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Effect of reactive group types on the properties of core-shell modifiers toughened PA6

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Summary

Reactive monomers such as acrylic acid (AA), maleic anhydride (MA) and glycidyl methacrylate (GMA) were grafted onto acrylonitrile-butadiene-styrene core-shell copolymer (ABS) by emulsion polymerization method. These functionalized ABS were used to toughen PA6. FTIR and Molau tests showed that these monomers were introduced onto ABS copolymers and compatibilization reactions took place between PA6 and the AA, MA and GMA grafted ABS. TEM result showed that the modified ABS copolymer dispersed in PA6 matrix uniformly and no obvious difference could be found between the different PA6 blends. However, mechanical test showed that GMA and MA modified ABS achieved much better toughening effect than the AA grafted ABS copolymer due to the stronger interfacial reactions. Fracture characterization indicated that PA6 toughened with GMA and MA modified ABS showed higher G_i values according to the Vu-Khanh approach and much obvious shear yielding in the deformed zone could be found.

Keywords

PA6, core-shell modifier, compatibilization, interfacial strength

Introduction

Polyamide 6 (PA6) is an attractive polymer for engineering applications. It exhibits high resistance to crack initiation that imparts high unnotched impact toughness. However, its low resistance to crack propagation leads to embrittlement in the presence of a notch [1-2]. In order to modify the notch sensitivity and improve the notch impact strength of PA6, core-shell modifiers such as acrylonitrile-butadiene-styrene (ABS) has been used to toughen PA6 [3-20]. However, since SAN (shell phase of ABS) is not miscible with or is not adequately wetted by PA6, some strategies are needed to disperse the core-shell impact modifiers in the PA6 matrix. The most common compatibilization strategy has been to incorporate a functional copolymer which can react with the amine end groups of PA6 and is miscible with

SAN phase of ABS. Copolymers containing anhydride functional groups such as styrene-maleic anhydride copolymer (SMA) [9], styrene-acrylonitrile-maleic anhydride copolymer (SAM) [10] and imidized acrylic polymer (IA) [11-15] have been used to compatibilize PA6/ABS blends. Recently, epoxy-functionalized copolymers, such as glycidyl methacrylate copolymer, were synthesized as a compatibilizer of PA6/ABS blends [16-20].

This work adopted another option to compatibilize PA6/ABS blends. In the present paper, the grafted shell polymers containing different functional groups are chemically incorporated during the emulsion polymerization process, which are capable of reacting with PA6. During the synthesis of ABS, reactive monomer such as acrylic acid (AA), maleic anhydride (MA) or glycidyl methacrylate (GMA) was added to the reactive system. So ABS-g-AA, ABS-g-MA and ABS-g-GMA core-shell modifiers were obtained. Compared with PA6/compatibilizer/ABS blends, the functionalization of impact modifiers was carried out during the preparation process of ABS, so this method was much simpler. The focus of this study was to investigate the effect of reactive group types on the compatibility, morphology, mechanical properties and fracture behavior of PA6/ABS blends.

Experimental

Materials

The PA6 was purchased from Longjiang plastics plant, China. The concentrations of carboxyl and amine groups are 42.6μeq/g and 51.2μeq/g, respectively. Its intrinsic viscosity is 2.5dl/g (0.01g/ml, formic acid solution, 30°C) and Mn is 2.4×10^4g/mol. The ABS modifiers with different reactive groups were synthesized by emulsion polymerization method and the properties were list in Table1.

Table1 Properties of reactive monomers modified core-shell copolymers

Designation used here	Reactive monomer	PB content (wt%)	St/AN (wt/wt)	Reactive monomer content (wt%)
ABS	–	60	75/25	–
ABS-g-AA	AA	60	75/25	1
ABS-g-MA	MA	60	75/25	1
ABS-g-GMA	GMA	60	75/25	1

Preparation of core-shell modifiers

Functionalization of ABS core-shell modifiers with AA was achieved by emulsion polymerization method. PB latex used in this study was supplied by Jilin chemical industry group synthetic resin factory, China. $K_2S_2O_8$ was used as initiator and sodium dodecyl sulfate (SDS) was used as emulsifier. The reaction was performed in a 2L glass reactor under nitrogen at 80°C. First, the water, PB, $K_2S_2O_8$, and SDS were added to the glass reactor and stirred five minutes under nitrogen, and then the mixer of St/AN/AA was added by continuous feeding way to the glass reactor in about 4h. As for ABS-g-MA modifier, the water, MA, PB, $K_2S_2O_8$, and SDS were added to the glass reactor and stirred five minutes under nitrogen, and then the mixer of St/AN (75/25) was added by continuous feeding way. The polymers were isolated from emulsion by coagulation and dried in a vacuum oven at 60°C for 24h before being used. The preparation of ABS-g-GMA has been introduced in the other paper [20].

Reactive blending and molding procedures

PA6 blends were prepared in a twin-screw extruder. Constitutes were set at 70/30(wt/wt). The temperatures along the extruder were 210, 220, 240, 240, 240, 240, 240°C, and the rotation speed of the screw was 60 rpm. The melt stripes of blends were cooled in a water bath and then palletized.

The blends were dried in a vacuum oven at 80°C for 24h. Then injection molding was carried out to prepare Izod impact specimens and tensile specimens. The notch of the Izod impact specimens was milled in by the machine having a depth of 2.54mm, an angle of 45^o and a notch radius of 0.25mm.

FTIR analysis

The functionalized ABS modifiers were dissolved in acetone and the solution was ultracentrifugated at room temperature at 10000rpm using a GL-21M ultracentrifuge. After 30min, clear separation was achieved. The un-grafted SAN and/or SAN copolymers are soluble in acetone, while the grafted modifiers are insoluble. The insoluble part is concentrated in a white layer at the tube bottom and was used to analyze the grafting reaction by FTIR tests.

Morphological properties

The microstructure of the PA6 blends was observed by TEM (model Japan JEM-2000 EX). Ultramicrotomed sections were obtained using a Leica ultramicrotome at -100°C and stained with an OsO_4 solution for 8h before observation.

Mechanical properties

The notched Izod impact strength of PA6 blends were measured by a XJU-22 Izod impact tester at 23°C according to the ASTM D256. The tensile tests were carried out using a Shimadzu AGS-H tensile tester at a cross-head speed of 50mm/min at room temperature according to the ASTM D638.

Results and discussion

FTIR analysis and Molau test

Figure1 shows the FTIR spectra of ABS and the functionalized ABS modifiers with different reactive groups. As for the ABS-g-AA modifier, two absorbance peaks at $1735cm^{-1}$ and $1711cm^{-1}$ appear due to the carbonyl groups absorbance corresponding to the grafted AA. In the ABS-g-GMA spectrum, the absorbance peak of carbonyl groups at $1727cm^{-1}$ comes from the grafted GMA monomer. As for the ABS-g-MA core-shell modifier, the peak at $1778cm^{-1}$ is the strong characteristic absorption of maleic anhydride groups. Since the ungrafted copolymers have been separated form the modifiers, the FTIR results show that the reactive monomers such as AA, MA and GMA have grafted onto the ABS modifiers.

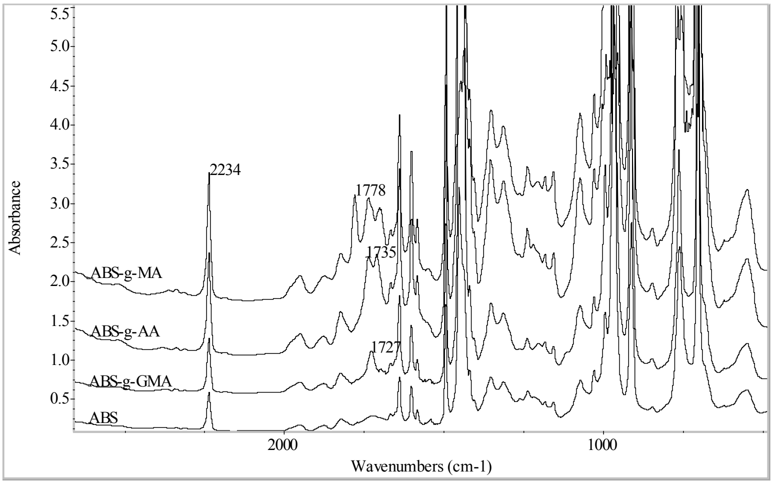


Figure1 FTIR of ABS and the functionalized ABS with different reactive groups

The grafting of AA, MA or GMA on ABS modifiers can improve the compatibility and interfacial strength between PA6 and the functionalized ABS due to the compatibilization reactions. Molau test was used to testify the formation of grafted copolymer between PA6 and functionalized ABS. In the study, formic acid was used as solvent of PA6 and nonsolvent of core-shell modifiers and the result was shown in Figure2. It can be found that PA6/ABS blend shows phase separation after mixing and the unsoluble ABS lies on the top of the test tube. As for the PA6/ABS-g-AA, PA6/ABS-g-MA and PA6/ABS-g-GMA blends, milky and colloidal solutions appear which is undoubtedly attributed to the emulsifying effect of the graft copolymers formed in situ during the melt blending. No obvious differences can be found for the solutions though the different reactions between PA6 and the functionalized ABS. Molau test indicates the compatibilization reactions have taken place.

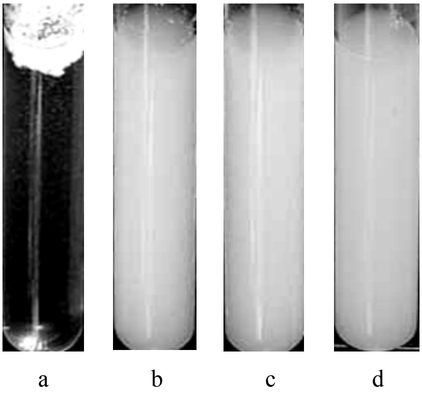
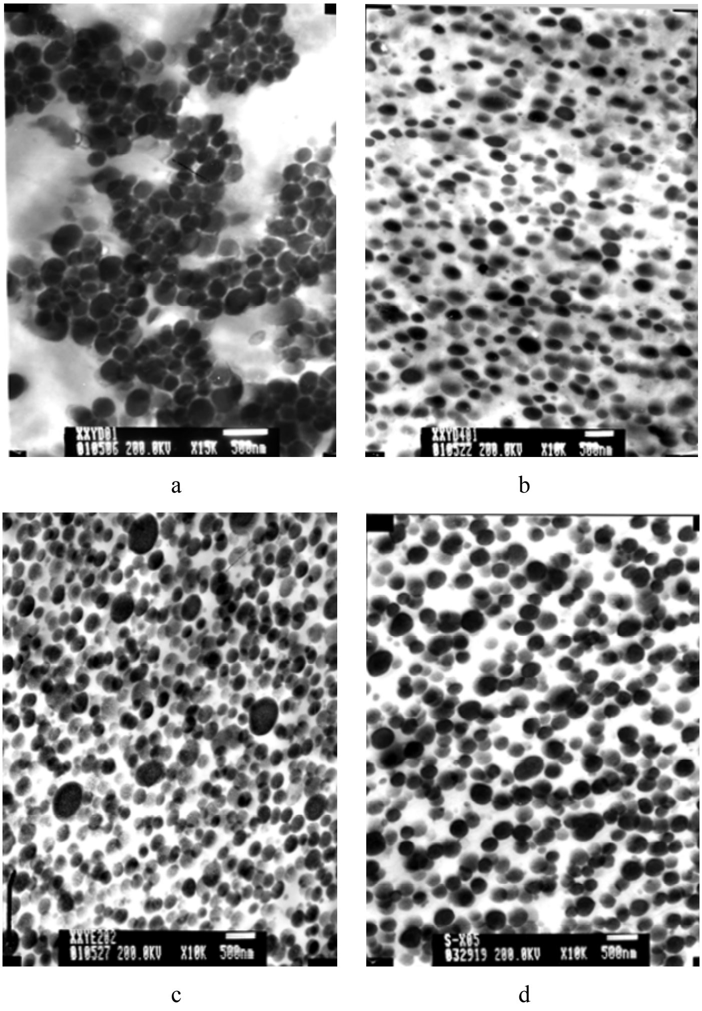


Figure2 Molau test of PA6 blends for a PA6/ABS, b PA6/ABS-g-AA, c PA6/ABS-g-GMA, d PA6/ABS-g-MA

Morphology

TEM was used to investigate the influence of compatibilization reaction types on the dispersed phase morphology of PA6 blends. The polybutadiene (PB) particles (the core phase of ABS) were stained black by OsO_4, which indicated the dispersed morphology of the core-shell modifiers. Figure3a shows the phase morphology of PA6/ABS blend. Obvious agglomeration can be found for ABS phase since no chemical reactions exist in this blend. The agglomeration of ABS indicates the poor compatibility between PA6 and SAN (shell phase of ABS). The introduction of reactive groups on ABS particles improves the dispersed phase morphology significantly. The core-shell modifiers disperse in PA6 matrix uniformly and no clusters can be found as can seen from Figure3b, c and d.



a

b

c

d

Figure3 TEM morphology of PA6 blends a PA6/ABS, b PA6/ABS-g-AA, c PA6/ABS-g-MA, d PA6/ABS-g-GMA

The improvement of the dispersed phase morphology identifies the compatibilization effect of PA6-co-ABS copolymer formed at the interface. The PA6-co-ABS copolymers decrease the interfacial tension, which is beneficial for the dispersion of core-shell modifiers according to Wu's study [21]. More important is that the coalescence of the dispersed phase is suppressed through the interfacial stabilization effect due to the in situ reactions between PA6 and core-shell modifiers. On the other hand, the influence of reactive group types on the dispersed morphology can not be found from the TEM pictures.

Mechanical properties

Figure4 shows the notched Izod impact strength of PA6 and its blends. Pure PA6 is a notch sensitive polymer, and its notched Izod impact strength is only 30J/m. The impact strength of PA6 is improved slightly by ABS and PA6/ABS blend still fractures in brittle way due to the poor compatibility between PA6 and ABS. With the introduction of AA, GMA or MA on ABS particles, the toughening effect improves significantly. However, the impact toughness is different obviously for the blends when the core-shell modifiers contain different reactive groups. As can be seen from Figure4, PA6/ABS-g-GMA and PA6/ABS-g-MA blends show high impact toughness and impact values of 900J/m and 950J/m are achieved respectively, which displays the super-tough property. Compared to ABS-g-GMA and ABS-g-MA, ABS-g-AA shows poor toughening effect. Impact strength value reaches 230J/m as for PA6/ABS-g-AA blends, which is much lower than the other two blends system. The different toughening ability for the three functionalized core-shell modifiers lies in the different compatibilization reactions.

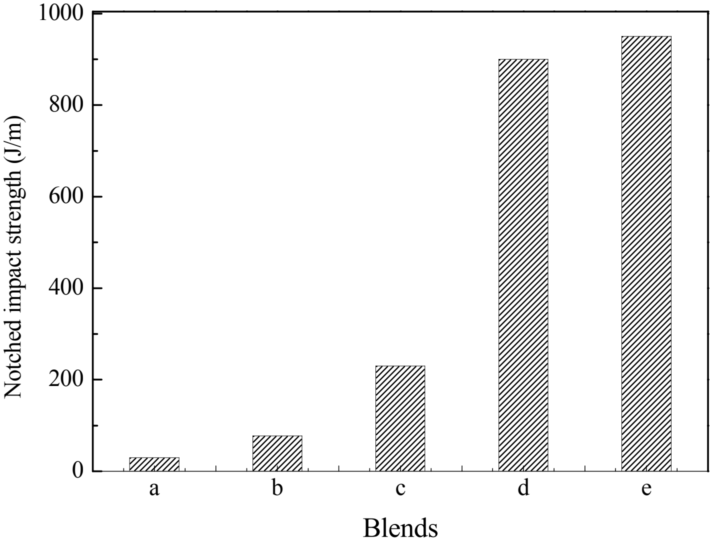


Figure4 Notched Izod impact strength of PA6 and its blends a PA6, b PA6/ABS, c PA6/ABS-g-AA, d PA6/ABS-g-GMA, e PA6/ABS-g-MA

Dispersed phase morphology and interfacial strength are two important factors that influence the toughness improvement of polymer blends. In PA6/ABS-g-AA blend, the compatibilization reaction comes from the reaction between carboxylic acids and amines, which is the basis for the synthesis of many polyamides. The reaction rate is slow, for example, batch processes for synthesis of polyamides usually need several hours [22]. The poor reaction properties lead to little PA6-co-ABS copolymers formation and weak interfacial strength at the interface during the melt blending process. So the uniform dispersion of ABS-g-AA in the PA6 matrix can not induce the prominent toughness improvement of PA6/ABS-g-AA blend due to the weak interfacial strength. Similar result has been found in the other paper [22]. The compatibilization reactions between the maleic anhydride and amines have been used extensively since the fast reaction ratio between them. So PA6/ABS-g-MA blends show fine dispersed phase morphology and strong interfacial strength, which induce high impact strength of the blends. As for the PA6/ABS-g-GMA blends, both the acid and amine end groups can react with the epoxy groups of GMA during melt processing and the reaction ratio is fast. So PA6/ABS-g-GMA blends show similar impact toughness with PA6/ABS-g-MA blend. The essential difference of the toughening effect between ABS-g-AA and the other two modifiers lies in the poor interfacial reaction.

Table2 shows the tensile properties of core-shell modifiers toughened PA6 blends. It has been studied that the tensile properties of polymer blends were very sensitive to the state of the interfacial adhesion. The poor interface behaves as a flaw, and the failure initiates at the interface, which results in low tensile strength and elongation at break. As can be seen from Table2, PA6/ABS blend shows lower yield strength, break strength and elongation at break than the other blends due to the lower interfacial strength. The introduction of reactive groups on the core-shell modifiers induces compatibilization reactions and higher interfacial strength, leading to higher tensile strength and elongation at break.

Table2 Tensile properties of PA6 blends with different core-shell modifiers

	Yield strength (MPa)	Break strength (MPa)	Elongation at break (%)
PA6/ABS	41	36	75
PA6/ABS-g-AA	42	41	152
PA6/ABS-g-MA	42	44	210
PA6/ABS-g-GMA	43	45	215

Fracture characterization

In the Izod test, only the total energy absorbed by the sample to break can be measured and it is well known that this value does not directly correspond to the fracture performance of the materials. Characterization of the impact resistance of the samples was made by different methods based on the fracture types, such as brittle, semi-ductile or ductile fracture. For the ductile fracture behavior, Vu-Khanh approach, which takes into account the crack initiation and crack propagation energies in the materials, has been proposed. Since the energy absorbed by the specimen is mainly dissipated in the fracture process, the energy absorbed by the specimen becomes

$$\frac{\mathrm{U}}{\mathrm{A}}=\mathrm{G}_{\mathrm{i}}+\frac{1}{2}T_a\cdot A$$

Where U is the total energy of fracture, A is the area of the fracture, G_i is called the fracture energy at the crack initiation and T_a is claimed to be a tearing modulus.

The plots of absorbed energy to fracture surface, U/A, against fracture surface, A, for the PA6 blends with different core-shell modifiers are shown in Figure5 for comparison. The corresponding G_i and T_a values are list in Table3. From Figure5 and Table3, it can be found the PA6/ABS blend shows lowest G_i and T_a values than the other blends. The PA6 blends that toughened with the functional core-shell modifiers show the similar T_a values. However, the G_i values increase with the improvement of interfacial strength and which is consistent with the change of Izod impact strength. So the compatibilization reactions improve the interfacial strength, which is not beneficial to the crack initiation process. The much stronger of the interfacial strength is, the much higher energy is needed to induce crack initiation and higher notched impact strength is achieved.

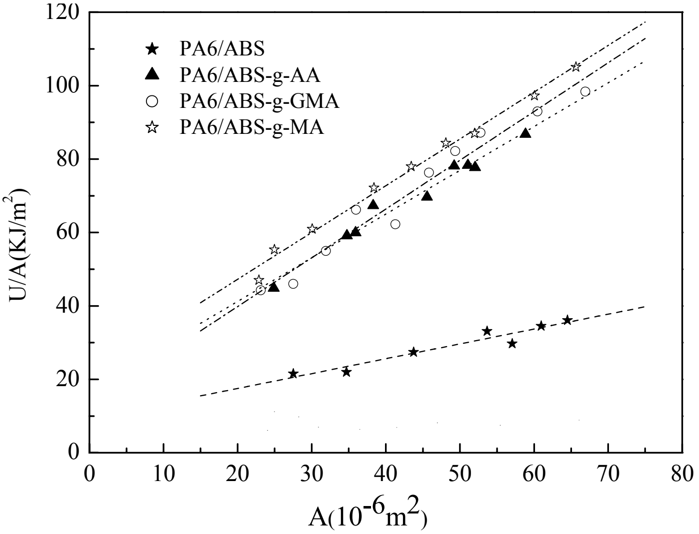
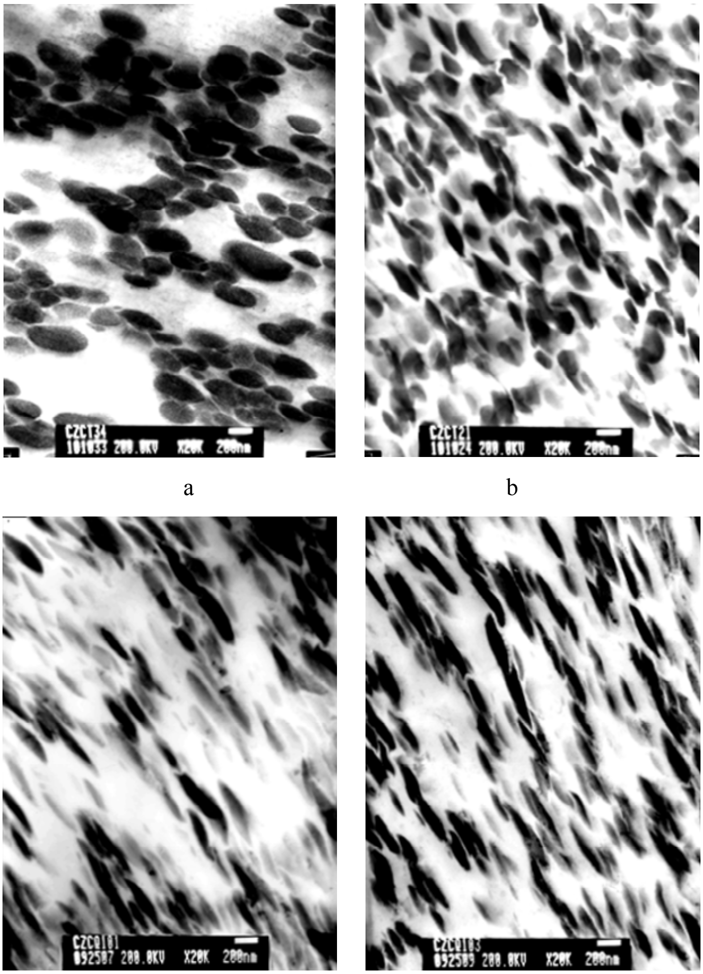


Figure5 U/A versus A plots for PA6 blends with different core-shell modifiers

Table3 G_i and T_a values for PA6 blends with different core-shell modifiers

	G_i(kJ/m^2)	T_a(10^9J/m^4)
PA6/ABS	9.42	0.91
PA6/ABS-g-AA	13.27	2.60
PA6/ABS-g-GMA	17.39	2.40
PA6/ABS-g-MA	21.76	2.55

Deformed morphology inside the fracture zone of PA6 blends is shown in Figure6. The black PB phase displays slight deformation in PA6/ABS blends as can be seen from Figure6a, which indicates that shear yielding of the PA6 matrix does not occur. As for the PA6/ABS-g-AA blend, the PB particles are elongated in some degree which shows that shear yielding takes place and the Izod impact strength of PA6 is improved as shown in Figure4. Figure6c and d show the deformed morphology of PA6/ABS-g-GMA and PA6/ABS-g-MA blends. The black PB particles are elongated remarkably and obvious deformation of PB particles can be seen which indicates shear yielding is the major energy absorbance way and PA6 blends display higher impact strength. So the fracture character further testifies that the GMA and MA are much suitable reactive monomers for the compatibilization effect in PA6 blends.



a b

c d

Figure6 TEM morphology in the deformed zone of PA6 blends a PA6/ABS, b PA6/ABS-g-AA, c PA6/ABS-g-GMA, d PA6/ABS-g-MA

Conclusion

Acrylic acid (AA), maleic anhydride (MA) and glycidyl methacrylate (GMA) modified ABS were prepared by emulsion polymerization method. The functionalized

ABS-g-AA, ABS-g-GMA and ABS-g-MA copolymers were used to toughen PA6 and the difference of the toughening effect was investigated. FTIR and Molau tests showed that the reactive monomers were grafted onto ABS copolymers and compatibilization reactions took place between PA6 and the AA, GMA and MA modified ABS. TEM result showed that, compared to PA6/ABS blend, the modified ABS copolymers dispersed in PA6 matrix uniformly due to the compatibilization reactions. No obvious difference could be found though the ABS grafted with different reactive monomers. The notched impact toughness showed obvious difference for the blends when the core-shell modifiers contained different reactive groups. GMA and MA modified ABS achieved much better toughening effect than the AA grafted ABS copolymer due to the stronger interfacial reactions. Fracture characterization indicated that PA6/ABS-g-GMA and PA6/ABS-g-MA blends showed higher G_i values according to the Vu-Khanh approach due to the higher interfacial strength. Morphology inside the deformed zone displayed that obvious shear yielding took place in the PA6/ABS-g-GMA and PA6/ABS-g-MA blends and only slight deformation could be found in the PA6/ABS-g-AA blend.

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