Mechanical Behavior, Thermal Properties and Microstructure Analysis of Marine ABS/PC Alloy

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Abstract — It is well known that in blend modification, PC(Polycarbonate)/ABS(Acrylonitrile-Butadiene -Styrene) alloy polymers were used very common , but because of its high production cost and poor processing performance limited its application in marine materials. To improve the problem, We studied the behavior of ABS/PC alloy performance, and made a lot of exploration to increase the toughness, made it meet the use requirement for marine. In order to determine the mechanical properties of ABS/PC alloy, we adopted a way that melt blending, extruding, injection molding and standardized tests, also launched microstructure analysis. The results shows that by adjusting the ratio of the blend, choosing the polymer alloys which meeting the use requirements of marine magnetic compass cover, we can get a more reasonable, better and more economical cost formula plastic for marine.Exploring the way that use plastic instead of wood or instead of steel to cut the cost.

Keywords - ABS/PC; Mechanical Behavior; Thermal Properties; Processability ; Microstructure

I. INTRODUCTION

Acrylonitrile-Butadiene-Styrene (ABS) resin is a kind of material which between engineering plastics and general plastics, because of its excellent mechanical properties and molding performance ABS was widely used. However, compared with engineering plastics, its poor heat resistance also mechanical performance limited its application range.

Polycarbonate (PC) is a kind of thermoplastic engineering plastics with excellent comprehensive properties, it has high impact strength, creep resistance, good dimensional stability, heat resistance, transparency, low water absorption, non-toxic, good dielectric properties, etc, the impact strength and transmittance are high, good dimensional stability, easy coloring, aging resistance, also has excellent electrical insulation, but there are shortcomings like poor wear resistance and processing at the same time. The ABS / PC composite was prepared by blending ABS with PC. The complementary properties and improved impact strength can be got by blending [1].PC and ABS / PC composites are widely used in building materials, electrical appliances, automotive and shipping industry [2].

In 1963, Borg-Warner Company in American successfully developed the first generation of ABS/PC alloy. With the brand Cycoloy800 put on the market, thereafter, the major companies in Germany, Japan and other countries also studied the different brands of ABS/PC alloy. Because of its excellent comprehensive performance, ABS/PC alloy has developed rapidly in recent years. Since 2003, ABS/PC alloy's production in the world was about 100 thousand ton per year and growth at a rate of 10% per year [3].

In 1995, the ABS/PC alloy was developed by the American GE company which can be used as the special material for automobile. Don't need to paint, good heat resistance and impact resistance, excellent technology, can be used for car dashboard, steering wheel cover, can be recovered 100%.

The research work of ABS/PC alloy in our country started at the period of "seven five". In recent years, due to the demand of the market, we accelerating the pace of research and development of ABS/PC alloy, the direction of development is to improve the flow of processing, to make blow molding processing come true, to improve the rigidity of the products and develop low gloss varieties, etc. At present, the application of ABS/PC alloy has been developed in China independently, including resistance, heat resistance, flame retardant and other varieties. A series of PC/ABS alloy was prepared by Cao Mingan et al. [4], they determined the static mechanical properties, hardness, VEKA softening point, water absorption, dynamic mechanical properties of PC/ABS blends and other indexes，studied the relationship between the proportion and the compatibility, fluidity and mechanical properties, the comprehensive research result considered that the overall performance also impact property of the 50%ABS and 50%PC blends was good. Cai Changgeng [5] studied the effect of ABS and PC blend ratios on mechanical properties, heat resistance, dynamic mechanical properties and fracture morphology of ABS/PC polymer alloys containing a certain amount of compatible agent. The result shows that the addition of PC can improve the tensile strength, bending strength, thermal deformation temperature and glass transition temperature of polymer blends. Jim Min San [6] chosen two different grades of ABS resin and PC blended, and studied the relationship between the composition and performance in the system. The result shows the introduction of PC can significantly improve the softening temperature of ABS resin. There is a big difference between the compatibility of different composition of ABS and PC. There was a big influence on the tensile property and notched impact property of ABS/PC alloy with different composition of ABS.

Studding and promoting the marine non-metallic materials' modification also localization can improve the overall technical level of the ship industry because of our proportion of ship export is more and more big in recent years. ABS, as a kind of special plastic which was rubber toughened, was widely used with its excellent comprehensive performance. In order to improve the poor heat resistant performance, mechanical properties performance of ABS, good performance of PC (Polycarbonate) is often used for ABS' modification. ABS/PC alloy can be successfully used in parts such as Marine pipeline, magnetic compass cover, instrument shell and Marine electric fan etc. But there is a big nature difference between PC blend with different brands of ABS. This paper is according to the experimental results of Liang Ji-zhao[7] which studied mechanical properties of binary alloy. Selecting PA747 ABS resin, different ratio of ABS/PC alloy was prepared, the mechanical properties, thermal performance and processability also microstructure was also be analyzed, thus determining the more reasonable formula.

II. EXPERIMENTAL METHODS

A. *The raw material*

ABS：brand PA-747，Tai Wan Industrial Factory；

PC：brand 141R-111，General Electric Company；

All materials are dried before experiment. The ABS resin in 80 ℃ drying 8 h, and PC must be dried 12h in 120℃ before use. The effect of raw material properties in the experiment as shown in table1.

TABLE I THE PROPERTIES OF ABS AND PC USED IN THE EXPERIMENT

Polymer	Properties					
	Tensile strength /MPa	Bending modulus /Gpa	Bending strength /Mpa	Vicat softening temperature/ ℃	Notch impact strength $/ KJ \cdot m^{-2}$	MFR / $g \cdot (10\,\text{min})^{-1}$
ABS	43.0	1.9	54.0	101	17.5	11.7
PC	62.0	2.4	76.4	105	39.2	5.4

B. *Experimental instruments*

Double screw plastic extruder，SHJ-36(L/D:34/1)，Nanjing Giant mechinery；

Injection molding machine，130F2V，DongHua Machinery Co. Ltd.；

HAKKE Rheometer，RC-90，HAKKE company；

HD-10 thickness meter，Shanghai chemical machinery equipment factory；

Plastic hardness tester，DShaw，Shanghai XianFeng machinery factory；

Automatic electro-optical analytical balance，TG328A，Shanghai balance instrument factory；

Electronic tensile testing machine，AI-7000M，Taiwan Gotech testing machines Inc；

Cantilever beam impact testing machine，XC-22，Hebei ChengDe precision testing machine factory；

Charpy impact testing machine，JC-25，HeBei ChengDe precision testing machine factory；

Melt index tester，GT-7100-MI，Taiwan Gotech testing machines Inc；

VEKA thermal denaturation temperature testing machine，

GT-HV2000，Taiwan Gotech testing machines Inc；

Scanning electron microscope (SEM)，JSM-6700F, JEOL company in Japan

SEM observation

Sample was cut by ultra-thin slicing machine, observing section morphology of notched impact specimen section after spraying gold. Metal spraying current is 5 ~ 7 mA, metal spraying time is 15 ~ 20 mins.

C. *Experimental apparatus*

1. The process flow diagram

In this section, we had taken the preparation and testing process of ABS/PC alloy as an example，flow chart of preparation and testing of ABS alloy samples is given.

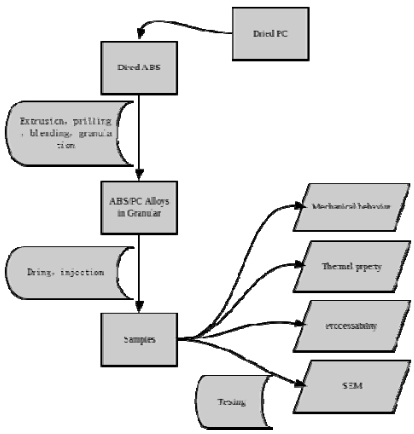

Fig. (1). Flow Chart of ABS/PC Alloy Samples Preparation and Tests

2. Premixed material

Such as flow chart figue1, the raw materials will be blended(the ABS must be drying at 80℃ for 8h before used, PC must be drying at 120℃ for 12h before used) ,mixed with a certain proportion to the twin screw extruder (length diameter ratio of screw is 34/1）.After full kneading（keep the speed in 80r/min）,extruded, Water cooling, pilled.The extruding temperature:(℃) as shown in tableII.

3. Molding system

TABLE II THE TEMPERATURE OF EVERY EXTRUDER'S ZONE(℃)

Area 2	Area 3	Area 4	Area 5	Nose
205	210	210	220	230

The granules after blended extrusion must be drying again, they were poured into the injection machine hopper then fed into the heating tube, after heating and melting in a flow state, injected into the closed mould through the injector which in front of the charging barrel by the screw driven, to keep the pattern given by injection mold cavity after cooling and solidifying, we got the products by released mould, a complete molding cycle was done in operation.

The injection molding pressure was 120Mpa; molding cycle was 1 minute.

The temperature for injection machine：(℃) was shown in table3.

TABLE III THE TEMPERATURE OF EVERY INJECTION MOLDING MACHINE'S ZONE(℃)

Nozzle	T1	T2	T3	T4	T5	Oil temperature
280	260	245	220	25	25	15

4. Experiment methods

（1）Tensile test

The tensile test was carried out in GT-10S-2000 tensile machine. Test standard for GB/T1040-92. The Starting measurement length was 50mm, test environment for the room 25□，the tensile speed was 50mm/min.Test results are taken from the average of 5 samples.

（2）The impact experiments at room temperature.

In order to detected the response of blends at a high speed under load. In order to evaluate the impact ductility of the material, the notch impact test on the blends were held at room temperature. The test pieces were standard sample with V notch bar. The standard was GB/T1843-96、GB/T16420-1996.

（3）Bending test

The bending strength reflects rigidity of material. This experiment adopts the method according to the principle of a simple beam. The span of L was 10cm, test speed was 25mm/min, the standard was GB1042-79。

（4）Hardness test

The experiment of Rockwell hardness was according to the standard GB2411-80.

（5）Melt flow rate test

Polymer especially the fluidity of thermoplastics can be simply represented by melt flow rate (MFR).The MFR measurement of ABS and its blends were carried out according to GB3682-83 standard in PXRZ-400C. Test temperature was 220 ℃, load was 10kg.

III. EXPERIMENTAL RESULTS and DISCUSSION

A. PC content effect on the tensile strength and impact strength of ABS/PC alloy

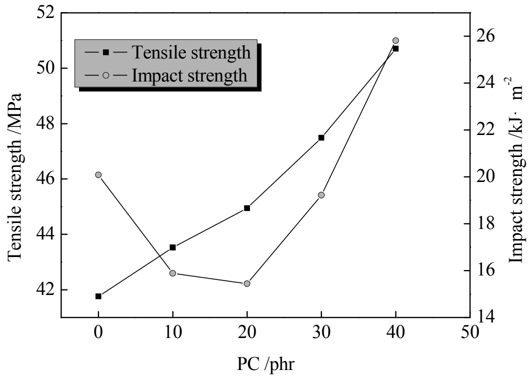

Fig.2 PC Content Effect on Tensile and Impact Strength of ABS/PC Blends

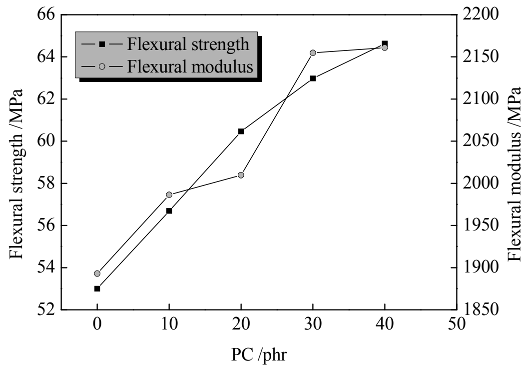

Fig. 3 PC Content Effect on Flexural Strength and Modulus of ABS/PC Blends

Figure (2)is a curve of tensile and impact strength with the variation on PC content of ABS/PC alloy. With benzene ring structure exists, the intermolecular force is large, PC has a better mechanical strength. Especially in ductibility, PC is much higher than PS, PMMA and so on amorphous thermoplastic plastics, the improvement of the flexibility in the molecular chain mainly due to the ether oxygen bond in PC ,increasing the ductibility; a large number of microspores exist among the original fiber reinforced skeleton of PC lead to slip in the original fiber structure , so micropore itself can also absorb some of the impact energy in the impact energy absorbing deformation [8] .

The tensile and impact strength variation of ABS/PC alloy was shown in Figure (2). As can be seen from Fig. (2), with the increase of PC content, the tensile strength increased, the notched impact strength decreased first and then increased gradually, it decreased rapidly when the content of PC is 0~10 range, the rate of decline was gradually slow when the content of PC exceeded 10 percent, the turning point appears in the PC content was 20 phr, more than 30% can improve the impact ductibility of polymer alloy significantly. Because of the high impact performance of PC, when PC content was more than 20%, there was a substantial increase in the impact strength of the mixture with a further increased of PC content. But with the increaseing of PC content, the cost and the viscosity of alloy increased too.

B. PC content effect on the flexural strength and flexural modulus of ABS/PC alloy.

Figure (3)shows the variation of bending properties of ABS/PC alloy with PC content, Because of the viscosity of PC is higher than ABS, PC is easy to be the dispersed phase. The bending strength, bending modulus of the blends showed a good linear relationship with content of ABS, keeping with superimposed effect in blend component.

As shown in Figure (3): with the increase of PC content, the flexural strength of the composite was improved which is consistent with the reported results[7],The flexural modulus increased, indicating that the rigidity is greatly improved by increasing PC content in alloy system. The flexural strength of ABS / PC alloy approximation was a linear function of PC content, suggesting that the flexural strength was accord with with the mixture principle roughly in ABS / PC alloy.

C. PC content effect on the flow rate and the VEKA melt softening point of ABS/PC alloy

The continuous phase composition, molecular weight structure also had effect on heat resistance of ABS, the higher the molecular weight of the continuous phase, the better heat tolerance. If the polar group with strong interactions were introduced in the molecular structure, Or made the large side groups insert into the molecular chains, will improved the heat resistance of ABS. Figure (4)is a trend chart with melt flow rate and VEKA softening point changed with the content of PC of ABS/PC alloy. The melt viscosity of ABS was rose because the introduction of PC, challenged machining， improved the VEKA softening temperature ABS resin significantly at the same time. The maximum operation temperature of ABS was determined by the continuous phase, the thermal deformation temperature of ABS will not exceed the continuous phase’s.

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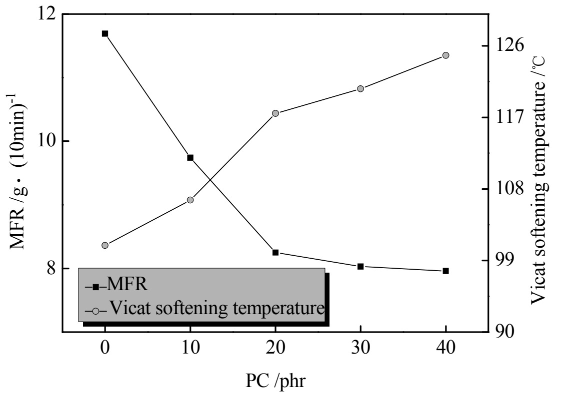

Fig. 4 Different PC Types Effect on Thermal Properties of ABS/PC Blends

As shown in Figure (4): with the increase of PC content, the alloy melt flow rate was declined, especially in the ABS/PC of 80/20, the fall range was bigger, then tended to be gentle . This shows that it will affect the alloy processing performance because of high melt viscosity of PC. Due to the molecular chain structure with high rigidity and high steric hindrance of PC which make a strong interaction between the macromolecular chains of ABS / PC alloy, Internal frictional resistance between the molecules is larger, the relative motion between the polymer molecular chains is difficult, the melt flow rate of the alloy was increased. This will increase difficulty of ABS/PC alloy on the molding process especially large thin-wall injection molding, so it is necessary to add some flow modifier in the preparation process of ABS/PC alloy, to improve the processability of ABS/PC alloy and to reduce the residual stress of the product. Avoiding possible stress cracking, surface defect, warping phenomenon [9].

VEKA softening point of alloy increased with PC raising in the system. The polar group linkage effect acrylonitrile (AN) of SAN in ABS and the benzene ring effect in PC, leading a high polarity of alloy, the intermolecular interactions between macromolecular chain molecules is strong, internal frictional resistance was large, The relative motion was difficult between the segment and segment in polymer, so there was better heat resistance and high heat distortion temperature in the alloy system.

D. PC content effect on other properties of ABS/PC blends

TABLE IV. PC CONTENT EFFECT ON OTHER PROPERTIES OF ABS/PC BLENDS

ABS/PC	100/0	90/10	80/20	70/30	60/40
Yield strength /Mpa	41.28	43.76	47.12	48.10	51.85
Elongation at break /%	47.47	39.39	37.04	35.88	33.42
Hardness /HD	76	80	79	80	80

It was can be seen from table IV, with the increase of PC content, yield strength of the alloy system increased constantly, that suggests more and more external force was needed when the molecular chains started to move in system; The elongation at break of the system decreased with the increase in content of PC, the hardness increases gradually indicated that the plasticity of the alloy is getting smaller and smaller and more and more rigid.

The results are a sign that in order to get an ABS/PC alloy with better mechanical performance, heatresistance and lower production cost, the mass ratio of ABS and PC was more suitable for 80/20.

E. SEM observation of marine ABS/PC alloy cross-section morphology

In order to understanding the compatibility of ABS/PC alloy system intuitively, Scanning Electron Microscopy (SEM) was used to analyze the impact of the cross section morphology (figure (5)) of ABS/10% and ABS/20%PC alloy respectively.

Since ABS is a complex phase structure, including two main components: SAN and grafted rubber, when ABS was blended with PC, the phase morphology is more complicated. As can be seen from the figure (5) (b), ABS/PC blend morphology is mutiple level, it can be divided into two parts of PC and ABS phase at first, in the ABS phase, it is divided into SAN and grafted rubber particle phase, the grafting of rubber particles dispersed in SAN phase, that is to say, the SAN phase is between PC and rubber particles. For nearly a decade, researchers using SAN/PC system instead of ABS/PC system, exploring the relationship between the AN in SAN content and the ABS/PC system from different views, finding that when the AN content was 24% in SAN, the mechanical properties and micro morphological structure of ABS/PC system can be optimal [10].

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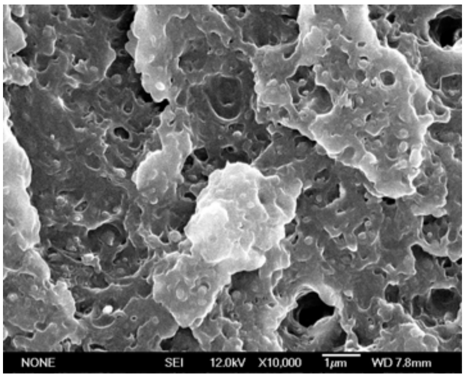
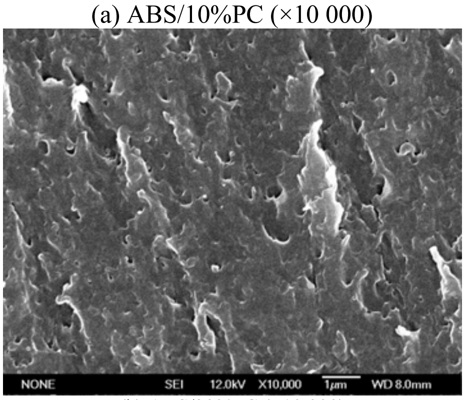


(a) ABS/10%PC (×10 000)



(b) ABS/20%PC (×10 000)

Fig.5 SEM photographs of impact surfaces of ABS/PC alloys with different ratios

As can be seen from figure (5), In ABS/10%PC alloy (figure (5) (a)), PC is dispersed phase, ABS is the continuous phase, PC was presented as granular distributed in ABS, and the particles are elongated along the injection direction. In ABS/20%PC alloy (figure (5) (b)), while the PC is still as the dispersed phase, but the phase interface tends to mistiness with an increase of PC, the Section texture is more comminuting, fracture surface is more complex, the break superficial area getting bigger, the surface energy of fracture surface increased, it explained that when the impact break occurred, more energy was needed[11]; In addition, the whole section is smooth, but there are still a tear characteristics, brittle and ductile rupture exist at the same time, the compatibility of alloy is good. It is consist with the mechanical properties analysis of binary alloy in literature [12]. The AN content is 19.8% in ABS was adopted in this research. The discrete phase in alloy distribute relatively uniform, the particle size is about 1 ~ 2μm as shown in figure 5 (a), but the combination between the phase interface is not very strong, many globular bumps and empty can be seen from the section, interface layering is obvious. When PC with high viscosity dispersed in ABS with low viscosity, PC as dispersed phase is condensed. Because in the continuous phase ABS with low viscosity, PC has the very high diffusion rate [13]. With the increase of content of PC, coagulation rate also gradually increased as can be seen in figure 5 (b), it lead to diameter of dispersed phase particle increasing, interfacial area getting smaller in a certain area [14]. Also can be seen from figure 5 (b), except empty there are some diameter is about 0.5 ~ 1μm dimples in the section, they are the microporous gathered when material destroyed, the size and depth are related to the size of the plastic deformation when materials damage [15]. This crater-like morphology, has been observed in some toughening in the cross section morphology of polymer, we considered that it is formed to non-uniform expansion because of the triaxial stress in crack tip in the toughening particles and around [16]. Through experimental observation, it is believed this crater and the hole play an important role in the toughening mechanism of the ABS/PC alloy.

IV. CONCLUSIONS

For ABS/PC alloy, the compatibility of the two was obviously improved with an increase of PC, so as to improve the mechanical properties of alloy.

After testing, the performance of ABS/10%PC alloy reached the requirements of mechanical properties of Marine ABS alloy, and the alloy's flow properties is fine, the extrudate appearance is smooth the processability is good; the compatibility of ABS/20%PC alloy had some improvement, mechanical properties was enhanced, but the extrusion processing was depredated, there is a sharkskin distortion phenomenon in extrudate appearance, it can be improved by introducing processing agent.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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