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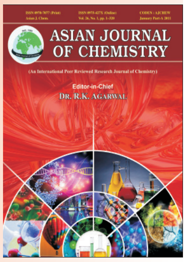

Micromorphology and Thermostability of PEEK/PEI/PES Plastics Alloys†

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PEEK/PEI/PES plastics alloys were prepared by twin-screw extrusion molding. Microstructure analysis showed that poly(ether imide) (PEI) and poly(aryl ether sulfone) (PES) can be well-balanced dispersed in poly(ether ether ketone) (PEEK) matrix. The PEEK has better compatibility with PEI than that of PES and that PEI can improve the compatibility between PEEK and PES and that there is a certain interaction between three components. But there are some regions in alloys without interaction between PEEK and PEI when PES was increased. Thermostability of materials could not be affected by alloying and there is little influence on the stability of ternary alloys for the heat treatment process of thermal compression molding.

Keywords: Poly(ether ether ketone), Poly(ether imide), Poly(aryl ether sulfone), Plastics alloy, Micromorphology, Thermostability.

INTRODUCTION

It is well concerned by people that plastic alloys with excellent comprehensive performance could be obtained by alloying modification in the recent years. Poly(ether ether ketone) (PEEK), a kind of semi-crystalline high performance engineering plastics, has prominent advantages in mechanical strength, thermal stability, electrical insulativity and chemical stability[1], but with the high price and significantly lower glass transition temperature than some high heat-resistant amorphous plastics such as poly(ether imide) (PEI) and poly(ether sulphone) (PES), so PEEK was improved by alloying modification, which has become one of research hotspots. Blend of PEI, PES and PEEK[2-4], such as were used to increase their high-temperature rigidity and reduce costs. The blends between PEEK and PEI, PES, PPS were also studied to obtain excellent comprehensive properties[5-9]. The both amorphous high performance engineering thermoplastics, PEI and PES, display high heat resistance, high glass-transition temperature (T_g: 215 and 220 ºC), high strength and modulus and good electrical insulativity[2,8,9], but PEI has a low chemical resistance[3,4] and PES has a poor organic solvent resistance. It is well known that plastics alloys with excellent comprehensive performance could be obtained by blending. However, only binary alloys among these three plastics such as an alloy of PEEK and PEI or PES, were investigated and reported in literatures[8,10]. The three components alloys based on PEEK had been reported in few literatures. Several ternary plastic alloys of PEEK, PEI and PES with lower cost could be prepared by extrusion blending process and structures and thermostability of the alloys with the different content of PEEK, PEI and PES were investigated in this paper.

EXPERIMENTAL

The PEEK of 012P, whose number-average molecular weight (Mn) was 60000 and PES, whose Mn was 65000, with powder of 250 μm in diameter, were supplied by Changchun Jida Engineering Plastics Research Co., Ltd., in which PEEK material had a T_g of 143.3 ºC and a Tm of 335 ºC and PES had a T_g of 230.2 ºC. PEI, Mn 50000, had a T_g of 216.5 ºC, whose powder of Ultem1000 was supplied by SABIC Co., Ltd. PEEK, PEI and PES were blended in weight ratios of 70/30/0, 70/0/30, 70/25/5, 65/30/5, 60/30/10, 60/35/5 and 60/10/30, 100/0/0, 0/100/0 and 0/0/100, respectively, by TSE-30A twin-screw extruder supplied by Nanjing RuiYa Polymer Co., Ltd.

General procedure: Before blending, the three polymers were completely dried overnight in an air-circulated oven at 150 ºC. The parameters: temperatures of extruder sections for 310-370 ºC, screw speed 10-30 rpm and head pressure 9-11 MPa. Compression moulding was used to prepare the specimens, whose parameters: molding temperature for 370 ºC, molding pressure for 5 MPa at 350-370 ºC and for 10 MPa at 275-350 ºC, holding molding pressure temperature of 370 ºC for 20 min, stripping temperature 150 ºC.

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Detection method: The surface and morphology of the samples had been observed by scanning electron microscope (S4800 type, HITACHI, Japan). The cross-section was frozen in liquid nitrogen and then brittle fracture to form cross-section and cross-section was sprayed by gold. The samples had been analyzed by the Fourier transform infrared spectrometer and the attenuated total reflection flourier transformed infrared spectroscopy (NEXUS-870, Thermo Nicolet, USA) at room temperature, with scanning wave number range 4000-650 cm^{-1} and scanning interval 4 cm^{-1}. Thermostability of samples and samples soaked by solvent of ternary plastic alloy had been tested by the thermogravimetric analyzer (HTG-type, Beijing Henjiu scientific instrument, China) at room temperature. The temperature range is 0-900 ºC and the heating rate is 20 ºC/min.

RESULTS AND DISCUSSION

Compression molding: Molding temperature has great influence on mechanical properties, physical properties and size stability of materials. In Fig. 1, the plate sample molding temperature is 370 ºC, as if the temperature is too high, the plate sample would be degraded and if the temperature is too low, the plate sample would not be fully molten and thus affects the material properties. Therefore, 370 ºC was selected as the molding temperature of the alloy materials. At the same time, the pressure was 5 Mpa. It can be shown in Fig. 1 that the pressure and temperature can certainly make cross function.

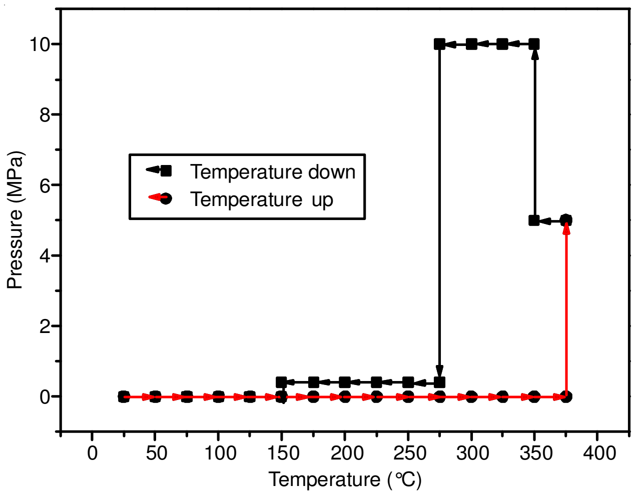
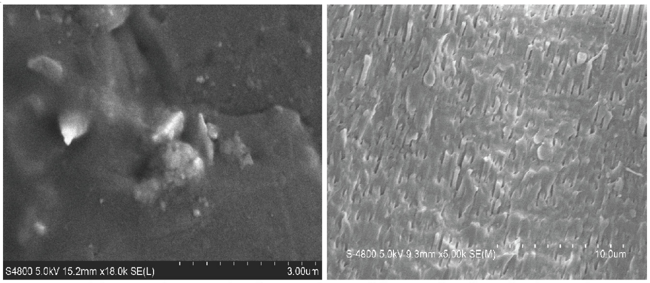


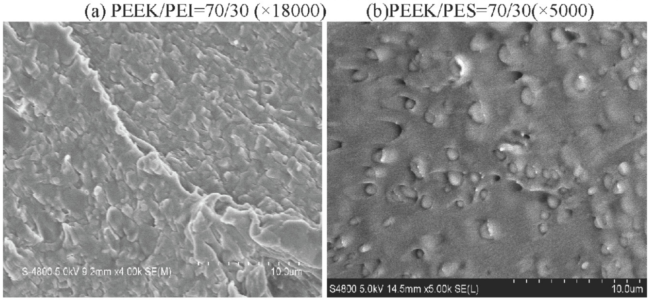
Fig. 1. Curve of temperature and pressure in the process of compression molding

As thermoplastic resin has consolidation molding under the glass transition temperature, 150 ºC was selected as the mold release temperature.

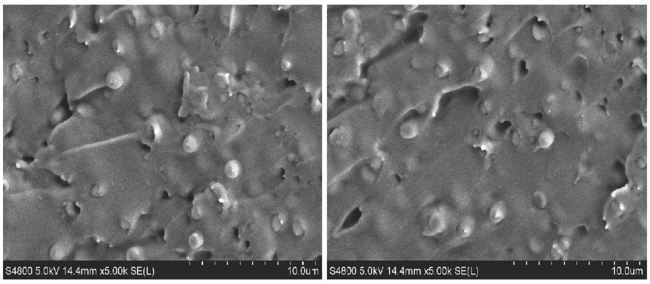
Microstructure analysis: As shown in Fig. 2, it can be seen in Fig. 2(a) that there are two phase regions and PEI which presents the bald irregular shape is dispersed in the PEEK matrix phase and there is not a clear interface to exist in two phases. In Fig. 2(b), the accumulation phenomenon exists locally in the PEEK matrix phase and only a few of PES is dispersed in PEEK matrix and it could be inferred by the fact that PEEK has better compatibility with PEI than that of PES because of the interaction of functional groups between PEEK and PEI. It had also been reported that the blends of PEEK and PEI would present a good compatibility between the both plastics[11].



(a) PEEK/PEI=70/30 (×18000) (b)PEEK/PES=70/30(×5000)



(c) PEEK/PEI/PES=60/10/30 (×4000) (d) PEEK/PEI/PES=60/30/10 (×5000)



(e) PEEK/PEI/PES=60/35/5 (×5000) (f) PEEK/PEI/PES=65/30/5 (×5000)

Fig. 2. SEM images of PEEK/PEI and PEEK/PEI/PES

It can be seen in Fig. 2(c) and (d) that the content of PEI or PES has affected the distribution of PEEK, PEI and PES. With increasing contents of PEI or the decreasing contents of PES, PEI and PES or PEI, or PES can be dispersed evenly in the matrix phase, at the same time, two phase regions still exist and it would be further inferred that PEI can improve the compatibility between PEEK and PES. The phenomenon can also be seen in Fig. 2(e) and (d) when PEI content is more than 30 wt %.

It can be further observed that, with the change of the PES content, the number of particles of Fig. 2(e) and (f) in the incompatible areas are significantly less than that of Fig. 2(d) and it could be inferred that the particles in the incompatible areas should be PES.

Interaction analysis: As shown in Fig. 3, the samples of PEEK, PEI, PES, PEEK/PEI, PEEK/PEI/PES had been analyzed by the Fourier transform infrared spectrometer, The characteristic absorption peaks were shown in Table-1. The difference of -C=O and -C-N vibration absorption peak in binary alloy of PEEK/PEI can be observed, which are from 1652.1-1647.3 cm^{-1} and from 1355.7-1350.6 cm^{-1}, respectively, therefore, it can be inferred by the difference that there would be interaction between PEEK and PEI.

The difference of -C=O , -C-N and Ø-(S=O)-Ø vibration absorption peak in the ternary alloy of PEEK/PEI/PES can be observed, which are from 1649.9.1-1647.3 cm^{-1}, from 1355.2-

TABLE-1
FTIR CHARACTERISTIC ABSORPTION PEAKS (cm^{-1}) OF PEEK, PEI, PES, PEEK/PEI, PEEK/PEI/PES

Samples	PEEK	PEI	PES	PEEK/PEI	PEEK/PEI/PES
-C=O	1647.3	–	–	1652.1	1649.9
Ø-O-Ø	1217.1	–	–	1218.4	1217.2
-C-O	1010.4	–	–	1009.6	1010.3
Ø-(C=O)-Ø	926.4	–	–	924.3	926.0
-C=O (Imide ring)	–	1777.4	–	1777.5	1777.5
-C-N	–	1350.6	–	1355.7	1355.2
Ø-(S=O)-Ø	–	–	1319.6	–	1310.7
	–	–	1144.7	–	1145.8

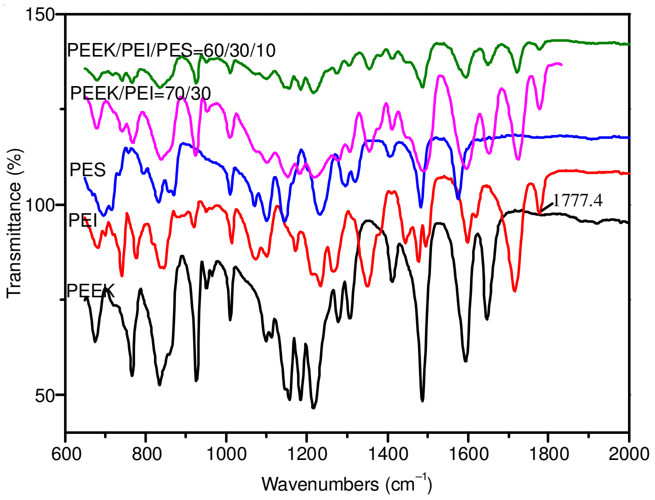


Fig. 3. FTIR curves of PEEK, PEI, PES, PEEK/PEI, PEEK/PEI/PES

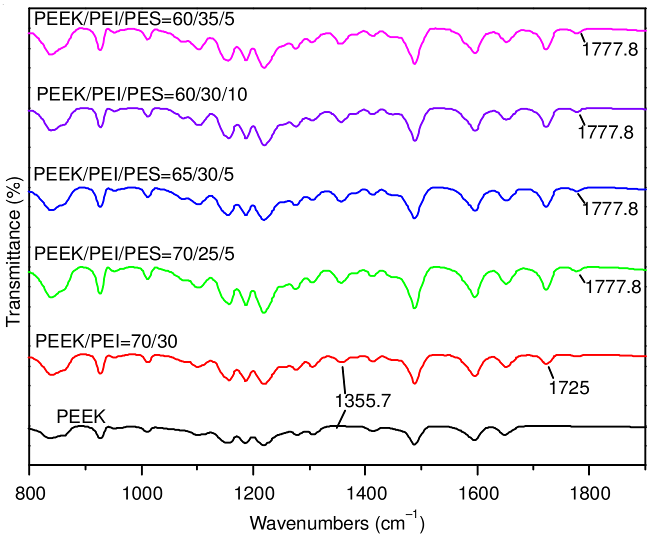


Fig. 4. FTIR-ATR curves of PEEK, PEEK/PEI, PEEK/PEI/PES

1350.6 cm^{-1} and from 1144.7, 1319.6-1145.8 and 1310.7 cm^{-1}, respectively, therefore, it can also be inferred by the difference that there would be interaction between PEEK, PEI and PES, so it would be presented in the results that the polar group of PEEK, PEI and PES made some interaction, because they contains a large number of polar groups, such as ether, acetone functional groups. FTIR-ATR had been used to analyze the samples because the results of FTIR can not enough to detect the variation of vibration absorption peak.

As shown in Fig. 4, the samples of PEEK, PEEK/PEI, PEEK/PEI/PES had been investigated by the attenuated total reflection flourier transformed infrared spectroscopy, the characteristic absorption peaks were shown in Table-2.

Figs. 3 and 4 showed that 1777.8 cm^{-1} is the -C=O (imide ring) vibration absorption of PEI. In the Table-2, the variation of -C=O peak in binary alloy of PEEK/PEI can be observed, which is from 1777.8-1725 cm^{-1} and it could be inferred that there are interaction between the ether, acetone functional groups of PEEK and the -C=O functional groups of PEI, which means that it results in a red shift phenomenon of >C=O.

It can be seen in Table-2 that -C=O (imide ring) vibration absorption of PEI have the 1777.8 and 1725 cm^{-1} vibration absorption peak. It would be inferred that the interaction of PEEK and PEI had been weakened, or shielded by PES, therefore, in the curve of the FTIR-ATR, not only red shift phenomenon existed, but it also had vibration absorption peak -C=O (imide ring) functional groups of PEI.

As shown in Fig. 5, in order to investigate the influences of compression molding on the interaction of functional groups, the ternary alloy plate prepared by compression molding had been detected by FTIR-ATR. It can be seen in Fig. 5 that -C=O (imide ring) vibration absorption of PEI in the plate sample have still the 1777.8 and 1725 cm^{-1} vibration absorption peak, thus it may be inferred that high temperature molding almost does not affect the interaction of functional groups or structures of ternary alloy materials to some extent.

It had been reported that there could be an intense reciprocity between PEI and PES which have a good compatibility[12] and the blends of PEEK and PEI would present a good compatibility between the both plastics[11], PEI as a coupling agent could improve the compatibility between PEEK and PES and only a single T_g for the alloys of PEEK/PEI/PES have been obtained in these tests[13]. So the interaction between functional groups of ternary alloy materials explains why does PEI as a

TABLE-2
FTIR-ATR CHARACTERISTIC ABSORPTION PEAKS (cm^{-1}) OF PEEK, PEEK/PEI, PEEK/PEI/PES

Samples	PEEK	PEEK/PEI	PEEK/PEI/PES (70/25/5)	PEEK/PEI/PES (65/30/5)	PEEK/PEI/PES (60/305/10)	PEEK/PEI/PES (60/35/5)
-C-N	–	1355.7	1355.7	1355.7	1355.7	1355.7
-C=O (Imide ring)	–	1725.0	1725.0	1725.0	1725.0	1725.0
	–	–	1777.8	1777.8	1777.8	1777.8

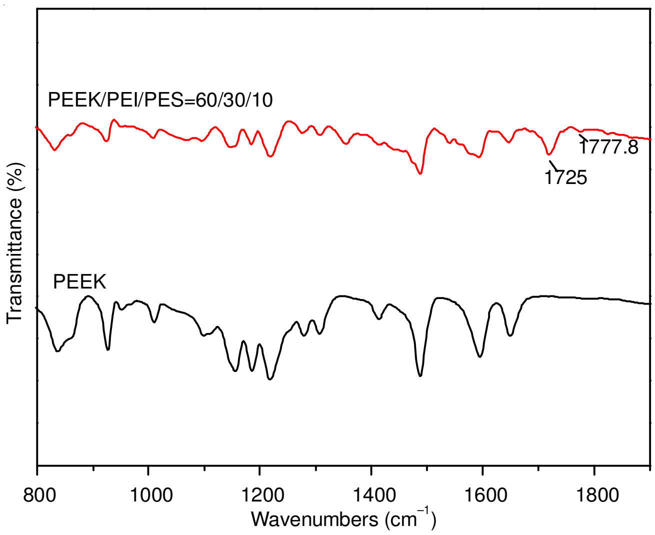


Fig. 5. FTIR-ATR curves of samples between PEEK/PEI/PES and PEEK

coupling agent improves the compatibility between PEEK and PES through these tests of FTIR and FTIR-ATR.

Thermostability: As shown in Fig. 6, the samples of PEEK, PEI and PEEK/PEI had been analyzed by thermogravimetry. The thermal decomposition temperature of PEEK and PEI are about 502 and 546 ºC, respectively. With the rising of temperature, the thermal pyrolysis is not obvious before the decomposition temperature, but for the alloy of PEEK/PEI/PES, the thermal pyrolysis is more obvious than that of PEEK or PEI and the thermal decomposition temperature of PEEK/PEI is about 503 ºC. Therefore, thermostability of materials could not be affected by alloying. The influences of compression molding on the thermostability had been evaluated (Fig. 7).

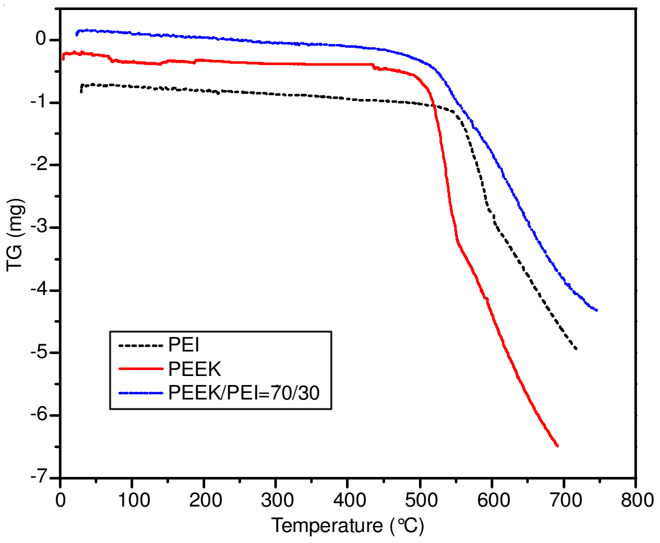


Fig. 6. TGA curves of PEEK, PEI and PEEK/PEI

It can be seen in Fig. 7 that the thermal pyrolysis of ternary alloy particle of PEEK/PEI/PES almost does not exist before the thermal decomposition temperature and the thermal decomposition temperature is about 499 ºC. As for the ternary alloy plate of PEEK/PEI/PES, The thermal decomposition temperature is about 501 ºC. With the rising of temperature, the thermal pyrolysis is not obvious before the decomposition temperature, therefore, it can be inferred that thermostability of alloy materials could not be affected by compression molding.

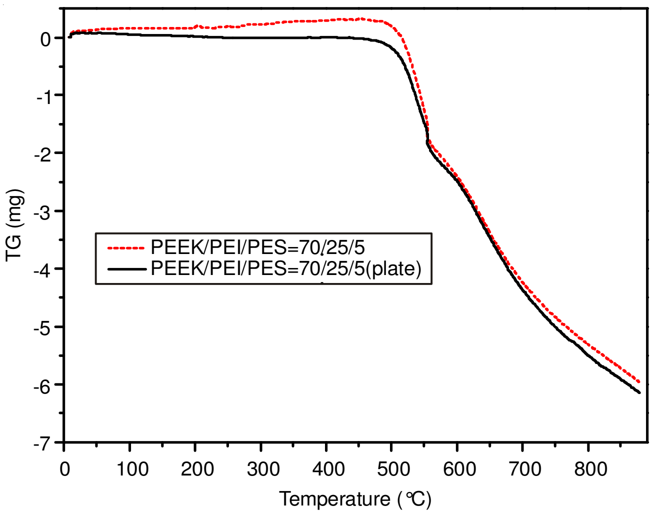


Fig. 7. TGA curves of ternary alloy particle and plate of PEEK/PEI/PES

Thermostability soaked by concentrated H_2SO_4 of ternary plastics alloy: As shown in Fig. 8, the alloy samples soaked by concentrated H_2SO_4 for 12 h had been analyzed by thermogravimetry. With the increasing of temperature, the alloy samples soaked by concentrated H_2SO_4 for 12 h all have some weightlessness. The thermal decomposition temperature of PEEK/PEI and PEEK/PEI/PES in weight ratios of 70/25/5 are about 490 ºC. The thermal decomposition temperature of PEEK/PEI/PES in weight ratios of 60/30/10 and 65/30/5 are about 450 and 499 ºC, respectively.

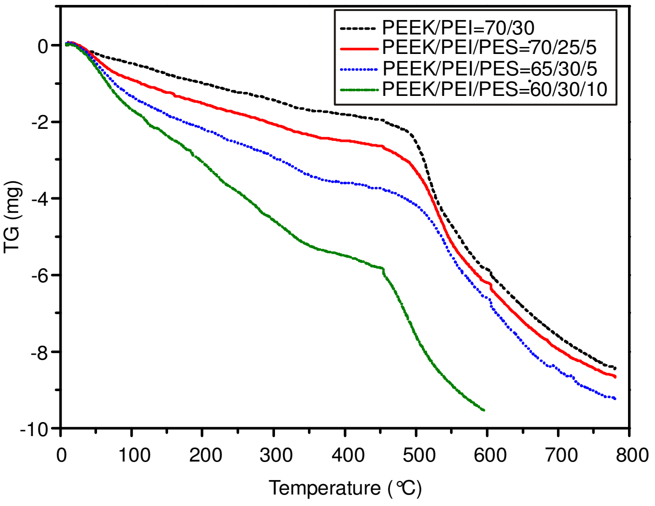


Fig. 8. TGA curves of the alloy samples soaked by concentrated H_2SO_4 for 12 h

It had been reported that PEEK, PEI, PES can be sulfonated by sulfuric acid and thermostability of samples sulfonated by concentrated H_2SO_4 declined[14,15]. The alloy samples after sulfonation have degradation in the range of 230-370 ºC, so it could be inferred that thermostability of samples decreased. Therefore, thermostability of materials soaked by concentrated H_2SO_4 could be affected by alloying.

Conclusions

- Poly(ether ether ketone) (PEEK) has better compatibility with poly(ether imide) (PEI) than that of poly(aryl ether sulfone) (PES) because of the interaction of functional groups between PEEK and PEI. The content of PEI or PES has affected the distribution of PEEK, PEI and PES.
- Poly(ether imide) can improve the compatibility between PEEK and PES. The interaction of functional groups between PEEK and PEI had been weakened, or shielded by PES. The interaction between functional groups of ternary alloy materials explains why PEI as a coupling agent improves the compatibility between PEEK and PES. At the same time, the high temperature molding almost does not affect the interaction of functional groups or structures of ternary alloy materials to some extent.
- Thermostability of materials could not be affected by alloying and there is little influence on the thermostability of the ternary alloy materials for the heat treatment process of compression molding. However thermostability of materials soaked by concentrated H_2SO_4 could be affected by alloying.

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