Blends of Polyethyleneterephthalate with EPDM through Reactive Mixing

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ABSTRACT: Ethylene-propylene-diene elastomer (EPDM), which is grafted with an isocyanate-containing monomer (HI), was blended with polyethyleneterephthalate (PET) and its morphological, thermal, rheological, and mechanical properties were studied. HI was incorporated onto EPDM backbone through a solution graft reaction. When the PET was blended with HI-grafted EPDM (EPDM-g-HI), the morphologies of dispersed phases showed considerable differences in the aspects of particle size and interfacial adhesion compared with those of a PET/EPDM blend. DSC analysis showed that, when blends are cooled slowly, the PET phase in PET/EPDM-g-HI is somewhat amorphous compared with that in the PET/EPDM blend. The increase in complex viscosity, storage modulus and impact strength of PET/EPDM-g-HI blends enabled us to ensure that the compatibility between PET and EPDM improved through functionalization of EPDM with the isocyanate moiety. These results are mainly due to graft PET-EPDM copolymer in situ formed through the chemical reaction between the isocyanate group of EPDM-g-HI and hydroxyl or carboxyl end groups of PET. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2227–2233, 2000

Key words: isocyanate; morphology; compatibility; chemical reaction; impact strength

INTRODUCTION

Polyesters such as polyethyleneterephthalate (PET) and polybutyleneterephthalate (PBT) have been widely used as engineering thermoplastics for packaging, electronics, and other applications. When blended with other polymers they offer an attractive balance of mechanical and barrier properties.[1] In spite of these desirable properties of polyester, the applications of these engineering plastics are quite limited because of their inherent notch-sensitivity in fracture mode.[2–4] Thus, numerous research groups have studied the impact modification and toughness enhancement of polyester.[5,6] However, most of the studies of polyesters have focused on PBT rather than PET.

Thus, it is of interest to examine specially the issues in toughening PET.

Based on structural considerations, PET is capable of specific interactions (e.g. H-bonding), but, also, chemical reactions with a variety of other polar polymers. Ester groups, and terminal carbonyl and hydroxyl groups, that were inherently present or formed by thermal decomposition, may participate in interchange reactions,[7,8] esterification,[9] amidation, etc. A general approach to impact-modification of condensation polymers like polyester involves incorporation of a reactive functional moiety into the elastomer.[10–12] The in situ graft copolymer formed by reaction with the thermoplastic matrix reduces interfacial tension to improve dispersion during processing, and improves adhesion of the rubber to the thermoplastic in the solid state.[13]

In our previous study, polyolefin that is grafted with an isocyanate group-containing monomer showed appreciable compatibility with poly-

amide, polyester, and other engineering plastics.[14–16] In this study, an isocyanate (—NCO) group was introduced as a reactive functional group onto the ethylene-propylene-diene monomer terpolymer backbone with an expectation to enhance the compatibility and mechanical properties of the immiscible PET/EPDM blend. The isocyanate group has a good reactivity towards amine, hydroxyl, and carboxyl groups. Furthermore, it reacts with the above functional groups rapidly at high temperature during the blend process.[17] In order to investigate the compatibilizing effect of the isocyanate group on immiscible PET/EPDM blends, EPDM was grafted with unsaturated molecules containing isocyanate groups (EPDM-g-HI) and then melt blended with PET. The thermal, morphological, rheological, and mechanical properties of the PET/EPDM-g-HI blends are discussed along with those of the PET/EPDM blends.

EXPERIMENTAL

Materials

PET (Mn = 24,000) was a bottle grade polymer kindly supplied by SK Chemical (Korea). It was always used after drying at 150°C for 15 h to remove sorbed water completely in vacuo. EPDM elastomer (KEP 570P, C_2 content 67 wt %, ENB content 4.8 wt %, Kumho Polychem Co., Korea) having Mooney viscosity of 53 at 125°C was used. 2-hydroxyethylmethacrylate (2-HEMA) and isophorone diisocyanate (IPDI) were purchased from Aldrich Chem. Co. Dicumyl peroxide (DCP, Akzochem), a radical initiator was used as received.

Graft Copolymerization of HI onto EPDM

A functional monomer, HI was synthesized by the reaction of 2-hydroxyethyl methacrylate and isophorone diisocyanate with a molar ratio of 0.95 to 1. The reaction was carried out for 6 hrs in a round-bottomed glass reactor equipped with a reflux condenser, a nitrogen inlet, and a mechanical stirrer at the temperature of 45°C. The molecular structure of functional monomer, HI has been confirmed in our previous study.[15,18]

Grafting of HI onto EPDM was carried out at 120°C in xylene with dicumyl peroxide (DCP) as an initiator. EPDM (20 g) was dissolved in xylene (180 g) and heated to 120°C with stirring under nitrogen atmosphere, followed by the addition of HI (30 phr)/DCP (0.2 phr)/xylene (20 g) solution at once. After completion of reaction over 5 hrs, the reaction mixture was cooled and precipitated by adding sufficient acetone. The product (EPDM-g-HI) was washed several times with acetone to remove unreacted HI and/or residual initiator and then dried at 45°C in vacuo for 24 hrs. Graft reaction was confirmed from FT-IR (Nicolet, Mahgna IR-550) spectroscopy. The graft ratio of HI to EPDM was 3.2% as measured by elemental analysis (Yanaco, MT2 CHN coder).

Blend Preparation

PET and EPDM-g-HI were premixed and then melt blended in a Brabender-like internal mixer. The temperature inside the mixing chamber was 265°C, and the roller speed was 55 rpm. After mixing for 10 min, the blends were cooled slowly under N_2 atmosphere and stored in a drying oven at room temperature. The compositions of the PET/EPDM-g-HI were varied over the ratios of 95/5, 90/10. 85/15, 80/20, 75/25, and 70/30 by weight. Another series of PET/EPDM "bare" blends were also prepared for comparison.

Morphological Observation and Thermal Analysis

For comparison of the morphology of each blend, the cryogenically fractured surfaces were investigated using scanning electron microscopy (JEOL, JSM-6300).

Thermal analysis was carried out using a differential scanning calorimeter (Perkin-Elmer, DSC-7) to study the influence of elastomer containing isocyanate functional group on thermal behavior of PET/EPDM blends. The temperature was raised from 50 to 275°C at a rate of 10°C/min, then two minutes was allowed to erase the thermal history, and then, it was cooled to 50°C at −10°C/min. All measurements were performed under nitrogen atmosphere.

Rheological and Mechanical Properties

The rheological measurements were carried out on a rheometric dynamic spectrometer using parallel-plate geometry (R = 25 mm). In all cases, sample response linearity with respect to strain amplitude was verified and nitrogen gas was used to prevent thermal oxidation. The parallel-plate system was pre-heated to the temperature of the experiment. The sample was put in between the plates once the target temperature was reached.

Strain was maintained at 15% for all samples and the test was carried out at 265°C.

The specimens of the blends for Izod impact tests were molded using Mini Max Molder (SC-183MMX, Custom Scientific Instruments, Inc.). All specimens were stored in a desiccator before testing to avoid moisture absorption completely. Izod bars were tested at room temperature according to ASTM D256 method. All these values of the measurements are the average of 10 runs.

RESULTS AND DISCUSSION

Blend Morphology

The cryogenically fractured surfaces of blends of PET with EPDM and EPDM-g-HI are shown in Figure 1.

In the SEM micrograph of 80/20 PET/EPDM blend (Figure 1 (a)), there exists a very sharp interface between EPDM domain and PET matrix. EPDM domains have a spherical shape and very broad size distribution. Moreover, there are many large voids from which the dispersed EPDM was pulled out. This is typical morphology of an incompatible blend. When, instead of EPDM, EPDM-g-HI is blended with PET (Figure 1 (b)–(d)), the domain size of the dispersed phase is significantly reduced and partial adhesion between dispersed EPDM phase and PET matrix can be observed. As the content of EPDM-g-HI increased, this adhesion between matrix and dispersed phase seemed to be weaker, which is attributed to the increase in volume fraction of the elastomeric domain (Figure 1 (e)).

In this study, the reaction of isocyanate group, grafted on EPDM, and hydroxyl (or carboxyl) groups of PET was a key to improving the compatibility between PET and EPDM. There is no doubt that the chemical reactions between —NCO groups in EPDM and —OH (or —COOH) groups of PET occur during melt processing, which in turn generate in situ graft copolymers (PET-g-EPDM) at the interface. Consequently, these newly formed graft copolymers can cause the interfacial tension to reduce or the interfacial adhesion to increase, acting as compatibilizing agents.[19] This result leads us to expect that the compatibility of the PET/EPDM blend can be improved by modifying EPDM with HI.

Thermal Properties

Heating and cooling thermograms of PET/EPDM 75/25 blend and PET/EPDM-g-HI 75/25 blend are compared in Figure 2.

In the PET/EPDM blends, the cold crystallization temperature, T_{cc}, was not detected. It has been known that amorphous PET, processed with rapid cooling of the melt, crystallizes at T_{cc}, while no crystallization occurs in the DSC heating run for highly crystalline PET formed by the slow cooling at room temperature. Thus the absence of T_{cc} in the PET/EPDM blend was the result of slow cooling at room temperature in our blend preparation. However, there is evidence of T_{cc} in the PET/EPDM-g-HI blend although the melts of these blends were cooled slowly at room temperature. From this presence of T_{cc}, we expected that some parts of PET were amorphous, with low crystallinity due to the chemical bonding between PET and EPDM-g-HI. This chemical bonding caused the PET not to crystallize fully even in the slow cooling process, which induced the cold crystallization of PET near 120°C in the heating run for the PET/EPDM-g-HI.

More clear evidence of chemical bonds between PET and EPDM-g-HI can be found in the DSC cooling run in Figure 2 (b). The EPDM-g-HI also displayed nucleated crystallization from the melt by shifting the crystallization temperature, T_c. However, it should be noted that the crystallization peak in Figure 2 (b) was slightly higher and narrower than that of the PET/EPDM blend, as was often the case when a reactive second component was added to PET.[20] These results confirm that the chemical reaction between isocyanate in EPDM and hydroxyl or carboxyl group in PET occurred.

Rheological Properties of Each Blend

The complex viscosities of PET and EPDM are shown in Figure 3. The viscosities of PET and EPDM show typical Newtonian behavior and pseudo-plastic behavior within the frequency range investigated, respectively.

Plots of complex viscosity (η^*) versus angular frequencies (ω) for the PET/EPDM blend and PET/EPDM-g-HI blend are given in Figure 4.

It is seen that the viscosities of the PET/EPDM-g-HI blends were much higher than those of the PET/EPDM blends at each blend composition. Figure 5 shows the plots of storage modulus (G') versus angular frequencies (ω) for the PET/EPDM blends and the PET/EPDM-g-HI blends. As in the complex viscosity, the PBT/EHI blend shows a strong increase in the storage modulus (G') compared with the PBT/EPM blends over an extended range of frequencies (ω).
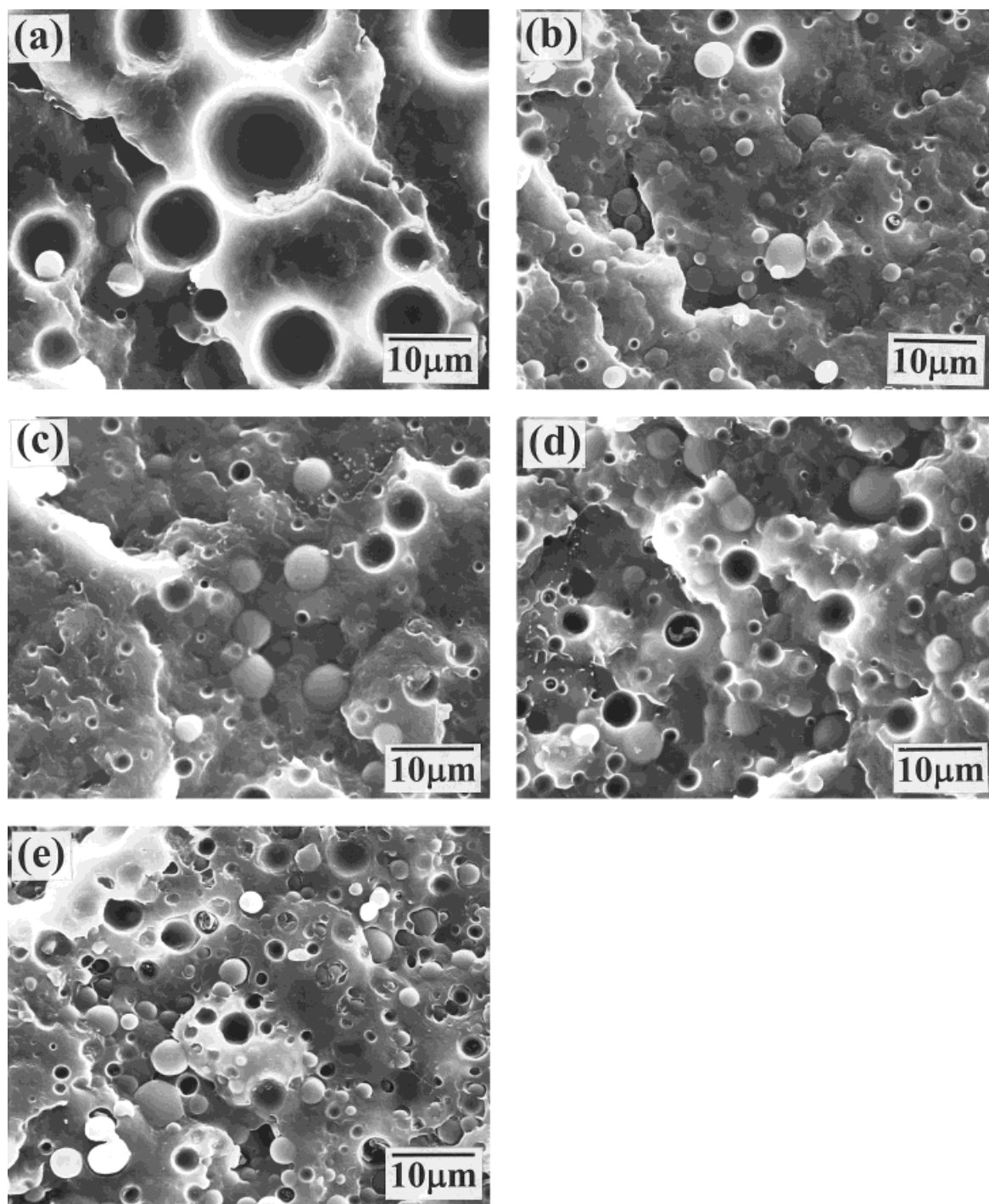
Figure 1 SEM images of uncompatibilized (a) PET/EPDM 80/20, and compatibilized (b) PET/EPDM-g-HI 90/10, (c) PET/EPDM-g-HI 85/15, (d) PET/EPDM-g-HI 80/20, and (e) PET/EPDM-g-HI 70/30, respectively.
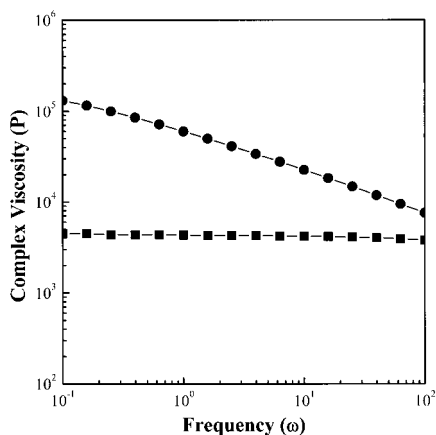
The strong increase of η^* generally occurs either when there are strong interactions between the phases[21,22] or when the blend has an interlocked morphology.[23,24] In this study, a chemical

reaction takes place between —NCO groups in EPDM-g-HI and —OH (or —COOH) end groups of PET during melt blending. Such a chemical bonding will induce a strong interaction between
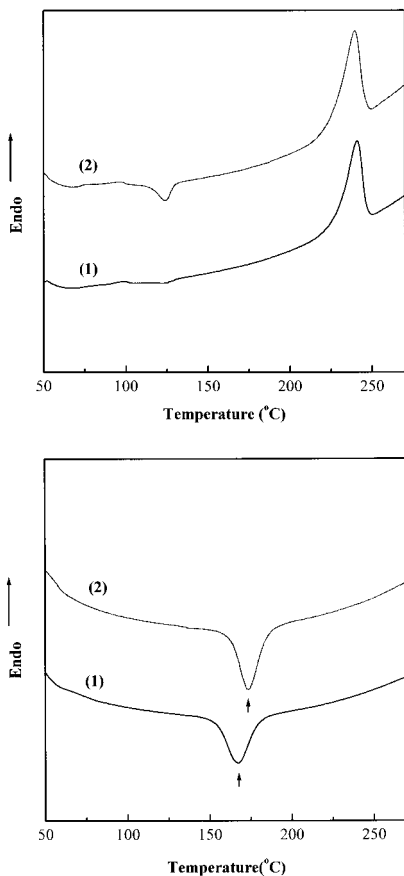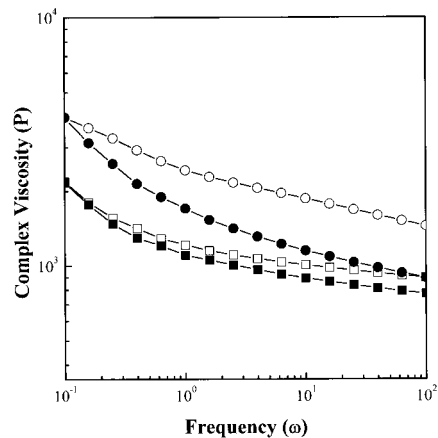
Figure 2 DSC heating (a), and cooling (b) thermograms of (1) PET/EPDM and (2) PET/EPDM-g-HI blend, respectively.

the two phases and the matrix gives more resistance to flow, resulting in a high viscosity. Also, the strong increase of G' in the low frequency
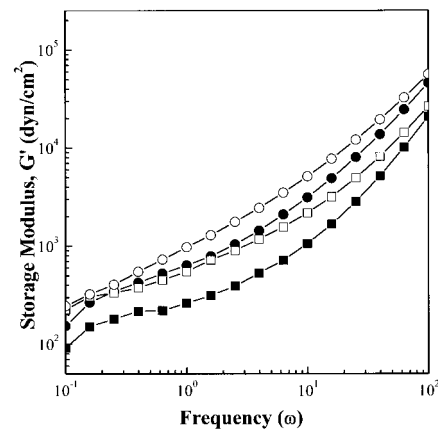

Figure 4 Complex viscosity vs. frequency for PET/ EPDM (closed symbols) and PET/EPDM-g-HI (open symbols) blends: (—■—, —□—) 90/10; (—●—, —○—) 75/25; (w/w).

range results from the molecular build-up by the reaction between the two polymers.

To validate the above-mentioned molecular build-up induced by chemical bonding, the relationship between storage modulus and loss modulus of the blend was investigated. Figure 6 shows the log G' versus log G'' plots for PET/ EPDM and PET/EPDM-g-HI blends. When EPDM-g-HI is used as a blend component, the curve shifts from the viscous-dominant region to the elastic-dominant region, and its slope increase slightly. These findings suggest that EPDM-g-HI react with PET, resulting in some branching and molecular weight broadening.
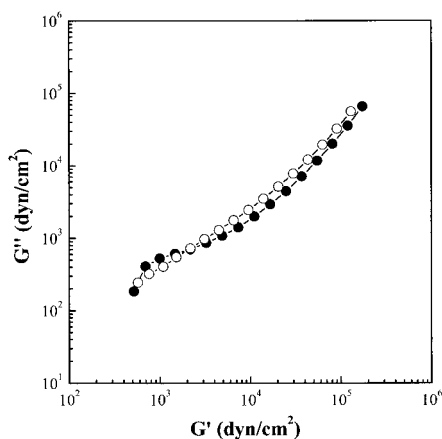

Figure 3 Complex viscosity of PET (—■—) and EPDM (—●—).

Figure 5 Storage modulus vs. frequency for PET/ EPDM (closed symbols) and PET/EPDM-g-HI (open symbols) blends: (—■—, —□—) 90/10; (—●—, —○—) 75/25; (w/w).
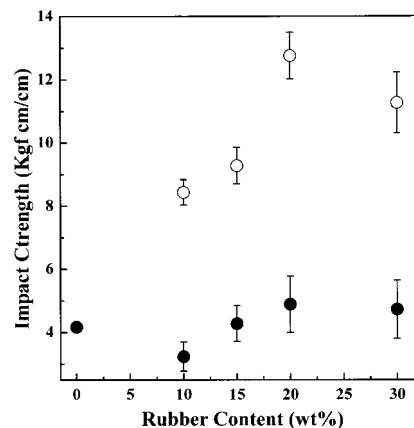
Mechanical Properties

The impact strengths of both compatibilized and uncompatibilized blends are compared in Figure 7. Within the range of rubber content investigated, the impact strengths of PET/EPDM-g-HI blend were higher than those of PET/EPDM. In PET/EPDM blends, there was no dependence of strength on rubber content. On the contrary, there was clear dependence of impact strengths on blend composition in PET/EPDM-g-HI blends. The slight decrease in impact strength at 30wt% of EPDM-g-HI can be related to the overall increase in rubber volume fraction, which in turn may have a negative effect on the impact strength of the blends.

The impact strength of the polymer blends depends on several factors like dispersed particle size, interfacial adhesion, and interparticle distance, etc. As can be seen in Figure 2, it is clear that impact strength of the blends is dependent strongly upon the blend morphology. When EPDM was blended with PET, the dispersed EPDM could not act as an effective stress dispersant due to large particle size and the lack of adhesion between the phases. However, when EPDM-g-HI was blended with PET, the dispersed EPDM phase became small enough to act as a stress dispersant. Moreover, the partial adhesion between the phases would transfer the stress field from the PET matrix to the dispersed elastomer phase effectively. All these results are due to the PET-EPDM in situ copolymer generated during the process.

Figure 7   Izod impact strength of PET/EPDM (closed symbol) and PET/EPDM-g-HI (open symbol) blend.

CONCLUSION

Ethylene-propylene-diene terpolymer containing isocyanate group was blended with PET and compared with blends of PET and EPDM. In view of the blend morphology, dispersed particle sizes of the PET/EPDM-g-HI blends were finer than those of the PET/EPDM blends, and the PET/EPDM-g-HI blends showed homogeneous dispersions and even partial adhesions between the dispersed and matrix phases. This indicates that PET-g-EPDM graft copolymers were generated during the melt processing and acted as a compatibilizer. From thermal analysis, we could confirm that PET in the compatibilized blend has relatively low crystallinity compared with that of a "bare" blend because of the chemical reaction between dispersed phase and matrix. In rheological measurements, increases of complex viscosity and storage modulus were observed for the PET/EPDM-g-HI blends, which were also related to the chemical reaction. In mechanical properties, the PET/EPDM-g-HI blends showed improved notched-Izod impact strengths over the PET and the PET/EPDM blends. From above results, it could be concluded that the isocyanate-modified EPDM has potential for toughening of PET.

Figure 6   Plots of G'' vs. G' of PET/EPDM 75/25 (closed symbol) and PET/EPDM-g-HI (open symbol).

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