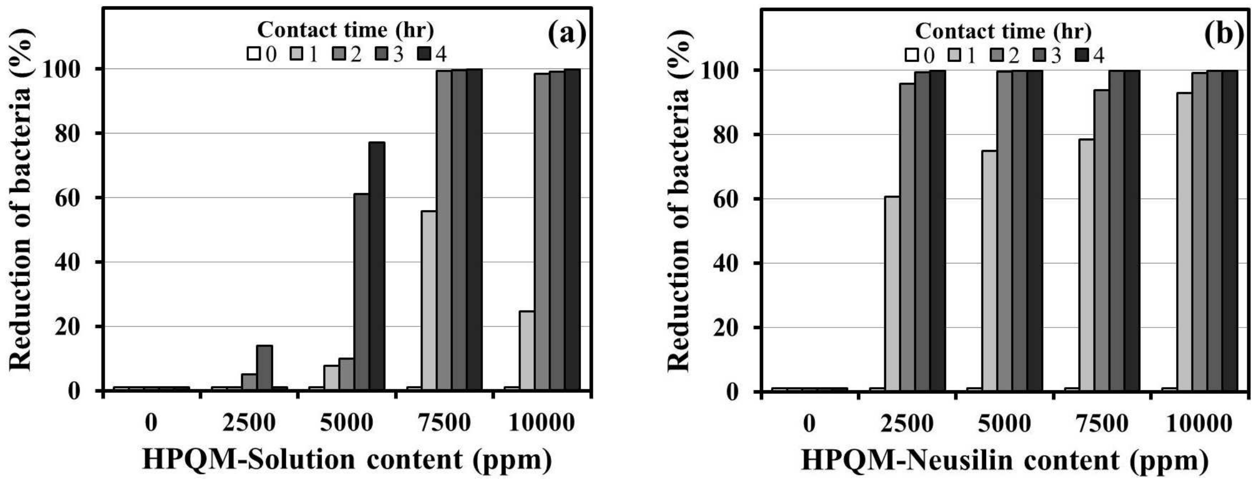

Figure 1 Percentage of bacteria reduction for HPQM incorporated PP:
(a) HPQM-Solution and (b) HPQM-Neusilin

The discolorations of PP surfaces comparing between HPQM-Solution and –Neusilin, via CIE-LAB color system, are demonstrated in Fig. 2. It can be observed that the addition of HPQM-Neusilin in PP matrix showed more significant changes in the total color difference (*ΔE**), the lightness (L*) and chromatic coordinate values (a* and b* values). The more lightness value when introducing the HPQM-Neusilin would be a result of a whiteness property of the Neusilin powder used (see Table 1). By considering the a* and b* chromatic coordinates, it was found that adding HPQM-Neusilin in the PP had a tendency to turn green, and blue.

Summary

HPQM-based water (HPQM-Solution) and HPQM-based Magnesium aluminometasilicate, Neusilin (HPQM-Neusilin) were used as anti-bacterial agent for PP material in this study. The PP doped with HPQM-Neusilin had much greater anti-bacterial efficacies than that with HPQM-Solution, this being confirmed by Halo and dynamic shake flask methods. To achieve 99.9% of bacteria reduction in the PP, 2,500 ppm of HPQM-Neusilin, or 7,500 pp, of HPQM-solution were recommended for the contact time of 3 or 4 h. Discolorations of PP samples markedly changed with HPQM-Neusilin addition. The results by chromatic coordinate values (a* and b* values) suggested that surface color of PP had tendency to turn green, and blue when adding with HPQM-Neusilin.

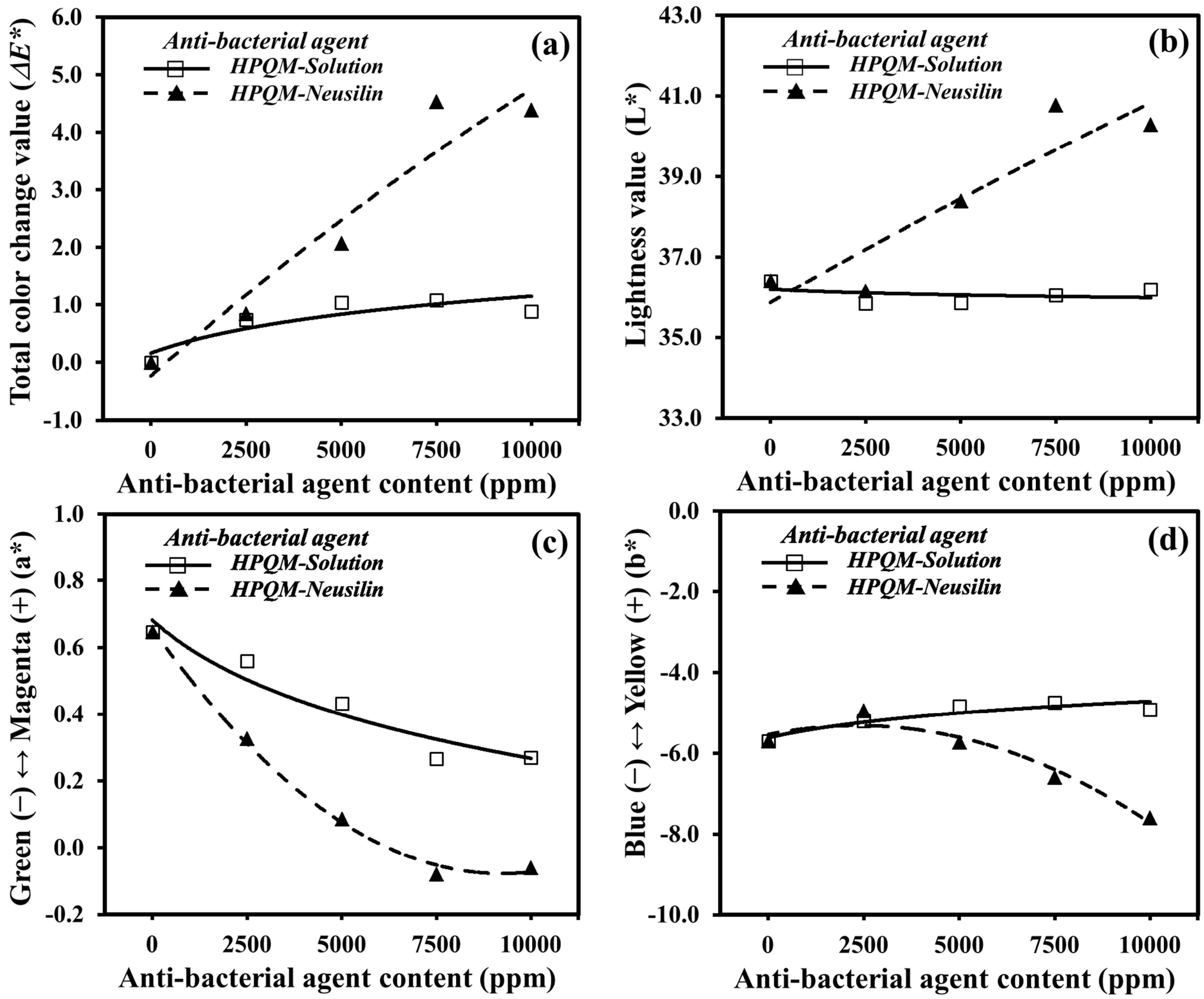

Figure 2 Color changes of PP samples added with HPQM:
where (a) ΔE^* value, (b) L* value, (c) a* value and (d) b* value

Acknowledgement

The authors thank for the Thailand Research Fund (RTA 5580009 and MRG555S053), and the Office of Higher Education Commission under the National Research University Program and Koventure Co., Ltd. for co-financial supports. Thanks are also to the College of Industrial Technology at KMUTNB for the laboratory facilities.

References

[1] P. Chammanee, K. Sombatsompop, A. Kositchaiyong, N. Sombatsompop, Effects of anti-bacterial agents, sample preparation and contact time on anti-bacterial efficacy in MDPE film, J. Macromol. Sci. Phys. 48 (2009) 755-765.

[2] K. Taptim, N. Sombatsompop, Effect of UV weathering on mechanical and anti-bacterial performances for peroxide-cured silicone rubber with HPQM, J. Vinyl. Addit. Techn. (2012) (accepted)

[3] R. Chimkamolkul, A. Kositchaiyong, N. Sombatsompop, Effects of thermal and UV aging on anti-bacterial, physical and mechanical performances for LDPE and PVC films incorporated with silver colloids, J. Plast. Film Sheet. (accepted)

[4] K. Hanušová, M. Šťastná, L. Votavová, K. Klaudisová, J. Dobiáš, M. Voldřich, M. Marek, Polymer films releasing nisin and/or natamycin from polyvinyldichloride lacquer coating: Nisin and natamycin migration, efficiency in cheese packaging, J. Food Eng. 99 (2010) 491-496.