Effect of Chemical Structure of Thermoplastics on Antibacterial Activity and Physical Diffusion of Triclosan Doped in Vinyl Thermoplastics and Their Composites with $CaCO_3$

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ABSTRACT: Triclosan was used as antibacterial agent in various vinyl thermoplastics and calcium carbonate ($CaCO_3$)/thermoplastic composites and the antibacterial performances were studied through Halo and Plate-Count-Agar (PCA) test methods. The thermoplastics used were polyethylene (LDPE, MDPE, HDPE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC). *Escherichia coli (E.coli*, ATCC 25922) and *Stapphylococcus aureus* (*S.aureus*, ATCC 25923) were used as the testing bacteria. The color index results suggested that introducing triclosan did not change the color of all thermoplastics used. The antibacterial results showed that the inhibition zone increased with increasing triclosan for nonpolar thermoplastics like LDPE, MDPE, HDPE, PP, and PS films whereas the opposite effect was observed for polar PVC film. The antibacterial efficacies of the triclosan decreased in the order of LDPE > MDPE > HDPE > PP > PS > PVC and this was confirmed by the triclosan releasing and FT-IR results. The differences in the antibacterial performances of the studied thermoplastics with triclosan were associated with their rigidities, abilities to crystallize, and free volume or molecular density. The sensitivities of *E.coli* and *S.aureus* bacteria to the triclosan were found to be dependent on the testing methods used for the antibacterial performance evaluations. The addition of $CaCO_3$ worsened the antibacterial performances in the triclosan filled HDPE and PS blends, but had a benefit for improved bacterial reduction in the triclosan-filled PVC blend. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 253–261, 2011

Key words: additives; thermoplastics; polymer composites; antimicrobials

INTRODUCTION

Because of the increasingly high demands for hygienic thermoplastic products, attention has been extensively placed on active thermoplasticic materials in food packaging applications, the medical professions, and household products. The thermoplastics used for such applications include polyolefin, poly(vinyl chloride), polyamide, and polyurethane and are usually incorporated with antimicrobial agents.[1,2] There are a number of antimicrobial agents available and used, including Carbendazim, 2-Hydroxypropyl-3-Piperazinyl-Quinoline carboxylic acid, Methacrylate, Silver and Silver substituted zeolite, Triclosan, Benzoic acid, Benzoic anhydride, Sorbic acid, Potassium sorbate, Nisin, Lysozyme, Glucose oxidase, Cinnamic Caffeic, nano-Titanium dioxide, *p*-Coumaic acid.[3–10] The efficacies of these antimicrobial agents are dependent on mixing method, contact time, carrier and thermoplastic types, standard testing methods.[5]

A number of scientific research evidences[8–14] have been made on antimicrobial efficacies of polymeric packaging products, mostly considering the effects of polymer matrix selection, type and loading of antibacterial agents, and processing conditions. Pei et al.[8] investigated the releasing of loaded-triclosan on the synthesized hollow TiO_2 nanocapsules using UV-vis absorption technique, and found that the releasing rate of triclosan was rapid in the initial stage then slow down. Zhang et al.[9] used plasma immersion ion implantation (PIII) to modify the surface of medical-grade PVC and then coated with triclosan and bronopol for the enhancing antibacterial properties via plate count agar technique. They

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found that the plasma technique produced more hydrophilic functional groups and subsequently, resulted in more effective coating of the triclosan and bronopol on the modified PVC surface. The results showed that the plasma-modified PVC with tricloan had more antibacterial efficiency against *E. coli* than that with bronopol. Similar results were found for polyethylene surface-modified by plasma immersion ion implantation.[11] Recent work by Asadinezhad et al.[12] developed a novel surface active antibacterial medical-grade PVC by coating Irgasan as antibacterial agent onto the PVC, which was surface-modified by a multistep physicochemical approach, to impart antimicrobial properties, that was assessed through the agar diffusion test method. They found an improved hydro-philicity on the sample surface and bacteriostatic characteristics of the Irgasan coated samples. Similar approach was used for other antimicrobial agents including bronopol, benzalkonium chloride, and chlorhexidine, which were also coated onto the functionalized PVC samples.[13] Park et al.[14] indicated that thermoplastics synthesized from vinyl monomer derivatives in different forms of phenol and benzoic acid exhibited different bacteria inhibition zones. The polymers with greater glass-transition temperatures tended to show lower antimicrobial performances. Chung et al.[15] suggested that the effect of triclosan in a styrene-acrylate cothermoplastic on diffusion performance using water, ethanol and *n*-hexane as diffusion media. It was found that the efficiency for killing bacteria was dependent on the diffusion ability in the media, and diffusion in the ethanol exhibited the highest antimicrobial efficiency. Camilloto et al.[16] developed antimicrobial extruded PE films containing triclosan at 2000 and 4000 mg kg^{-1} for sliced cooked ham. The PE films efficacies were studied against *Escherichia coli, Staphylococcus aureus, Listeria innocua, Salmonella choleraesuis*, and *Pseudomonas aeruginosa* growth using agar diffusion test. They found that the addition of triclosan did not affect the mechanical properties of the films. Films containing triclosan showed an antimicrobial effect for *E. coli* and *S. aureus* detected by formation of an inhibition halo, but this was not the case for *L. innocua, S. choleraesuis*, and *P. aeruginosa*.

The chemical structures of thermoplastics, which are usually used as packaging products, can be considered as one of the important factors to affect the antimicrobial performance of the thermoplastic products. This involves their polarities and hydrophilic properties,[9] molecular orientations,[7] abilities to crystallize, and the bulk density. Iconomopoulou et al.[7] studied the effect of molecular orientation of uniaxially drawn triclosan doped HDPE flims on controlled release of triclosan using UV-Vis absorption spectroscopy up to 15-month period. They found that the relevant release rate of triclosan from the drawn specimens was lower than the non-stretched samples due to the molecular orientation developed during the drawing process. Kalyon et al.[17] assessed the antibacterial efficacy of triclosan-incorporated PS disks against *Escherichia coli* and *Bacillus thuringiensis*. The results suggested that triclosan-filled PS inhibited the bacteria growth for some periods, after which bacteria growth resumed and the bulk of the triclosan in the polymer was not available for interaction with bacteria.

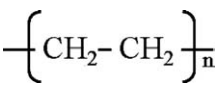
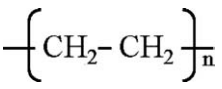
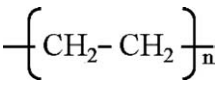
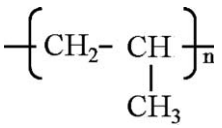
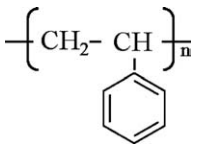
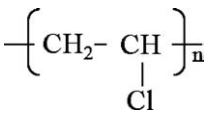
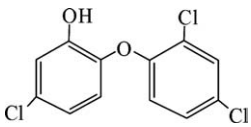
Available literatures have shown that the antibacterial performances of triclosan-incorporated thermoplastics have been studied extensively, but most of them have been carried out separately for individual thermoplastics with unfilled thermoplastic systems.[7–17] None of these studies have addressed relationship between triclosan and chemical structure of thermoplastics on the antibacterial activities. Besides, In practical point of view, fillers (reinforcing and extending fillers) are usually required for promoting the physical and mechanical properties, for stabilizing the chemical structures, and for reducing the product costs. But the information on the effect of filler addition on the antibacterial performance of triclosan-doped thermoplastic blend has not been conducted thoroughly. These missing information have, therefore, led to this present work on the effects of chemical or molecular structures of six thermoplastics on the antibacterial performance and physical diffusion mechanism of triclosan/thermoplastic blends with and without calcium carbonate ($CaCO_3$) filler. *Escherichia coli (E.coli*, ATCC 25922) and *Staphylococcus aureus* (*S.aureus*, ATCC 25923) were used as the testing bacteria.

EXPERIMENTAL

Materials and chemicals

Six thermoplastics used were a low-density polyethylene (LDPE, 1902F, SCG Public, Thailand), a medium-density polyethylene (MDPE, M380RU/RUP, Thai Polyethylene, Thailand), a high-density polyethylene (HDPE, HD6000F, PTT Thermoplastic Marketing, Thailand), a polypropylene (PP-401S, SCG Public, Thailand), a polystyrene (PS, Styron-656D267, Siam Polystyrene, Thailand) and a poly(vinyl chloride) (PVC, SIAMVIC 258RB, V.P.Wood, Thailand). Calcium carbonate ($CaCO_3$, Hicoat-410, Sand and Soil Industry, Thailand) was used as filler to make thermoplastic composites. Triclosan (2,4,4′-trichloro-2′-hydroxlydiphenylether, 24USP, Koventure, Bangkok, Thailand) was used as the antibacterial agent. The specifications, including suppliers, grades, physical and thermal properties and chemical structures, for all thermoplastics and additives used are given

TABLE I
Specifications and Physical and Thermal Properties for Thermoplastics, $CaCO_3$, and Triclosan (Bulk Density and Hardness Shore D at 25°C)

Materials	Grade	Supplier	Physical and thermal properties	Chemical structure
Low density polyethylene (LDPE)	1902F	SCG public Co., Ltd. (Thailand)	Density 0.919 g cm^3 Hardness = 48 $T_m = 110°C$ $T_g = -110°C$	
Medium density polyethylene (MDPE)	M380RU/RUP	Thai polyethylene Co., Ltd. (Thailand)	Density 0.940 g cm^3 Hardness = 52 $T_m = 126°C$ $T_g = -100°C$	
High density polyethylene (HDPE)	HD6000F	PTT polymer marketing Co., Ltd. (Thailand)	Density 0.956 g cm^3 Hardness = 55 $T_m = 131°C$ $T_g = -90°C$	
Polypropylene (PP)	401S	SCG public Co., Ltd. (Thailand)	Density 0.910 g·cm^3 Hardness = 62 $T_m = 163°C$ $T_g = -20°C$	
Polystyrene (PS)	Styron 656D267	Siam polystyrene Co., Ltd. (Thailand)	Density 1.05 g cm^3 Hardness = 83 $T_g = 95°C$	
Polyvinylchloride (PVC)	SIAMVIC 258RB	V.P. wood Co., Ltd. (Thailand)	Density 1.380 g cm^3 Hardness = 78 $T_g = 82°C$	
Calcium carbonate ($CaCO_3$)	Hicoat 410	Sand and Soil Industry Co., Ltd. (Thailand)	Average diameter of 1 micrometer	–
Triclosan (2,4,4′-trichloro-2′-hydroxlydiphenylether)	24 USP grade	Goventure Co., Ltd. (Thailand)	White powder from Average size of micrometer $T_m = 56–58°C$ $T_d > 280°C$	

in Table I, the experimental procedures for obtaining the physical and thermal properties being obtained elsewhere.[18] *Escherichia coli (E.coli*, ATCC 25922) and *Stapphylococcus aureus* (*S.aureus*, ATCC 25923), as gram negative and gram positive, respectively, were used as the testing bacteria.

Specimen preparation

All triclosan/thermoplastic blend and $CaCO_3$/thermoplastic composite specimens were molded in film test-piece form which was prepared by melt-blending triclosan with thermoplastics using an internal mixer (Haake Rheomix5000, Germany) to obtain a good dispersive blend, before made into the film form by using a compression molding technique. The processing temperatures for LDPE, MDPE, HDPE, PP, PS, and PVC in the compression mold were 160, 170, 180, 210, 150, and 170°C, respectively. The triclosan/thermoplastic blend was placed on a square mold at the desired mold temperature and then preheated for 10min under a pressure of 100 kg/cm^2 before cooled down to an ambient temperature (30°C) to obtain the resultant film of 0.2 mm thick. The films were made in a circular disc of 6 mm in diameter for the halo test, and in a square piece of 5 × 5 cm^2 for the plate count agar (PCA) method as will be detailed later. The triclosan concentration used was between 0 and 1.5×10^4ppm.

Antibacterial efficacy evaluations

Halo test

Inhibition zone was examined to qualitatively assess the antibacterial efficiency through the growth of bacteria by diffusion of antibacterial agent onto the agar media. In this work, the soft agar technique was introduced to prepare the testing media. The soft agar was performed by mixing nutrient agar and nutrient broth in the bottle at the ratio 50 : 50. After that, the agar

was calibrated at an initial concentration of 10^6 cfu/mL using a UV spectrometer. The prepared soft agar of 5 mL was poured on the solidified nutrient agar as substrate. The triclosan/thermoplastic blend test-pieces were carefully placed over the soft agar at the determined position. Finally, the plates were incubated at 37°C ± 0.5°C for 24 h. The results were reported in terms of "inhibition zone" as given by Eq. (1)[5] where D_C and D_S were diameters of inhibition zone and testing specimen, respectively.

$$\text{Inhibition zone} = \frac{D_C - D_S}{2} \quad (1)$$

Plate count agar method

Plate Count Agar (PCA) is appropriate for quantitative evaluation of bacteria-colony reduction in triclosan incorporated thermoplastic specimens.[5,9] The PCA test followed the ASTM E-2149 (2001) test method. The bacteria were inoculated overnight in 5 mL of nutrient borth (NB) at 37°C. The growing medium for the tested bacteria was peptone solution (prepared by 1 g/L peptone at pH of 6.8–7.2). The initial concentration of bacteria cell in 50 mL of peptone was 10^6 cfu/mL. The required bacteria suspensions were then added by the film specimens and then shaked by a reciprocal shaker at a speed of 100–120 rpm at 37°C ± 0.5°C for a desired contact time. Contact time, defined as the time that the triclosan incorporated thermoplastic specimens were shaken in the peptone solution which contained either *E.coli* or *S.aureus*, used was 60 min throughout this work. Then, a 10-fold serial dilution was conducted for bacteria colony counting. This was done by putting 100 μL of the bacteria solution over the agar in sterilized Petri dishes. Finally, the inoculated plates were kept at 37°C ± 0.5°C overnight before evaluating the antibacterial efficacy. The results were reported in terms of percentage reduction of bacteria-colony via Eq. (2).[9,11]

$$R = \frac{A - B}{A} \times 100 \quad (2)$$

where, R is the percentage reduction of bacteria (%), A is the average number of bacteria colonies from unfilled thermoplastic blend (CFU/mL), and B is the average number of bacteria colonies from triclosan filled thermoplastic blend (CFU/mL).

Materials characterizations

Triclosan releasing study

The releasing rate of triclosan form testing specimens was performed by measuring the UV absorbance of triclosan solution.[7,8] The specimens were put in the flask containing 50 mL of ethanol solution (95% v/v) and then the flask was shaked under the same conditions with shake flask method (37°C, 100 rpm for shaking speed and 1.0 h contact time). After the determined contact time, the ethanol solution was pipetted for 20 mL into cuvet to measure UV absorbance value using UV-Vis spectrophotometer (HACH DR/4000U) at the wavelength of 287–290 nm. The absorbance value was translated in triclosan concentration using a calibration curve (not shown here).

Color change test

The color changes of triclosan-filled thermoplastic were observed using UV-Vis spectrophotometer. The CIE-LAB color system, $L^*a^*b^*$ coordinates, were collected and calculated based on a D65 light source L^* represents the lightness whereas a^* and b^* are the chromatic coordinates. The higher the L^* value the lighter the sample. The a^* coordinate represents red-green coordinate while the b^* coordinate represents yellow-blue coordinate. The total color changes or discolorations of the triclosan/thermoplastic blend test-pieces were calculated from differences in lightness and chromatic coordinates (ΔE) were calculated based on a D65 light source. Eq. 3 was used to express the lightness and chromatic alterations of the test-piece specimens.[19]

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (3)$$

RESULTS AND DISCUSSION

Physical appearance of thermoplastic films added with triclosan

This section studied the physical appearances of the vinyl thermoplastic films without triclosan addition, and with 1.5×10^4 ppm triclosan (i.e., maximum dosage). This was achieved by assessing the changes in color and %light transmission, whose results are given in Table II. It can be seen that all the color indices (L^*, a^*, b^*, ΔE) and %light transmission (%T) for the thermoplastic films with and without triclosan were very similar, the differences being within the experimental errors (±2.0%). This suggested that the addition of triclosan had no significant effect on the physical appearances of the thermoplastic films, which appeared to be beneficial in practical point of view. The reason may be because the amount of the triclosan incorporated into the thermoplastics was relatively small (even up to 15,000 ppm triclosan). The unaffected mechanical properties of thermoplastics added with triclosan were also noted by Camilloto et al.[16]

TABLE II
Changes in Color and Light Transmission for Triclosan Incorporated Thermoplastics

	Thermoplastics with Triclosan ($\times 10^4$ ppm)											
	LDPE		MDPE		HDPE		PP		PS		PVC	
Color Index	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5
L^*	37.54	41.3	39.26	39.02	47.77	41.31	34.39	33.84	37.6	37.26	29.68	32.77
a^*	0.06	−0.12	0.14	−0.19	−0.3	−0.76	−0.07	−0.23	−0.09	−0.2	2.68	2.63
b^*	−2.85	−3.79	−2.99	−2.01	−7.01	−1.5	−1.63	−0.31	−1.13	−0.46	2.81	2.88
ΔE^*	–	3.88	–	1.06	–	8.50	–	1.44	–	0.76	–	3.09
$\%T$	88	83.2	86.3	85	78.3	82	89.4	90.1	89.3	88.1	70.9	72.5

Effect of triclosan content on inhibition zone

The halo test was used to qualitatively assess the antibacterial performance of triclosan-filled thermoplastics and the results are given in terms of inhibition zone. Figure 1 shows the effects of triclosan content on inhibition zone for all vinyl thermoplastic films for *E.coli* and *S.aureus* bacteria. The greater inhibition zone only indicated the ability of the triclosan to diffuse from the thermoplastic to react with and kill the bacteria. The results suggested that different thermoplastics had different effects on the inhibition zone. That was, LDPE, MDPE and HDPE and PP films showed relatively higher inhibition zone compared with PS and PVC films. Among the thermoplastics used, it was observed that at the lowest triclosan concentration (5000 ppm), the inhibition zone for PS was the smallest. Work by Kalyon et al.[17] suggested that the triclosan-filled PS could inhibit the bacteria growth (*E.coli* and *B.thuringiensis*) *only* for a short period of time because triclosan could not effectively diffuse through the PS to kill the bacteria.

In this work, three possible explanations for the differences in inhibition zones for all thermoplastics used were proposed, these including (i) rigidities of the thermoplastics, (ii) abilities to crystallize, (iii) free volume or molecular density. First, based on their glass transition temperatures and hardness results as given in Table I, the rigidities of the thermoplastics decreased in the order of PVC > PS > PP > HDPE > MDPE > LDPE. It was reasonable to state that it was more difficult for triclosan to diffuse through the thermoplastics with higher rigidities (like PS and PVC). Such claim could be substantiated by Park et al.[14] who suggested that, the polymers with greater glass-transition temperatures yielded lower antimicrobial activities. This was why relatively low inhibition zone was observed for more rigid thermoplastics like PS and PVC. Second, triclosan seemed to diffuse better in the crystalline thermoplastics (HDPE, MDPE, LDPE, and PP) compared to the amorphous thermoplastics (PS and PVC). It was thought that the triclosan could interact better with PS due to the benzene groups in PS and triclosan, and polarities of PVC and triclosan molecules. These interactions could probably cause difficulty for triclosan to diffuse away from the PS and PVC films to kill the bacteria, thus less inhibition zone being observed. Finally, the differences in inhibition zones among LDPE, MDPE,

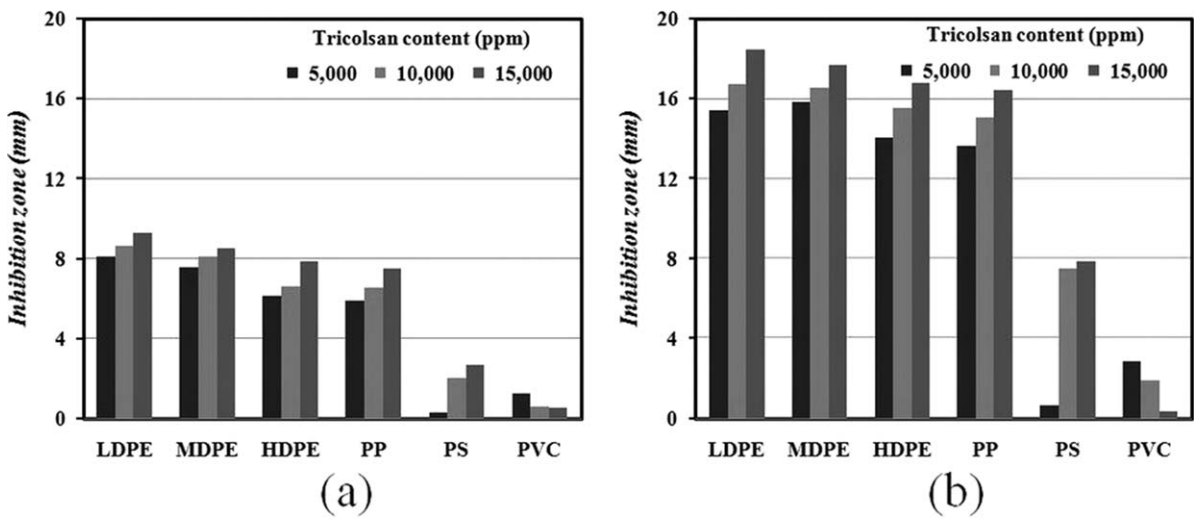


Figure 1 Inhibition zone results from Halo test for different thermoplastic film specimens for different loadings of triclosan (a) *E.coli* and (b) *S.aureus*.

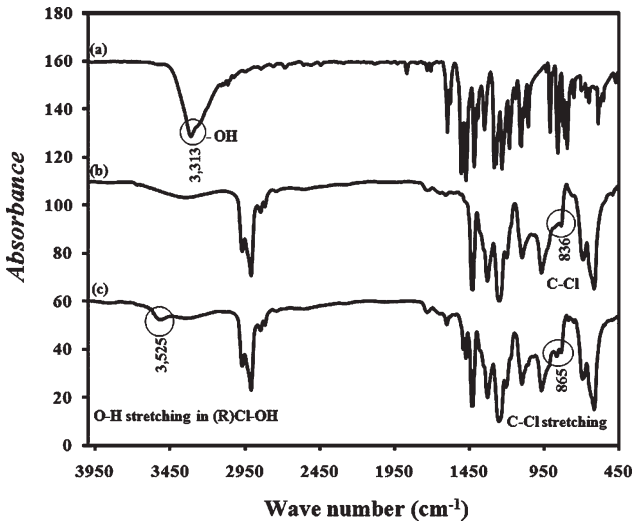


Figure 2 FT-IR spectra (a) Triclosan (b) PVC and (c) PVC containing 15,000 ppm triclosan.

HDPE, and PP were explained by differences in free volume or molecular orientations. That was, the greater the free volume the higher the triclosan to diffuse or release. This suggested why the LDPE had the greatest inhibition zone. This explanation could be linked and supported with the work by Iconomopoulou et al.[7] who investigated the effect of molecular orientation of uniaxially drawn triclosan doped HDPE films on controlled diffusion rate of triclosan. They found that the triclosan diffusion rate for the drawn specimens was lower than the nonstretched samples.

Considering the effect of triclosan content on the inhibition zone, one may expect that increasing triclosan loading would result in an increase in inhibition zone. This was not always true according to the results obtained in this work. The inhibition zone increased with increasing triclosan content for the nonpolar thermoplastics (LDPE, MDPE and HDPE, PP and PS) whereas the opposite effect was observed for the polar PVC. The decreases in inhibition zone as a result of increasing triclosan content in PVC could be explained through chemical and physical interactions between triclosan and PVC molecules as described here;

- Chemical interaction: This involved a polar-polar interaction between the PVC and triclosan molecules. An evidence to support such interaction was given using Fourier Transform Infrared (FT-IR) analysis [FTIR Spectrometer Spectrum One, Perkin–Elmer, with resolution of 4 cm^{-1} and scanning between 400 and 4000 cm^{-1}]. The FT-IR analysis was performed for pure triclosan, neat PVC, and triclosan/PVC blend and the results are given in Figure 2. The polar–polar interaction between triclosan and PVC could be evidenced by two shifted peaks, O—H stretching at 3525 cm^{-1} of R(Cl)—OH in triclosan/PVC blend, and C—Cl stretching at 865 cm^{-1} of PVC in the triclosan/PVC blend. However, the shifting of the peaks was not pronounced as one would expect, due to the small amount of the triclosan added into the PVC. This observation was similar to the work by Zhang et al.[9] who worked on the antibacterial properties of bronopol- and triclosan-coated PVC.

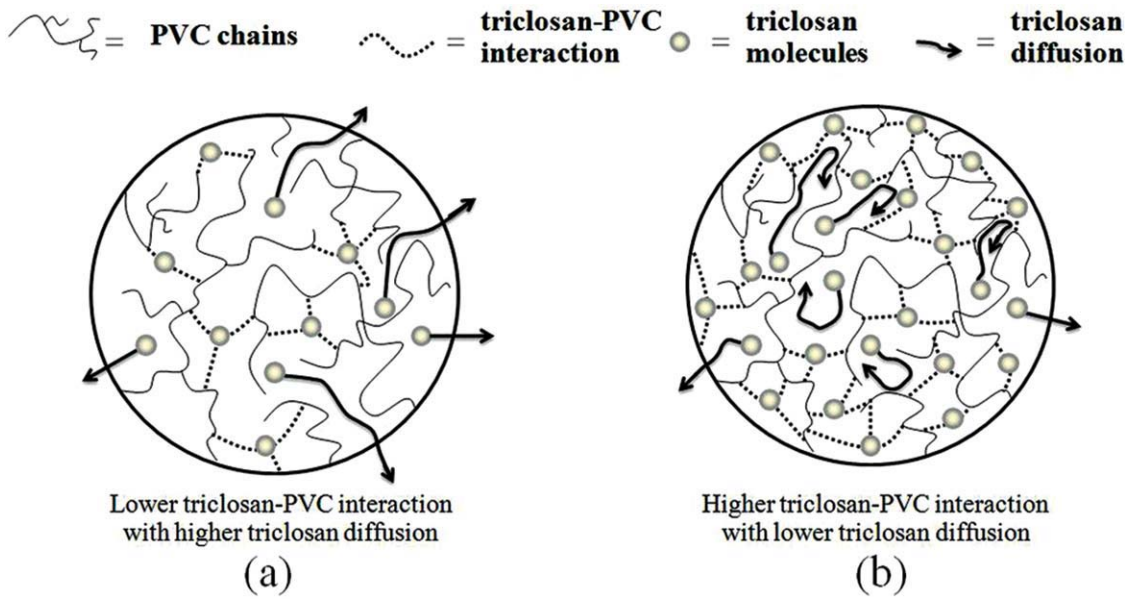


Figure 3 A proposed schematic model for diffusions mechanism of triclosan molecules in PVC (a) low triclosan concentration (b) high triclosan concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

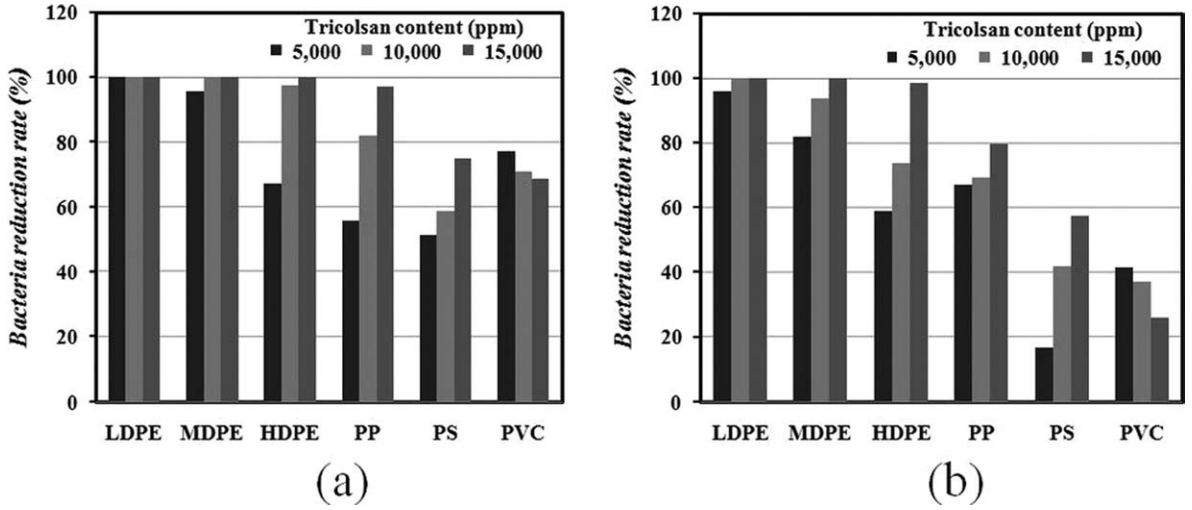


Figure 4 Percentage reduction rates for different thermoplastics at various triclosan contents by PCA method (a) *E.coli* and (b) *S.aureus*.

- Physical interaction: This can be referred to as diffusion of triclosan through the PVC matrix at different triclosan loadings. The results in Figure 1 suggested that the diffusion rate of triclosan was likely to differ with triclosan content. The explanation for this is schematically given in Figure 3, showing differences of triclosan diffusion-away within the triclosan/PVC blends with low and high triclosan contents. It was believed that the blend with high triclosan content was expected to have higher polar–polar interaction between PVC and triclosan molecules and this would probably retard further diffusions of triclosan to kill the bactetia at the sample surface. This was why the inhibition zone of PVC with higher triclosan content was lower than that with lower triclosan content.

The results in Figure 1 also indicate that the effects of triclosan loading and type of thermoplastics had a similar trend for both *E.coli* and *S.aureus* bacteria. But, for any given triclosan contents and types of thermoplastics, *S.aureus* appeared to be more sensitive to the triclosan loading than *E.coli*, considering the level of the inhibition zone.

Effect of triclosan content on percentage reduction of bacteria

Figure 4 shows the percentage reductions of *E.coli* and *S.aureus* for different vinyl thermoplastics for different triclosan loadings. It can be seen that the changing trends of the PCA results in Figure 4 for all thermoplastics corresponded well with those of the inhibition zone results in Figure 1. That was, the triclosan exhibited a most effective antibacterial agent for nonpolar polymers with high free volume structure (LDPE). The results and explanations for the triclosan diffusion in the different thermoplastics were substantiated by the triclosan releasing rate results as given in Table III. Higher triclosan releasing rate directly indicates higher triclosan diffusion and greater antibacterial efficacy. The results in Table III clearly suggest that relatively greater triclosan releasing rates were noted for nonpolar thermoplastics, the most pronounced effect being observed for the LDPE (32.6 to 100.2 $\times$ 10^{-5} g). However, a slight decrease of triclosan releasing rate with changing triclosan contents was observed for PVC matrix. It was worth mentioning that the magnitude changes in the results of inhibition zone in Figure 1, reduction rate of bacteria in Figure 4 and the triclosan releasing rate in Table III were different for all thermoplastics with various triclosan contents, although their changing trends of the results were similar. This may be expected since these three test-results were performed in different environments; i.e., the inhibition zone carried out in the soft agar, the %reduction rate performed in peptone solution, and the triclosan releasing result obtained via ethanol solution. Work by Chung et al.[15] found that the efficiency for killing bacteria was dependent on the diffusion ability in

TABLE III
Triclosan Releasing Rate Results for Thermoplastic Films with Different Triclosan Loadings after 1.0-h Contact Time in Ethanol Solution

Triclosan content (ppm)	Triclosan releasing rate ($\times 10^{-5}$ g)					
	LDPE	MDPE	HDPE	PP	PS	PVC
5,000	32.6	20.4	10.2	8.7	8.0	9.5
10,000	85.2	24.2	13.7	9.4	8.0	8.4
15,000	100.2	29.5	14.2	9.8	8.3	8.1

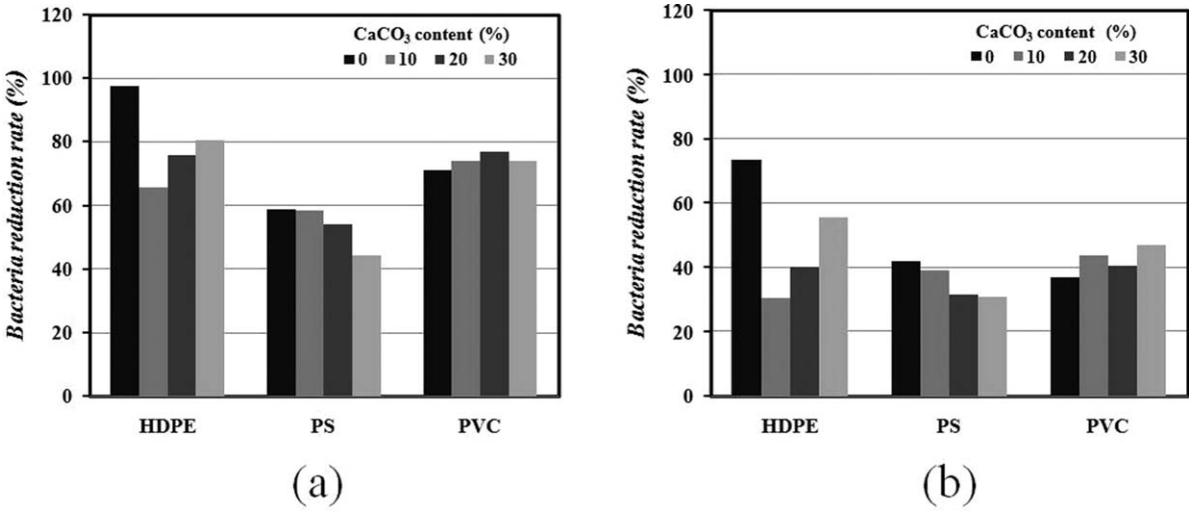


Figure 5 Effect of $CaCO_3$ content on percentage reduction rate for HDPE, PS, and PVC film specimens with 10,000 ppm triclosan content. (a) *E.coli* and (b) *S.aureus*.

the media. In the comparison of Figures 1 and 4 and Table III, it was found that even low triclosan releasing rates of MDPE, HDPE, and PP could result in high level of percentage reduction of the *E.coli* and *S.aureus* (up to 50–99% bacteria reduction).

Considering the triclosan sensitivities by *E.coli* and *S.aureus* bacteria in Halo test (Fig. 1) and PCA method (Fig. 4), it was surprising that the PCA method indicated higher triclosan sensitivity for the *E.coli* while the opposite effect was found for the Halo test. This difference was probably due to the fact that the *E.coli* in general have higher growth rate as compared to the *S.aureus*. Besides, in PCA method which was performed in peptone solution, the bacteria had made contacts very thoroughly with triclosan. The newly grown *E.coli* during the shaking in peptone was probably weak, and was easily killed by the triclosan as compared to the *S.aureus* which have lower growth rate. This was the reason of why the %reduction rate of the *E.coli* by triclosan was higher than that of the *S.aureus* in the PCA method. This finding was in good agreement with Zhang et al.[11]

Effect of $CaCO_3$ incorporation

In this section, three vinyl thermoplastics, namely HDPE, PS, and PVC, with 10,000 ppm triclosan content were selected based on their differences in abilities to crystalize and polarities, and the PCA method was used for antibacterial performance evaluations. Figure 5 shows the effect of $CaCO_3$ content on percentage reduction for *E.coli* and *S.aureus* for triclosan-HDPE, -PS, and -PVC blends. The %reduction rates of bacteria for triclosan-HDPE and -PS films appeared to reduce with $CaCO_3$ loading as compared with the films without $CaCO_3$. It was probably because the presence of $CaCO_3$ resulted in increases in rigidity and hardness of the thermoplastics,[20] and then this led to difficulty in the diffusion of the triclosan through the triclosan-HDPE and -PS films. It should be noted that the differences in the bacteria reduction rates as a function of $CaCO_3$ loading for each thermoplastic with triclosan were dependent on dispersion level of $CaCO_3$ which may be associated with $CaCO_3$-thermoplastic[20] and triclosan-$CaCO_3$ interactions, which is beyond the scope of this work, but to be explored for our future works.

In the case of the PVC film, the addition of $CaCO_3$ was found to improve the %bacteria reduction. This could be associated with an interfering effect of the polar–polar interaction between the PVC and the triclosan by presence of $CaCO_3$ filler. In connection with the proposed schematic model in Figure 3, if the polar–polar interaction of PVC and triclosan was interfered and reduced, the diffusion rate of triclosan through the PVC should probably be facilitated. As a consequence, the %bacteria reduction for the triclosan/PVC blend would be improved. The results were in a similar trend for both *E.coli* and *S.aureus* bacteria.

CONCLUSIONS

Triclosan was proposed to be suitable for nonpolar thermoplastics with high free volume structure. The effectiveness of the triclosan added in the vinyl thermoplastics decreased in the order of LDPE > MDPE > HDPE > PP > PS > PVC. The rigidities, abilities to crystallize, and free volume and molecular density were proposed to be responsible for the differences in the antibacterial performances among the thermoplastics used. The addition of triclosan did not change

the physical appearances of all the thermoplastics. The results showed that the antibacterial performance was improved with increasing triclosan content for nonpolar LDPE, MDPE, HDPE, PP, and PS films, but worsened for polar PVC. The addition of $CaCO_3$ slowed down the %reduction rates of *E.coli* and *S.aureus* in the triclosan-filled HDPE and PS blends, but enhanced the bacteria reduction rate for the triclosan filled PVC blend. Triclosan had similar effect on the inhibitions of *E.coli* and *S.aureus* bacteria for any given thermoplastics and thermoplastic composites with $CaCO_3$, but their sensitivities to the added triclosan were dependent on the test methods used.

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