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Color Stabilization of Low Toxic Antimicrobial Polypropylene/Poly(hexamethylene guanidine) Phosphate Blends by Taguchi Technique

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Abstract: The color stabilization of antimicrobial blends was studied by using poly(hexamethylene guanidine) phosphate (PHMG) as a highly efficient biocidal and nontoxic agent. The Taguchi method was used to determine the optimum conditions for the blending of PHMG in polypropylene (PP) matrix. To improve the yellowing phenomena, two kinds of stabilizer were used together: tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)](IN1010) from phenol and tris(2,4-di-t-butylphenylphosphite) (IF168) from phosphorus. According to blend composition and mixing condition, six factors were chosen, with five levels being set for each factor. The orthogonal array was selected as the most suitable for fabricating the experimental design, L25, with 6 columns and 25 variations. The-smaller-the-better was used as an optimization criterion. The optimum conditions for these parameters were 10 phr for PHMG, 2 phr for IN1010, 1 phr for IF168, 10 min for mixing time, 210 °C for mixing temperature, and 30 rpm for rotation speed. Under these conditions, the yellowness index of the blend was 1.52. The processibility of the blends was investigated by Advanced Rheometric Expansion System (ARES). The blend with 0.5 w% PHMG content, diluted with PP, exhibited an antimicrobial characteristic in the shake flask method.

Keywords: poly(hexamethylene guanidine) phosphate, PHMG, antimicrobial blend, yellowness index, Taguchi method.

Introduction

Generally, antimicrobial agents are referred to functional substances that are able to prevent a human being or other objects from infection by microorganisms (e.g., bacteria, fungi, and pathogens). Their ability against the microorganisms is applied to fiber, wood, paper, glass, resins, and metals. For example, the antimicrobial agents for fibers include organic blends such as quaternary ammonium salts[1] and polyhexamethylene biguanidine salts[2] and are required to exhibit a safety for the human being, stability, and wash fastness for fibers, as well as excellent antimicrobial activity.

One of promising antiseptic cationic surfactants is PHMG salt that includes guanidine group giving biocidal properties in the backbone of the molecule shown in Scheme I. Its strong bactericidal activity with low toxicity can be used in textile for suppressing growing microorganisms,[3] in medicine for disinfection of medical fiber or film materials,[4,5] in operating and injection fields, in agriculture in storage of vegetables, in lumber industry as fungicides and preservatives, in wastewater treatment, in protection of metals from corrosion, biological overgrowing, and salt deposition,[6] etc.

However, in spite of excellent antimicrobial properties of PHMG, its thermal properties are very poor, which make high temperature processing difficult. For antimicrobial polymer blend and its various applications, understanding thermal behavior of PHMG is very useful. Thermogravimetric analysis (TGA) has been used widely as a effective tool for it.[7-10] Surprisingly, however, there were only a few publications on PHMG though it has attracted considerable attention as highly efficient biocidal and nontoxic agents. Recently, only the thermal degradation kinetics of PHMG was investigated by dynamic TGA and pyrolysis-GC/MS.[11] Although kinetic data obtained from TGA are very useful for understanding the thermal degradation processes and mechanism of PHMG, it doesn't explain effectively the thermal degradation without weight loss such as graying or yellowing. During a melt blending of PHMG with polyolefin resin for antimicrobial blend, yellowish product was found even a short residence time. It was believed due to the degradation of PHMG not to that of polyolefin. Commercially, minimization of yellowing phenomena has very important meaning and to solve that problem optimum condition should be found. However, there are so many process parameters that

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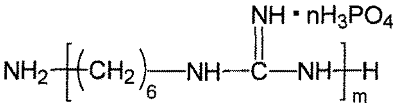
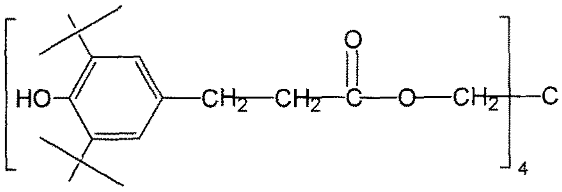
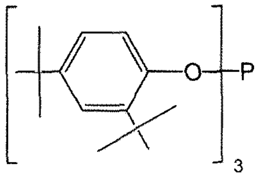
Scheme I.



Poly(hexamethylenguanidine) phosphate



Tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]



Tris(2,4-di-t-butylphenylphosphite)

can affect the yellowness of final product and a great number of experiments are required to figure out the optimum condition.

As an optimization technique, design of experiment (DOE) is a technique of defining and investigating all possible conditions in an experiment involving multiple factors. By using "partial" information obtained from the selected experiments, we can predict an entire picture. Analyzing the experiment results is based on analysis of variance (ANOVA), whose fundamental concept is to determine an "average-value" from all the responses, and their variations. The contribution of each factor and the interaction between various factors of an experiment can be quantitatively evaluated and the best condition set which gives the best response can be determined by using ANOVA.[12]

In recent years, the Taguchi method, also called the robust design method, has greatly improved engineering productivities. By consciously considering the noise factors and the cost of failure in the field, it helps ensure customer satisfaction. The complex systems with many variables could have been investigated by the Taguchi method, explained successfully, and optimized at the best conditions.[13,14]

In this study, PHMG and stabilizers were added in PP by taking into consideration the experimental parameters on the composition and on the processing condition (time, temperature, and speed of mixing), and Taguchi experimental design method was employed to determine optimum blending conditions.

Experimental

Materials. Poly(hexamethyleneguanidine) phosphate (SKYBIO 1100) (PHMG) in the form of powder was supplied by SK Chemicals Co., Korea. As a matrix polymer, polypropylene (F501, Hyosung Co.)(PP) was chosen. Two kinds of stabilizer, tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane (Irganox 1010, Ciba-Geigy Co.) and tris(2,4-di-t-butylphenylphosphite) (Irgafos 168, Ciba-Geigy Co.) were tested. The chemical structures of chemicals used and their characteristics are shown in Scheme I and listed in Table I. respectively.

Blend Preparation. PP and PHMG were dried in vacuum oven at 50 °C for at least 12 h before use. Dried pellets of PP and powers of PHMG were mixed in a container and blended in a melt mixer (Haake Reocord 9000) at a fixed temperature and rotation speed. The contents of PHMG, IN1010, and IF168 in blends system were 0~20, 0~3, and 0~3 phr, respectively. The processing conditions were 10~40 min of mixing time, 190~230 °C of mixing temperature, and 30~ 120 rpm of rotation speed, respectively. Specimens of blended samples were obtained by compression after mixing.

Color Measurement. The yellowness index (ASTM 1925) as a measure of color formation was evaluated by spectro-

Table I. Characteristics of the Materials

Material	Properties	
PP	MI=3 g/10 min	ρ=0.9 g/cm^3
PHMG	M_w=3,000	PDI=3.0, T_g=101 °C
IN1010	T_m=110.0~125.0 °C	$C_{73}H_{108}O_{12}$=1,177.63
IF168	T_m=183.0~187.0 °C	$C_{42}H_{63}O_3P$=646.92

Table II. Factors and Levels of the Experiments

Level	Composition			Processing Condition		
	PHMG (phr)	IN1010 (phr)	IF168 (phr)	Time (min)	Temp. (°C)	Speed (rpm)
1	0	0.0	0.0	10	190	30
2	2	0.5	0.5	15	200	50
3	5	1.0	1.0	20	210	70
4	10	2.0	2.0	30	220	90
5	20	3.0	3.0	40	230	120

Table III. $L_{25}5^6$ Orthogonal Array Diagram

Trial	Column					
	A	B	C	D	E	F
1	1	1	1	1	1	1
2	1	2	2	2	2	2
3	1	3	3	3	3	3
4	1	4	4	4	4	4
5	1	5	5	5	5	5
6	2	1	2	3	4	5
7	2	2	3	4	5	1
8	2	3	4	5	1	2
9	2	4	5	1	2	3
10	2	5	1	2	3	4
11	3	1	3	5	2	4
12	3	2	4	1	3	5
13	3	3	5	2	4	1
14	3	4	1	3	5	2
15	3	5	2	4	1	3
16	4	1	4	2	5	3
17	4	2	5	3	1	4
18	4	3	1	4	2	5
19	4	4	2	5	3	1
20	4	5	3	1	4	2
21	5	1	5	4	3	2
22	5	2	1	5	4	3
23	5	3	2	1	5	4
24	5	4	3	2	1	5
25	5	5	4	3	2	1

Table IV. Test Schedule

Batch Number	Composition			Processing Condition			Yellowness Index
	PHMG (phr)	IN1010 (phr)	IF168 (phr)	Time (min)	Temp. (°C)	Speed (rpm)	
1	0	0.0	0.0	10	190	30	0.74
2	2	0.5	0.5	10	200	50	10.69
3	5	1.0	1.0	10	210	70	8.69
4	10	2.0	2.0	10	220	90	12.88
5	20	3.0	3.0	10	230	120	19.99
6	5	2.0	3.0	15	190	50	8.54
7	10	3.0	0.0	15	200	70	11.62
8	20	0.0	0.5	15	210	90	10.03
9	0	0.5	1.0	15	220	120	2.88
10	2	1.0	2.0	15	230	30	7.87
11	20	0.5	2.0	20	190	70	5.67
12	0	1.0	3.0	20	200	90	0.38
13	2	2.0	0.0	20	210	120	9.23
14	5	3.0	0.5	20	220	30	12.56
15	10	0.0	1.0	20	230	50	19.23
16	2	3.0	1.0	30	190	90	25.87
17	5	0.0	2.0	30	200	120	29.52
18	10	0.5	3.0	30	210	30	14.36
19	20	1.0	0.0	30	220	50	27.21
20	0	2.0	0.5	30	230	70	5.89
21	10	1.0	0.5	40	190	120	6.18
22	20	2.0	1.0	40	200	30	13.09
23	0	3.0	2.0	40	210	50	2.63
24	2	0.0	3.0	40	220	70	10.39
25	5	0.5	0.0	40	230	90	28.74

photometer (CM-3500D, Minolta).

Experimental Design. To find optimum conditions a list of six factors, thought to be most important, was chosen, all of which were composition and processing condition. The four levels for each factor were set using information from material supplier and knowledge from personal experience. The factors and their levels were listed in Table II. The orthogonal array was chosen as the most suitable to make up the experimental design, L25, with 6 columns and 25 variations given in Table III. From the L25 array and the factor list, the test schedule was drawn up in Table IV. Performance characteristics chosen as the optimization criteria were divided by three categories, the larger-the-better, the nominal-the-best, and the smaller-the-better. Among these, the smaller-the-better was calculated by using eq. (1).[15]

$$SN = -10 \log \left[\frac{1}{n} \sum_{i=1}^{n} y_i^2 \right] \qquad (1)$$

Rheological Behaviour. Rheological properties of the blends and pure resins were measured using a ARES (ARES, TA Instrument) on which a 25 mm diameter parallel plate was mounted. The frequency range was set at 0.1~500 rad/sec and the applied strain was 10%. The plate gap was set at 1.2 mm.

Antimicrobial Properties. The blend composition prepared by optimum condition was diluted with PP to 0.5 w% PHMG content, the content of antimicrobial agent commercially adopted, in the blend through melt-mixing. To confirm the antimicrobial characteristic of the blend, shake flask method[16] was conducted. The activated sludge, used in this study, from an industrial wastewater treatment plant was aerated for 24 h before use.

Results and Discussion

The collected data were analyzed by using the MINITAB computer software. An analysis of variance was performed to see effective factors and their confidence levels on the yellowing phenomena. A statistical ANOVA was performed to determine whether process variables was statistically significant. With the performance characteristics and ANOVA analysis the optimal combination of blend compositions and mixing conditions can be predicted.

To obtain optimal blending composition and condition, the smaller-the-better performance characteristic, eq. (1) has been taken for yellowness index of the blend. The optimal level of a process variable is the level with the highest S/N ratio value calculated by eq. (1). The mean and the S/N ratio of factors with levels were summarized in Table V and plotted in Figure 1 and Figure 2, respectively.

Figure 1(d) shows the variation of performance characteristics with mixing time. To determine the experimental conditions for the first datum point, the mixing time of 15 min (level 2) was chosen. The experiments for mixing time is 15 min were batches 6,7,8,9, and 10. The first datum point in Figure 1(d) is the arithmetical average of the performance characteristics for these experiments. All the points in Figure 1(d) and other graphs were established by the same way. In each graph, the numerical value of a maximum point corresponds to the best value for that factor. These values are seen to be PHMG 0 phr, IN1010 2 phr, IF168 0.5 phr, mixing temperature 210 °C, and mixing speed 70 rpm.

Figure 2 shows the main effect of each factor on S/N ratio. The points in these plots were obtained in the same way as those in Figure 1, but instead of averages of the performance characteristics, the averages of the corresponding experimental data were taken. When Figures 1 and 2 are compared, it was seen that although they were similar for other factors, optimum conditions for the time, temperature,

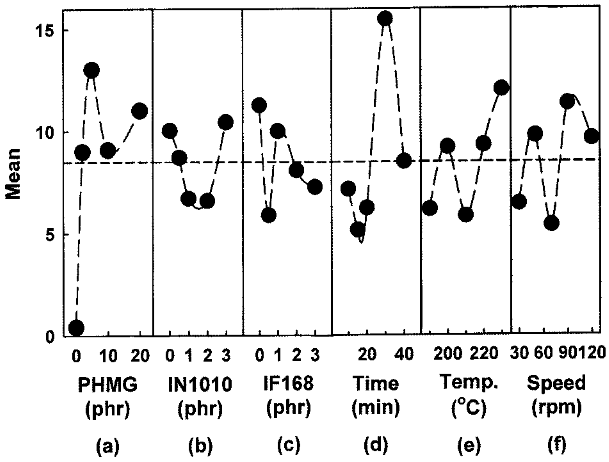


Figure 1. The effect of each factor on mean.

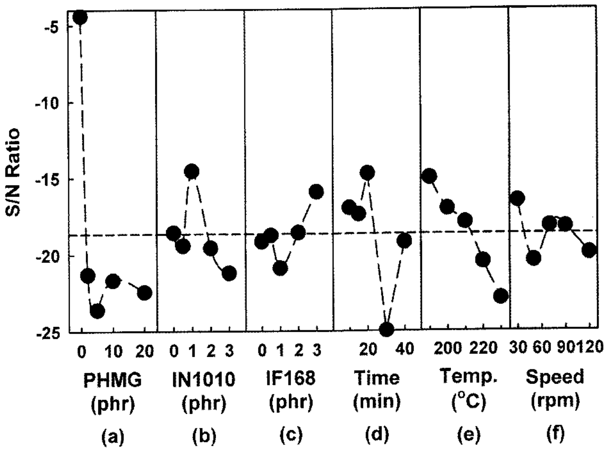


Figure 2. The effect of each factor on S/N ratio.

Table V. Mean and S/N Ratio of the Factors

		Composition			Processing Condition		
	Level	PHMG	IN1010	IF168	Time	Temp.	Speed
Mean	1	0.42	10.04	11.26	7.17	6.17	6.44
	2	9.01	8.72	5.89	5.16	9.22	9.77
	3	13.01	6.72	10.01	6.23	5.82	5.38
	4	9.10	6.61	8.10	15.48	9.32	11.32
	5	11.00	10.45	7.28	8.51	12.00	9.63
S/N	1	-4.4	-18.6	-19.2	-17.0	-15.0	-16.6
	2	-21.3	-19.4	-18.8	-17.4	-17.0	-20.4
	3	-23.6	-14.6	-20.9	-14.8	-17.9	-18.2
	4	-21.7	-19.6	-18.6	-25.0	-20.5	-18.3
	5	-22.4	-21.2	-15.9	-19.2	-22.9	-19.9

Table VI. Order of Influence of the Factors

Factor	Difference	V	Order
PHMG (phr)	19.20	322.36	1
IN1010 (phr)	6.63	30.79	4
IF168 (ph)	4.93	15.71	5
Time (min)	10.23	74.80	2
Temp. (°C)	7.83	46.61	3
Speed (rpm)	3.87	12.00	6

and speed were different. Optimum condition for mixing time was level 2 (15 min) in Figure 1(d), but level 3 (20 min) in Figure 2(d), mixing temperature level 3 (210 °C) in Figure 1(e), but level 1 (190 °C) in Figure 2(e), and speed level 3 (70 rpm) in Figure 1(f), but level 1 (30 rpm) in Figure 2(f).

The order of influence of the factors on the yellowness index was found by DOE and was shown in Table VI. Naturally, the amount of PHMG had the most influence on the yellowness index. The mixing time and the mixing temperature were next important factors and the mixing time had the least effect.

The optimum composition and the mixing condition having the lowest yellowness index could be estimated from the order between factor and degree of optimum level degree. As a matter of fact, if PHMG were not in blend, the color of the blend would not change and the more stabilizer was incorporated in blend, the better result we could get. Even though, however, the blend showed the lowest yellowness index, they would not correspond to the intention of this study. Therefore the amounts of PHMG and IN1010 were fixed as 10 and 2 phr, respectively and for other factors their optimum levels were chosen. In design of experiment, comparison of a confirmation experiment with an estimated result is important. A confirmation experiment was performed (Table VII) where optimum composition and mixing conditions were used. When IF168, mixing time, mixing temperature, and rotor speed were 0.5 phr, 15 min, 210 °C, and 70 rpm, respectively, the estimated value of yellowness index was 1.80 and the experimental value was 2.03 as shown. This difference might be somewhat attributed to interaction effects. To find the most optimum condition, as the second trial, additional experiments whose orthogonal array was L16 were conducted with fixed levels of PHMG and IN1010. Because of small number of experiments the general full factorial design of experiments was chosen and to prevent influence of differential elements from final results, the experiments were carried out randomly. The optimum results were showed in Table VII and the most optimum value was 1.52 in case 2 which was much lower than 2.03 in case 1.

Table VII. Optimum Composition and Processing Conditions

Factor	Case 1	Case 2
PHMG (ph)	10	10
IN1010 (phr)	2	2
IF168 (phr)	0.5	1
Time (min)	15	10
Temp. (°C)	210	210
Speed (rpm)	70	30
Yellowness Index (predicted)	2.03(1.80)	1.52

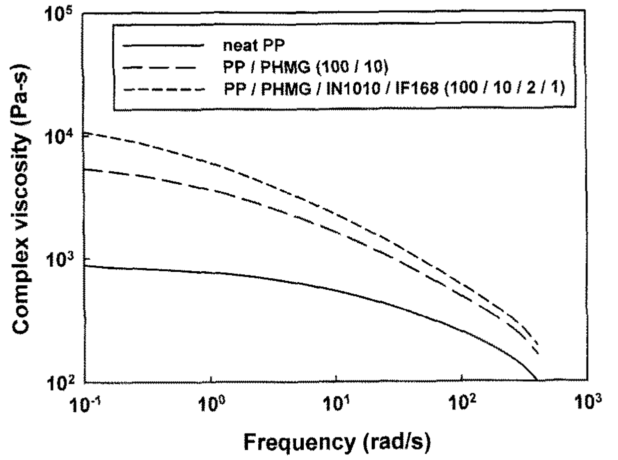


Figure 3. Effect of additives on the complex viscosity of the blends.

The processibility of the blends was investigated by ARES and the results were shown as a plot of complex viscosity versus frequency in Figure 3. Like a typical thermoplastic, the complex viscosities of the two kinds of blends as well as neat PP decreased as frequency increased. At a frequency of 0.1 rad/sec, the viscosities of blends were about-ten times larger than neat PP and it was more remarkable when antioxidants were incorporated. However, the large difference of complex viscosities between the blends and the neat resin decreased as the frequency increased and at a frequency of 500 rad/sec, the complex viscosities of blends were at most two times larger than neat PP. The frequency of 500 rad/sec corresponds to the range of general commercial processing condition, 100~2,000 s^{-1} and therefore these kinds of antimicrobial master batch blends could be easily prepared by a typical compounding machine and applied for further processing.

For final consumer use, master batch type blend was diluted with PP to 0.5 w% PHMG content, and its antimicrobial property was tested by shake flask method. The test results were shown in Figure 4. Lots of microorganisms were observed in a control sample (left) whereas any microorganism was not seen in the sample from diluted blend (right). This means that the diluted blend could be used as an antimicrobial material for final consumer product.

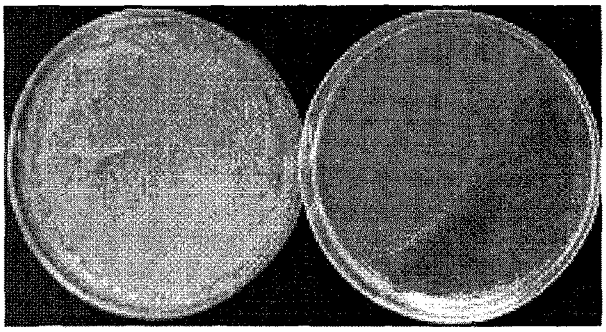


Figure 4. Antimicrobial test result by Shake Flask method.

From a manufacture's point of view, if the mixing temperature is standardized, the mixing time and the speed of screw have the potential to alter the yellowness index between testers. Sometimes, an unexplained bias in the test results exists between the raw material supplier and the processors, which makes the decision on raw materials more difficult. In this study, even though processing conditions are not always standardized between manufacturers, through this master batch type blend manufacturers could produce more easily final consumer goods with excellent antimicrobial properties and less yellowness index.

Conclusions

To lower yellowness index of PP/PHMG blends two kinds of stabilizer, IN1010 and IF168, were chosen and Taguchi method was used. Six factors for blend composition and mixing condition and five levels for each factor were chosen. As an experimental design, L25 with 6 columns orthogonal array was adopted and as an optimization criterion, the smaller-the-better was used. The first optimum factor levels were determined and an estimated result was compared with an experimental one for confirmation. The estimated value of yellowness index was 1.80 and the experimental one was 2.03. This difference might be somewhat attributed to interaction effects. The most optimum conditions for master batch type blend with fixed PHMG and IN1010 levels, were 10 phr for PHMG, 2 phr for IN1010, 1 phr for IF168, 10 min for mixing time, 210 °C for mixing temperature, and 30 rpm for rotation speed, respectively. Under these conditions, the yellowness index of the blend was 1.52, which was 0.51 lower than the first optimum value. For final consumer product, master batch type blend was diluted with PP to 0.5 w% PHMG content, and which was shown to have antimicrobial characteristic by shake flask method. This master batch type blend would help processors like injection molders and extruders to manufacture more easily final consumer goods with excellent antimicrobial properties and less yellowness index.

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