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Polypropylene(PP) 멤브레인 소재를 위한 이중 기능성 폴리구아니딘 염 첨가제의 난연 및 향균 특성 연구

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Flame Retardant (FR) and Antimicrobial Properties of Bifunctional Polyguanidine Salt Additives for Polypropylene (PP) Membrane Materials

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Abstracts: Two polymeric additives, polyhexamethyl guanidine-diphenyl hypophosphite (DPPA-PHMG) and polyhexamethyl guanidine-chlorobridging acid (HA-PHMG), were prepared to overcome aqueous solubility of polyhexamethyl guanidine (PHMG) through salinization with two acidic flame retardant intermediates, diphenyl hypophosphite and chlorobridging acid. Melting points of two water-insoluble organic salts were 176.49 ℃ and 172.20 ℃ tested by TG, which were both higher than PHMG's and brought better thermostability for the starting polymer. Their polypropylene (PP) blend films achieved 99.9% bactericidal rate for Escherichia coli and their suitable content improved flame-retardant performance in combustion experiments. PHMG serves as a useful platform for development of multifunctional additives.

Keywords: di-functional additives, bacteria inhibitor, flame retardant, polyhexamethyl guanidine salt.

Introduction

As the emphasis on public health and safety requirements, the desire for bacteriostatic plastic and rubber became stronger in medical and public goods manufacturing owing to their inhibition to destruction of microorganisms and pathogens spreading.[1-3] That reduces infection and makes more healthy life.[4,5]

Many long-lasting antibacterial polymer additives had been reported, including inorganic nano-particles, reactive organic anti-bactericides, metal-organic skeletons, and cationic polymers.[6,7] Organic antimicrobial agents gradually became popular in industry field due to the advantages of facile process, enduring effect coming from good compatibility and environmental safety because of easy degradation in nature.[8] Among them, oligomers of quaternary ammonium and phosphonium were confirmed quite effective, they could be introduced to polymer surfaces or matrices through blend, grafting, coupling, and other reactions, to disrupt proteins of cell wall of prokaryotic organisms when contact with them.[9] Chen *et al.*[10] developed a series of water-insoluble hyperbicycle-based biocidic complexes using poly-L-lysine (HBPL) and phosphate surfactant based on non-covalent superbranched interactions. The complexes showed excellent bactericidal ability to *S. aureus* even as small as 0.5 wt% in poly(ε-caprolactone) film. Qiu *et al.*[11] coated cationized polyquaternary ammonium salt-containing skin through co-deposition of catechol and polyethyleneimine (PEI) on a surface of polypropylene (PP) microfiltration membranes, which obtained 95% inhibition to Gram-positive *S. aureus*.

Some ammonium cation-containing compounds not only possess antibacterial activity but also are effective flame retardants since some N-contained groups, such as guanidine salt and iminazole have the function of flame retardant.[12] Zhao *et al.*[13] separately impregnated boric acid and amidinourea phos-

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phate into insulating paper and they respectively achieved 18.9% and 30.97% carbon residue, which are significantly higher than 1.97% of the original sample. When 10%-20% boric acid in their mixture, double salt between boric acid and amidinourea phosphate formed and could achieve the best flame retardant effect. Wan *et al.*[14] grafted guanidinium tetramethylene phosphine acetate onto cotton fibers to fabricate a flame-retardant fiber, which gave a 45.5% LOI even after 50 washing cycles. Fang *et al.*[15] constructed a multifunctional coat through layer-by-layer phytic acid and chitosan assembly on cotton fabric and then sprayed divalent Cu^{2+} and polydimethylsiloxane (PDMS). The coating layer was hydrophobic, flame retardant and antibacterial with a water contact angle of 150°, 32% LOI and 99% bacteriostatic rate for *E. coil* and *S. aureus*. It illustrated that plenty of ammonium cations on surface would provide the polymer both antibacterial and flame-retardant capacity.

PP, as a widely used polymer material, exhibits many beneficial properties, such as low density, high thermal stability, chemical resistance, good processability and recyclability,[16] Tensile strength of commercial PP ranges from 27 to 40 MPa, which makes it a good building packaging material.[17] The melting point of PP is about 160 ℃ to 180 ℃,[18] depending on its crystallinity. However, side methyl groups bring low structural regularity and crystallinity.[19] In addition, PP can be widely applied in medical area due to biocompatibility and non-toxicity.[20] The fully aliphatic hydrocarbon skeleton makes it low decomposition speed and high flammability compared to cotton materials.[21,22] However, the introduction of flame retardants, such as montmorillonite and C_{60}, can greatly improve flame retardant performance through increasing limiting oxygen index (LOI) and ignition time.[23,24]

Polyhexamethylene guanidine hydrochloride (PHMG), is a kind of antimicrobial water-soluble oligomer with amino groups that can dissociate into ammonium cations.[25,26] This provides a potential to be developed into multi-functional polymeric additives. Here, two water-insoluble organic salts were prepared by salinization reaction of PHMG and organic acids as the additives for PP. The structure of salts were characterized and they were blended with PP to prepare masterbatches through melting granulation. The bactericidal and flame retardant properties of the 2 salts were evaluated after masterbatches were prepared into PP films through thermally induced phase separation method. It was confirmed that suitable addition could provide PP good flame retardancy and 3 wt% addition could achieve 99.99% inhibition to *E. coil* and *S. aureus*. In plate count method test.

Experimental

Materials and Instruments. Materials. PHMG was obtained from Hunan Xuelian Fine Chemical Co., Ltd. Chlorobridged acid (HA) and polypropylene (PP) were acquired from Tianjin Maidin Science and Technology Co., Ltd. Diphenylphosphinic acid (DPPA) was sourced from J&K Scientific. Beef paste, peptone, and agar powder were provided by Beijing Auboxing Biotechnology Co. Dioctyl phthalate (DOP) Source Tianjin Guangfu Science and Technology Development Co.

Instruments: Chemical structures of samples were analyzed by a Nicolet iS50 Fourier Transform Infrared Spectrometer (Thermo Fisher, USA) and a ^1H NMR was measured by 400M03 liquid NMR (Bruker, USA) using *d*-DMSO as a solvent. Thermophysical properties were analyzed by TG 209 thermogravimetric analyzer and DSC204F differential scanning calorimeter (NETZSCH, Germany). Functional masterbatch and melt samples were extruded and pelletized by a small single-screw extruder (SJ-15, Jiangsu Orode Machinery Co., Ltd.). Combustion properties of samples were evaluated by an oxygen index meter (JF-3, Jiangning Analytical Instrument Factory, China), a vertical combustion meter (CFZ-1, Jiangning Analytical Instrument Co., Ltd., China), and a conical calorimeter (PX-07-007, Suzhou Phoenix Quality Inspection Co., Ltd.).

Synthesis of Polyhexamethylene Guanidine Salts. DPPA aqueous solution (7.55 g in 25 g water) was dropped in PHMG (53 g) saturated aqueous solution and stirred for 4 h. The white precipitate was vacuum-filtered and washed with deionized water. The filtration cake was dried at 40 ℃ to give 5.88 g white powder, DPPA-PHMG with a yield of 53.50%.

Similarly, HA-PHMG salt was synthesized under the same procedure of DPPA-PHMG by 2.93 g HA with a yield of 57.73%.

Preparation of Functional PP Masterbatch. DPPA-PHMG 1.0 g, PP masterbatch 98.5 g and 0.5 g antioxidant 1010 were mixed and then pelletized by a single-screw extruder with a screw speed of 50 r/min, heating temperature of 200 ℃ and cooling temperature of 30 ℃. The feeding and rotating speeds were 11.4 r/min. The as-produced masterbatch was dried at 40 ℃ for 4 h. HA-PHMG/PP blend masterbatch was prepared under the same procedure.

Preparation of Functional PP Membrane. 2 g PP-DPPA-PHMG masterbatch and 8 g DOP were mixed and heated at 200 ℃ under N_2 to complete melt and stood for 1 h. The melt was poured onto a smooth iron plate and scraped into a thin film by a casting stick of 200 μm edge thickness. The film was then put into 25 ℃ DI water and carefully scraped off after cooling down, which was washed by and immersed in anhydrous ethanol for further use. PP-HA-PHMG membrane was prepared under the same procedure.

Anti-bacterial Assessment. The antimicrobial performance of PP composite film was evaluated using *E. coli* as a target by plate counting method in National standard of P.R. China (GB/T20944.1: 2007).[27]

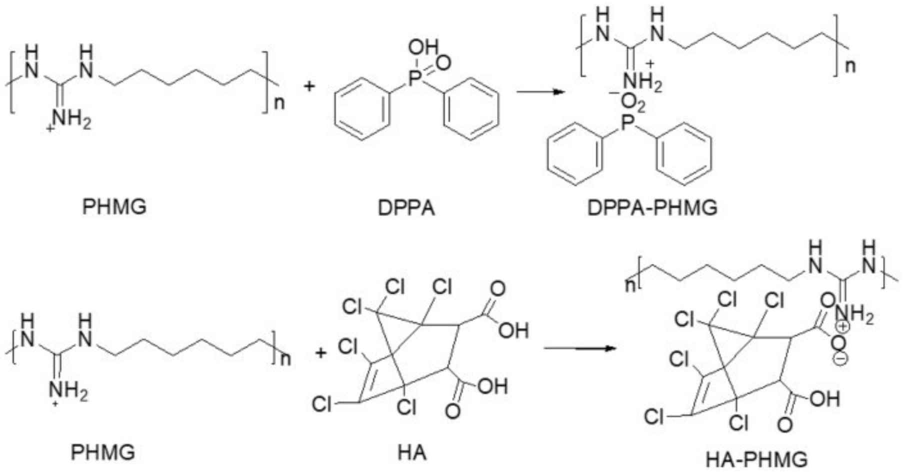
Flame Retardant Performance Test. The PP masterbatch is heated to 225 ℃ under nitrogen, stirred for 2 h and then allowed to stand at 225 ℃ for 1 h. The melt is then poured into silicone oil-coated molds and cooled to room temperature. Flame retardancy of strips is evaluated by vertical flame test of National standard of P.R. China (GB UL-94).

Results and Discussion

Synthesis and Structural Characterization of Additives. The salinization between PHMG and acids produced organic salts, DPPA-PHMG and HA-PHMG, which were both water-insoluble white powders (Scheme 1). The optimal ratio of PHMG to acid was 1:1 for two acids with the best yield of 57.73% and 53.5% for DPPA-PHMG and HA-PHMG, respectively.

FTIR and ^{1}H NMR characterized the chemical structures of DPPA-PHMG and HA-PHMG. In FTIR spectra (Figure 1(a)), the broad peak at 3259 cm^{-1} in PHMG curve was **-N-H** stretching vibration, which disappeared in curves of salts. The peak at 1620 cm^{-1} was stretching vibration of **-N**=**C-**, which was inconspicuous in both spectra of salts since **-**C=**N-H** in guanidine group took part in salinization and covered by acids sections. Absorption peaks at 1186 cm^{-1} in HA-PHMG and at 954 cm^{-1} in DPPA-PHMG spectrum were separately attributed to amide bond and hypophosphite groups, which illustrated the existence of HA and DPPA parts in new compounds. In ^{1}H NMR spectra (Figure 1(b)), PHMG possessed a doublet at 1.43 ppm of 8 C**H**$_2$ hexamethylene protons non-directly linking to N. The singlet at 3.09 ppm is 4 protons of C**H**$_2$ linking to guanidine group. The peak at 3.24 ppm in HA-PHMG curve was C**H**$_2$ protons in HA skeleton and the one at 11.4 ppm was carboxyl proton. In DPPA-PHMG curve, the singlet at 7.33 ppm is 4 N-linked C**H**$_2$ protons. The twin peaks at 7.33 ppm and 7.69 ppm are benzene ring proton peaks. Both FTIR and ^{1}H NMR confirmed the chemical structure of DPPA-PHMG and HA-PHMG. TG curves displayed that the onset and maximum decomposition temperatures of salts were both higher than those of PHMG (Figure 1(c)), which indicated their higher thermostability than PHMG. Although introduction of DPPA and HA destroyed intermolecular hydrogen bonds between PHMG chains, they increased molecular weight and enhanced new driving force of intermolecular interaction, involving π-π stacking and polar attraction, which led to higher thermostability. DSC curves (Figure 1(d)) showed that melting points of DPPA-PHMG and HA-PHMG were 176.49 ℃ and 172.20 ℃, which were higher than those of PHMG, 156.00 ℃. Since P, Cl and benzene cycle are all factors to increase decomposition temperature of materials, their introduction correspondingly increased melting points.

Preparation and Analyzation of Masterbatches. Table 1 listed recipes of DPPA-PHMG and HA-PHMG masterbatch and the best extrusion granulation parameters: screw speed 50 r/min, temperature of charging port 200 ℃, cooling temperature of feeding process 30 ℃ and rotational speed of pelletizing machine 11.4 r/min. When the additive content of HA was more than 5%, phase separation emerged and the master



Scheme 1. Synthesis of DPPA-PHMG and HA-PHMG.

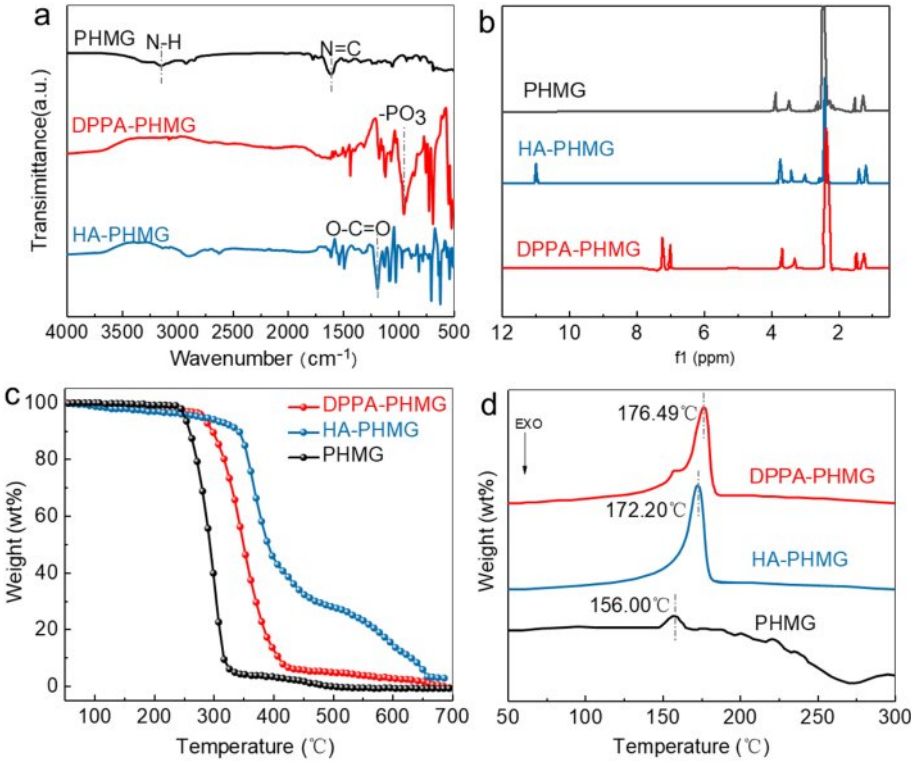


Figure 1. Characterization of smaples by: (a) FTIR; (b) ^{1}H NMR; (c) TG; (d) DSC spectra of PHMG, DPPA-PHMG, and HA-PHMG.

Table 1. Recipes of Masterbatch

Samples	PP (%)	DPPA-PHMG (%)	HA-PHMG (%)	Antioxidant 1010 (%)
1 wt%	98.5	1.0	1.0	0.5
3 wt%	96.5	3.0	3.0	0.5
5 wt%	94.5	5.0	5.0	0.5

match was unsuitable for later usage. Therefore, 1% and 3% were used to prepare films to evaluate antibacterial and flame retardant.

Figure 2 and Table 2 provided TG and DSC curves and data. The initial and maximum decomposition temperatures of PP-DPPA-PHMG and PP-HA-PHMG (289.8 ℃, 249.9 ℃ and

Table 2. Initial and Maximum Decomposition Temperature of Two Masterbatches

Masterbatch	T_{ind} (℃)	$T_{1/2}$ (℃)
PP	223.7	359.9
PP-HA-PHMG	249.9	369.6
PP-DPPA-PHMG	289.8	372.8

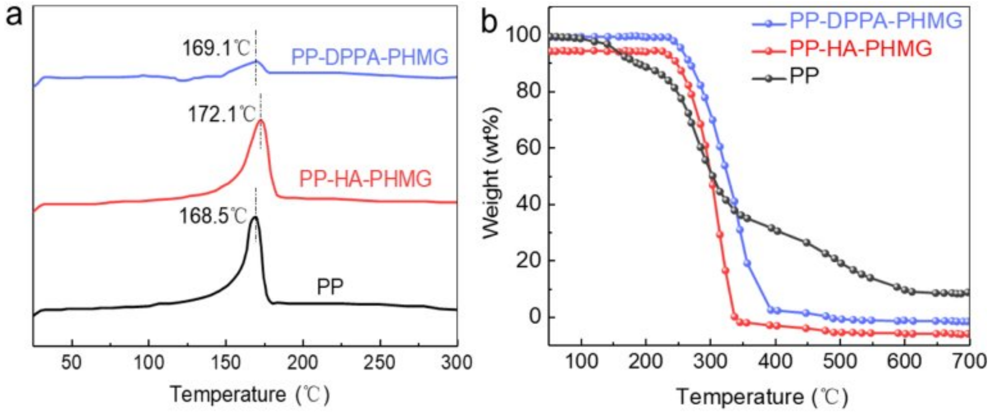


Figure 2. (a) DSC; (b) TG curves of PP, PP-HA-PHMG, and PP-DPPA-PHMG masterbatches.

372.8 ℃, 369.6 ℃), were both higher than those of PP (223.7 and 359.9 ℃), indicating enhanced thermostability. The melting point of PP and PHMG are 168.5 and 156.00 ℃, respectively. After mixed with additives, the melting points of modified PP increased to 169.1 and 172.1 ℃ for DPPA-PHMG and HA-PHMG. The introduction of acid segments increased both molecular weight and combination strength of intermolecular interaction among polymer chains. Consequently, this structural modification endowed the molecular chains with greater combining strength during heating process, thereby enhancing thermo-stability.

Antibacterial Performance of Membranes. Figure 3 was the digital photograph of petri dishes before and after 36h antimicrobial experiments. The pristine PP membrane did not exhibit any antimicrobial activity. Conversely, 0.02 g HA-PHMG or DPPA-PHMG provided 99.99% and 99.95% effective against *E. coli*. Both salts maintained antibacterial activity of PHMG, which confirmed that salinization reaction of -C=**N-H** in guanidine group with acids could not resist the dissociation of amine and imine groups into ammonium cations and did not affect antibacterial function of PHMG skeleton. Notably, HA-PHMG/PP membrane exhibits better bactericidal ability than DPPA-PHMG/PP, which was probably attributed to the multi-chlorine compound showing better antimicrobial activity.[28]

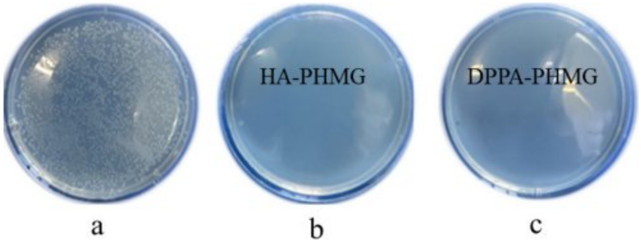


Figure 3. Digital photography of petri dishes after antimicrobial experiments of *E. coli* by: (a) PP; (b) HA-PHMG-PP; (c) DPPA-PHMG-PP membranes.

Flame Retardant Performance. Table 3 provided combustion properties of samples. When the salt content was 1%, the splines ignited quickly accompanying with molten droplets. 3% HA-PHMG provided better flame retardant performance than 3% DPPA-PHMG. Molten droplets disappeared and smoke release and carbon residue increased at the same time. However, the deterioration of combustion performance of 5 wt% HA was attributed to the uneven surface under higher concentration, which in turn impacted its flame retardancy.[29] The flame retardants would quickly form carbon layers in combustion process, which insulated heat transfer and O_2 and hence slowed down burning speed. In conclusion, 3 wt% HA-PHMG showed superior flame retardancy, while DPPA-PHMG showed better performance when more than 5 wt%.

Conclusions

Two composite functional additives, DPPA-PHMG and HA-PHMG were prepared and mixed with PP masterbatch, which were composed of both antibacterial and flame retardant parts. The antibacterial group, PHMG, endowed them excellent antimicrobial activity for solid polymers, such as PP, through the melting process. When combined with HA or DPPA, the salts obtained higher melting points and better thermal stability. They showed some flame retardant effect with 5% DPPA-PHMG and 3% HA-PHMG. Meanwhile, they decreased smoke emissions and increased carbon residue. It needs more work to improve flame retardant ability for the single additive, nevertheless, this work provided some ideas for developing multifunctional additives.

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Table 3. Combustion Characteristics of PP-HA-PHMG and PP-DPPA-PHMG

Additive		Time to ignition	Molten droplet	Quantity of smoke produced	Carbon residue
no		Swift	Yes	Major	None
HA-PHMG (wt%)	1	Fast	Yes	Large	Few
	3	Quick	No	Greater	Higher
	5	Fast	Yes	Large	Few
DPPA-PHMG (wt%)	1	Fast	Yes	Large	Few
	3	Fast	Yes	Large	Few
	5	Quick	No	Greater	Higher

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