

STUDIES ON FLAME-RETARDANT PC/ABS MULTIPLE-ELEMENT ALLOY

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Abstract The preparation technology of flame-retardant PC/ABS alloys was studied in this paper. Using a high-efficiency flame retardant system and by means of multiple-ingredient compatibilizing, PC/ABS alloys with excellent impact strength and flame retardant property were prepared. The experimental results showed that by using PS-g-MAH and SMA as synergistic compatibilizers, the notched Izod impact strength and flammability of PC/ABS alloy obtained in the present work can be up to 175 J/m and UL-94 V0, respectively.

Keywords Polycarbonate, ABS, Flame retardant, Compatibility, Blends, Alloy

INTRODUCTION

Polycarbonate (PC) is an important engineering polymer used in a wide variety of applications because of its excellent balance of properties, such as high strength, high dimensional stability, good electrical and chemical properties, high heat deformation temperature (HDT), good impact toughness and excellent optical clarity. It is widely used in electrical and electronic appliances, automobiles, industrial machinery, buildings and construction, consumer products, etc. PC, however, has many disadvantages, which deter its applications in some fields. For example, its high melt viscosity and low melt flowability have limited use in the injection molding of large-scale and thin-wall products. Consequently, the internal stress existing in the PC products easily brings about stress cracking. Additionally, the impact toughness of PC is very sensitive to sharp notch and sample thickness. So studies on the modification of PC attract much attention among polymer researchers. One of the most efficient methods is to blend PC with other polymers such as ABS (acrylonitrile-butadiene-styrene).

ABS has good melt flowability and excellent processability and relatively low price. The blends or alloys of PC/ABS combine the favorable properties of each component, i.e. PC/ABS alloys possess the good processability of ABS, high HDT of PC, good impact toughness even at low temperature and in sharp notched state. Over the past 30 years, many patents and papers pertinent to PC/ABS alloys have been issued^[1~10]. The first U.S. patent was issued to Grabowski in 1964^[11]. More recent U.S. patents cover various novel compositions, processes and applications^[12~16]. Many research results have shown that the compatibility between PC and ABS is not enough to make PC/ABS alloys with good properties, especially impact strength. In this work the compatibility enhancement of PC/ABS was investigated and the multiple-element PC/ABS alloy with good impact strength and retardant flammability up to UL-94 V0 level was prepared.

EXPERIMENTAL

Materials

PC, Lexan 144R with MI (300°C, 5 kg) of 9.5 g/10 min from GE Plastics, USA and ABS resin, PA-757 with MI (200°C, 5 kg) of 7.5 g/10 min from Chimei Chemical Co., Taiwan were used in this work. The flame retardants

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used in this work were BA-59P (tetrabromobisphenol A) with a molecular weight of about 354 and a bromine content of 58.8%, BC-52 (phenoxy-terminated carbonate oligomer of tetrabromobisphenol A) with a molecular weight of about 2500 and a bromine content of 51.3% and Reofos TPP (triphenyl phosphate). They are all from Great Lakes Chemical Corporation, USA. SMA (styrene-maleic anhydride copolymer) with a MA content of 18% made by Shanghai Oil & Chemical Research Institute, China and PS-g-MAH with a MA content of 15% made by Shanghai Sunning Chemical Co., China were also used.

Blending

Drying

Prior to melt blending, PC was dried in an oven with blower for 4–6 h at 120°C and ABS, SMA, PS-g-MAH etc. were dried in an oven with blower for 4 h at 80°C.

Mixing

All ingredients were weighed according to formulations and poured into the high-speed mixer (GA-10, made by Beijing Plastics Machinery Plant) and mixed at 1500 rpm for 3 min.

Melt blending

The mixture prepared from above was fed into a twin-screw extruder (Φ 30 mm, $L/D = 28$, Nanjing Rubber & Plastics Machinery Plant) and blended for ca. 3 min at 220–240°C. Through a die the melt was extruded into a water bath (water temperature = 50–60°C) and then cut into granules with a size of $\Phi = 2.5 \text{ mm} \times 2.5 \text{ mm}$ by a pelleter.

Sample injection

Prior to injection moulding, the granules obtained above were dried in an oven with blower for 4–6 h at 105–110°C. The dried granules were injected to form the test samples by an injection machine (CJ150NCII from Chen Machinery Co., Hong Kong). The injection temperature was set in the range of 230°C–240°C; injection time was 20 s; injection pressure was 75 MPa; the time of pressure retention was 30 s; the cooling time was 30 s; the mold temperature was in the range of 60–90°C.

Testing

Notched Izod impact testing was performed using a pendulum-type tester according to ASTM D256. The impact strength data are the average values of at least five test specimens. Tensile tests were performed using an Electronic Universal Tester Model CSS-1101 made by Changchun Tester Research Institute, China according to ASTM D638 type I at the crosshead speed of 50 mm/min. The tensile strength and elongation at break data are the average values of at least five test specimens. Flexural strength and modulus were measured according to ASTM D790. Retardant flammability testing was conducted using a Horizontal Vertical Flame Chamber made by Atlas Company, USA according to the UL-94 Vertical test method. The width and thickness of specimen were 10 mm and 4 mm. MI testing was conducted according to ASTM D1238. Vicat softening temperature testing was conducted according to ASTM D1525.

RESULTS AND DISCUSSIONS

The Miscibility of PC and ABS

The impact strength of a polymer blends depends strongly on whether or not the blend is miscible. ABS is a multiple-phase polymer and is composed of SAN and PB. The calculated solubility parameters of PC, PB, SAN (AN 26.8%) are $10.1 \text{ (cal/cm}^3)^{1/2}$, $8.25 \text{ (cal/cm}^3)^{1/2}$, $9.9 \text{ (cal/cm}^3)^{1/2}$, respectively^[9]. From these values, the differences in the solubility parameters of two polymers, i.e., $\Delta\delta$ are $0.2 \text{ (cal/cm}^3)^{1/2}$ for PC/SAN pair and $1.85 \text{ (cal/cm}^3)^{1/2}$ for PC/PB pair. This means PC and SAN is miscible, whereas PC and PB is immiscible. Therefore, the compatibility or miscibility of PC and ABS depends on the content of AN in ABS. On the whole, PC and ABS are partially compatible, but this level of compatibility is not enough to prepare PC/ABS alloy with good impact strength. So a compatibilizers should be added to the PC/ABS system to enhance the compatibility

of PC/ABS. Compatibilizers usually are branched or grafted copolymers which disperse in the interfacial domains between PC and ABS, and they improve the interfacial adhesion. By compatibilizing, the impact strength of PC/ABS alloy can be greatly improved. For flame-retarding PC/ABS system, the addition of a large amount of flame-retardants will greatly decrease the impact toughness. Therefore it is essential to add compatibilizers or impact modifiers to PC/ABS systems containing flame-retardants.

The Retardant Flammability of PC/ABS Alloy

Though PC has self-extinguishability, its flame resistance is still not up to UL-94 V0 level. For example, the flame resistance of Lexan 144R used in this work is only at UL-94 V2 level. The addition of ABS to the PC matrix further decreases the flame resistance of PC. Therefore, in order to meet the UL-94 V0 specification, a large amount of flame-retardants should be added to the PC/ABS system. It is very difficult to prepare flame-retarding PC/ABS alloy with good impact toughness. Low molecular weight brominated PC is suitable for PC and tetrabromobisphenol A or decabromodiphenyl oxide is suitable for ABS. As for flame-retarding PC/ABS alloy, united flame-retardants mentioned above were used in this work. Meanwhile, antimony trioxide (Sb_2O_3) was also used as cooperative flame-retardant.

The formulations and their related properties of trial experiments were listed in Table 1.

In Table 1, it is shown that the flame resistance of recipe 1, recipe 3 and recipe 4 can reach up to UL-94 V0 level, while recipe 2 was not up to UL-94 V0 level. This means that the addition of 15 phr (based on 100 weight part of PC/ABS) tetrabromobisphenol A or 15 phr decabromodiphenyl oxide plus 3 phr Sb_2O_3 can make the flame resistance of PC/ABS alloy up to the UL-94 V0 level, while the addition of 15phr TPP plus 3 phr Sb_2O_3 was not enough. The results show that the flame-retardant efficiency of TPP is lower than that of tetrabromobisphenol A or decabromodiphenyl oxide. The PC/ABS system containing TPP has better flowability and impact strength than the systems containing other flame-retardants. The properties of recipe 4 indicate that a combination of tetrabromobisphenol A with low-molecular-weight brominated PC can afford better impact toughness. However, the impact strength of all of the four recipes above is too low, which indicates that the miscibility of PC and ABS is not sufficient for improving the impact strength.

Table 1. Formulations and properties of trial experiments

Materials	Recipe 1	Recipe 2	Recipe 3	Recipe 4
PC, GE 144R	70	70	70	70
ABS, PA-757	30	30	30	30
Sb_2O_3	3	3	3	3
BA-59P	15			10
DE-79			15	
BC-58	5			5
TPP		15		
Properties				
Tensile strength (Mpa)	56	52	59	54
Elongation at break (%)	21	46	36	52
Flexural strength (Mpa)	92.9	90.2	111.5	96.5
Flexural modulus (Mpa)	2337	2345	2423	2386
Izod notched impact strength (J/m)	28.9	58.4	51.8	69.5
Flame resistance, UL-94 4 mm	V0	V2	V0	V0
Vicat softening temperature ($^{\circ}\text{C}$)	121	118	126	123
Flowability, MI, 260 $^{\circ}\text{C}$, 5000 g	22.4	25.8	24.4	23.6

The Compatibilization of SMA, PS-g-MAH and EVA

The compatibilization effects of SMA, PS-g-MAH and EVA were investigated in this work. The results are listed in Table 2.

Table 2. The compatibilization effects of several polymers on the compatibility of PC/ABS

Materials	Recipe5	Recipe 6	Recipe 7
PC, GE 144R	70	70	70
ABS, PA-757	30	30	30
BC-58	5	5	5
Sb ₂ O ₃	3	3	3
Anti-oxidant	0.5	0.5	0.5
BA-59P	10	10	10
PS-g-MAH	5		
SMA		5	
EVA, VA28%, MI 25, (from ATO Co.)			5
Properties			
Tensile strength (Mpa)	51.2	51.6	41.6
Elongation at break (%)	63.3	52.4	66
Flexural strength (Mpa)	88.4	61.5	64.6
Flexural modulus (Mpa)	2397	2548	2245
Izod notched impact strength (J/m)	92.4	78.4	93.3
Flame resistance, UL-94 4 mm	V0	V0	V0
Vicat softening temperature (°C)	121	125	115
Flowability, MI, 260°C, 5000 g	22.8	20.6	23.3

From Table 2, it can be seen that several polymers used in this work have certain compatibilization effects on the PC/ABS system. Through the addition of these polymers to the PC/ABS system, the impact strength of PC/ABS alloy is increased. From the viewpoint of impact strength, PS-g-MAH has the best effect. From the viewpoint of flexural strength, modulus and Vicat softening temperature, SMA has the best effect. That means that each compatibilizer has its own characteristic. It is noted that the increase of impact strength of PC/ABS alloy containing single compatibilizer is not so remarkable as expected.

The Synergistic Effects of Mixed Compatibilizers

Because the compatibilization effect of single compatibilizer is not satisfactory, multiple-component systems were used in this work. The results are listed in Table 3.

Table 3. The results of multiple-elements compatibilization

Properties	Recipe 8	Recipe 9
	Multiple-element system 1	Multiple-element system 2
Tensile strength (Mpa)	55.6	51.4
Elongation at break (%)	75	78
Flexural strength (Mpa)	87.8	80.4
Flexural modulus (Mpa)	2402	2355
Izod notched impact strength (J/m)	175	162
Flame resistance, UL-94 4 mm	V0	V0
Vicat softening temperature (°C)	125	122
Flowability, MI, 260°C, 5000 g	20.1	21.6

Table 3 shows that the compatibilization effects of multiple compatibilizers on PC/ABS alloy are very significant, and the impact strength is greatly increased. This indicates that the simultaneous addition of multiple compatibilizers will produce synergistic effects on the compatibility of PC/ABS. Meanwhile, the flame resistance attains the UL-94 V0 level, and other mechanical properties such as tensile strength, flexural strength and modulus, etc. are also very good.

CONCLUSIONS

By using multiple compatibilizers, PC/ABS alloys with good mechanical properties and flame resistance were successfully prepared. The experimental results show that the compatibility of PC/ABS was not enough and needed to be enhanced. Several polymers such as PS-g-MAH, SMA, EVA have noticeable compatibilization

effects on the PC/ABS system. The simultaneous addition of multiple compatibilizers will produce synergistic effects on the compatibility of PC/ABS, and the impact strength is greatly increased. Meanwhile, by use of united flame retardants such as tetrabromobisphenol A and low-molecular-weight brominated PC, the flame resistance of PC/ABS alloy can attain the UL-94 V0 level.

REFERENCES

- 1 Deanin, R.D. and Chu, C.W., *J. Elastomers and Plastics*, 1986, 18: 42
- 2 Jin, L., Shon, K.H., Jeong, H.M. and Kim, B.K., *J. Appl. Polym. Sci.*, 1998, 69: 533
- 3 Koo, K.K., Inoue, T. and Miyasaka, K., *Polymer Eng. and Sci.*, 1985, 25(12): 741
- 4 Yan, R.J. and Yang, B.X., *J. Appl. Polym. Sci.*, 1994, 52: 1063
- 5 Balakrishnan, S. and Neelakantan, N.R., *Polymer International*, 1998, 45: 347
- 6 Lee, M.P., Hilter, A. and Baer, E., *Polymer*, 1992, 33(4): 685
- 7 Lombardo, B.S., Keskkula, H. and Paul, D.R., *J. Appl. Polymer Sci.*, 1994, 54: 1697
- 8 Wu, J.S., Shen, S.C. and Chang, F.C., *J. Appl. Polymer Sci.*, 1993, 50: 1379
- 9 Chun, J.H., Maeng, K.S. and Suh, K.S., *J. Mater. Sci.*, 1991, 26: 5347
- 10 Chiang, W.Y. and Hwung, D.S., *Polymer Eng. and Sci.*, 1987, 27(9): 632
- 11 Grabowski, T.S., 1964, U.S.Pat. 3,130,177
- 12 Chao, H.S., 1993, U.S. Pat. 5,229,169
- 13 Dufour, H.S. and Denis, J.P.St, 1991, U.S. Pat. 5,061,754
- 14 Dujardin, R., 1993, U.S. Pat. 5,177,145
- 15 Fischer, J.D., Darmstadt, R.B., Numirch, U. and Siol, W., 1993, U.S.Pat 5,232,986
- 16 Udipi, K., 1992, U.S.Pat. 5,104,934