

## **Nanoparticles in Flame-Retardant Coatings for Flexible Polyurethane Foams: Effects on Flammability and Nanoparticle Release**

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### **Abstract**

Nanoparticles can effectively reduce polymer flammability; however, the impact of nanoparticles on environmental and health safety is still unclear. The purpose of this study is twofold: (1) to develop and investigate the effect of nanoparticle-rich-coatings on the flammability of polyurethane foam, and (2) to establish suitable techniques for measuring the release of the nanoparticles from the foam under simulated end-use stresses.

The nanoparticle-containing coatings were prepared by Layer-by-Layer self-assembly and included sodium montmorillonite, multi-wall-carbon-nanotubes or carbon nanofibers. The carbon-nanofiber-coated foams showed the highest reduction in flammability (40 % reduction in peak of heat release rate with 1.6 % by mass of nanoparticle) and out-performed 17 flame retardants commonly used in polyurethane foams (31 % reduction with 20 % mass fraction additive in the best formulation).

The nanoparticle release was investigated by exposing the coated foams to simulated chewing and wear-and-tear. The average release values ranged between 0.0003 % and 0.50 % by mass, as referred to the total nanoparticle content. The amount of nanoparticles released by simulated chewing was an order of magnitude greater than from wear-and-tear. Sodium montmorillonite yielded lower release values than carbon nanofibers and multi-walled nanotubes.

### **Introduction [1]**

First item ignited soft furnishings (mattresses, upholstered furniture) are annually estimated to account for 5 % of the residential home fires and a disproportionately

high amount of fire civilian fatalities in the United States (33 %) [2,3]. The fire hazard of these items can be mitigated by using barrier fabrics to protect the highly-flammable polyurethane foam (PUF) or by flame-retarding the polyurethane foam itself [4].

Nanoparticles can significantly decrease the heat release rate of PUF, for example carbon nano fibers (CNFs) homogeneously dispersed into the PUF allowed a reduction of about 35 % in peak heat release rate [5]. As an alternative, nanoparticle-rich films can be applied to the foam substrate as a coating. This approach offers two advantages as compared to the incorporation of nanoparticles into the PUF: first, this post-manufacturing process does not affect foaming and does not require a re-tuning of the formulation; second, the nanoparticles are localized at the surface of the foam struts and membranes, rather than homogeneously mixed throughout the polymer, promoting a continuous percolated network with reduced flammability at a lower nanofiller content [6].

Layer-by-Layer (LbL) assembly has been extensively studied for the past 20 years as a methodology to create multifunctional films [7,8]. LbL thin film coatings were commonly fabricated by alternate deposition of a positively charged layer and negatively charge layer. LbL thin films have been used in an extensive breadth of applications, such as oxygen barriers [9], sensors [10], and, lately, flame-retardants [11].

Potential environmental and health safety issues (EHS) still remain a limiting factor for nanotechnology development and commercialization [12]. Nanoparticle release appears to be particularly likely to occur when nanoparticle-containing coatings are applied to flexible (*e.g.*, textiles) and porous (*e.g.*, foams) substrates due to potential debonding/fracturing of the coating and high specific surface area.

In this work, a flexible open-cell polyurethane foam was used as a substrate and was coated with thin nanoparticle-rich films to potentially generate flame-retardant soft furnishings. LbL assembly was used to prepare alternated multi-layer coatings of nanoparticles (sodium montmorillonite clay, carbon nanofibers or multi-wall-carbon nanotubes) and polyelectrolytes on PUF. In order to enable regulatory agencies to assess the environmental, health, and safety risk of using this nanoparticle-based technology, this project developed the methodology to promote, collect, and quantify nanoparticles release in various conditions.

**Experimental Part** (uncertainties are reported as  $\pm 2\sigma$ ).

*Materials.* All materials were used as-received from the supplier unless otherwise indicated. Branched polyethylenimine (PEI, 25 kg/mol molecular mass, branched) and poly(acrylic acid) (PAA, 100 kg/mol molecular mass ) were obtained from

Sigma-Aldrich (Milwaukee, WI). Baytubes C150HP multi-walled carbon nanotubes (MWCNT, average diameter was 14 nm, length was 1  $\mu\text{m}$  to 10  $\mu\text{m}$ ) were obtained from Bayer MaterialScience AG (Pittsburgh, Pennsylvania). PR-24-XT-PS carbon nanofibers (CNF, average diameter = 100 nm, length was 30  $\mu\text{m}$  to 100  $\mu\text{m}$ ) were obtained from Pyrograf Products Incorporated. Sodium montmorillonite clay (MMT, trade name is Cloisite Na<sup>+</sup>) was obtained from Southern Clay Products Inc. (Gonzales, TX). The standard (untreated) polyurethane foam was supplied by Future Foam Inc.

The polyelectrolyte (0.1  $\pm$  0.03 % by mass) and deionized (DI, < 0.5  $\mu\text{S}$ ) water solutions were prepared as follows. A 2 L glass container was charged with DI water (1.3 L) and PEI (1.3 g  $\pm$  0.4 g). This PEI cationic stock solution was slowly agitated for 6 h at room temperature before using. The preparation of the PAA anionic stock solution was similar to the PEI cationic solution, except PAA (1.3 g  $\pm$  0.4 g) was used instead of PEI. The pH value was 10 and 3 for the PEI and PAA solutions, respectively. The CNF/PEI suspension in DI water was prepared by dispersing CNF powder (0.30 g  $\pm$  0.02 g) in the PEI cationic stock solution (150 mL  $\pm$  1 mL). The suspension was sonicated at 40 W using a Sonics VCX130 sonicator with a 13 mm probe for 1 h. The sonicated suspension was diluted with more PEI stock solution (450 mL) and immediately used for coating. The MWCNTs were first functionalized with PEI (MWCNT-PEIs) to facilitate dispersion and distribution in DI water and to improve retention of the MWCNTs in the coating. Amination of MWCNTs was prepared according to the procedure by Liao et al [13]. The preparation of MWCNT-PEI water dispersion was similar to the CNF dispersion, but the nanoparticle content was doubled (0.60 g  $\pm$  0.02 g). The MMT in DI water suspension was prepared by dispersing MMT (2.6 g  $\pm$  0.8 g) in DI water (1300 mL) and stirring for 12 h.

*CNF-based bilayered nanocoatings.* The substrate was submersed and squeezed four times into the CNF/PEI cationic suspension, and then soaked in the suspension for an additional 5 min. The excess solution was squeezed out and the samples thoroughly rinsed in deionized water. Excess water was removed by passing the substrate through a hand wringer (Dyna-Jet Products, Overland Park, KS). The same procedure was repeated for PAA anionic solution. This deposition of the CNF+PEI layer followed by the PAA layer created a single BL (CNF+PEI/PAA). This procedure was repeated to build a total of four BLs (soaking time 1 min).

*MWCNT-based trilayered nanocoatings.* The substrate was submersed into the PAA anionic solution and after squeezing and releasing the substrate four times, the substrate was soaked in the PAA solution for an additional 5 min. The excess solution was squeezed back into the container. To remove unbound PAA, the substrate was thoroughly rinsed in water. Excess water was removed by passing

the substrate through a hand wringer. The foam was then submersed in a MWCNT-PEI cationic suspension for 5 min and the unbound MWCNT-PEI was removed by rinsing in water. The polymer only cationic layer (PEI only) was then deposited by dipping in a PEI solution for 5 min. This deposition of a PAA layer, a MWCNT-PEI layer, and a PEI layered created a single TL (PEI/MWCNT-PEI/PAA/substrate). The procedure was repeated to build four TLs (dipping time 1 min).

*MMT-based trilayered nanocoatings.* A substrate was submersed into the PEI cationic solution and after squeezing and releasing the substrate four times, the substrate was soaked in the PEI solution for an additional 5 min. The substrate was removed and the excess solution was squeezed back into the container. To remove unbound PEI, the substrate was thoroughly rinsed in water. Excess water was removed by passing the substrate through a hand wringer. The MMT anionic layer was deposited onto the PEI/substrate and the unbound MMT was removed using water. The second anionic (PAA only) layer was deposited onto MMT/PEI/substrate and washed using the same procedures described above. This deposition of a PEI layer, a PAA layer, and a MMT layered created a single TL (PAA/MMT/PEI/substrate). The procedure was repeated to generate a total of eight TLs (dipping time 1 min).

*Sample Characterization.* All specimens were dried in a convection oven ( $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ , 12 h) and stored in a dessicator (at least 3 days) with anhydrous calcium sulfate before weighing and analyzing.

A Head Over Heels shaker (HOH) simulated the type of stresses expected from chewing on a piece of soft furnishing [14]. A polymer coated glass bottle (300 mL) was charged with a simulated saliva solution (100 mL,  $0.9\% \pm 0.08\%$  by mass of sodium chloride in deionized water) and four substrates. Each substrate had a mass of  $0.6\text{ g} \pm 0.06\text{ g}$ . The HOH spun at a rate of 6.3 rad/s (60 rev/min) for 30 min. The four substrates were removed after squeezing all the simulated saliva solution back into the bottle. Four new substrates were added to this bottle and the stressing and squeezing process was repeated. This process was repeated a total of 10 times; therefore, the simulated saliva extraction suspension to be analyzed contained nanoparticles released from 40 PUF. The so-obtained extracted nanoparticle dispersions were dialyzed (Snakeskin pleated tube, 10,000 g/mol relative molecular mass cut-off) to reduce the electrical conductivity from the initial value of  $16,000\text{ }\mu\text{S} \pm 300\text{ }\mu\text{S}$  to less than  $0.5\text{ }\mu\text{S}$ . Sodium dodecyl sulfate ( $0.23\% \pm 0.02\%$  by mass) was added to the dialyzed extracts to stabilize the nanoparticles in the suspensions.

A mechanical pounder simulated the type of “wear and tear” expected from routine use of soft furnishings. The “Pounder” was constructed of a hard plastic (diameter of  $8.9\text{ cm} \pm 0.1\text{ cm}$ ) pounding element that had a slight convex curvature attached

to a pneumatic driven vertical piston. The substrate dimensions (length / width / thickness) for the pounding studies were (10.2 / 10.2 / 5.0) cm  $\pm$  0.1 cm for the PUF. The substrate was placed in a polyolefin bag then secured under the pounder by set screws positioned around the edge of the substrate. A substrate was pounded for 100,000 cycles (approximately 28 h) at 1 cycle/s at a force pressure of (20.7  $\pm$  0.1) kPa. After pounding was complete, the substrate was removed from the bag and the bag was washed with a SDS water solution (100 mL, 0.23 %  $\pm$  0.02 % by mass of SDS in water). The same wash solution was used for 10 experiments; therefore, the 100 mL simulated wear and tear suspension contained the nanoparticles released from 10 substrates.

Foam samples were sputter coated with 4 nm of Au/Pd and scanned with a Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY). A Q-500 GA Thermal Gravimetric Analyzer (TGA, TA Instruments, New Castle, DE) was used with 20 mg  $\pm$  3 mg samples and ceramic pans under nitrogen. The temperature was stabilized at 90 °C  $\pm$  1 °C (30 min) then ramped to 800 °C  $\pm$  2 °C at 10 °C/min. A Lambda 950 Ultraviolet-Visible (UV-VIS, Perkin Elmer, Waltham, MA) spectrometer with a 10 mm ES quartz cuvette was used to measure the absorbance spectrum between 185 nm and 1800 nm for the CNFs and MWCNTs dispersions. An Optima 5300 DV Inductively Coupled Plasma – Optical Emission spectrometer (ICP-OES, PerkinElmer Inc., Shelton, CT) was used to measure MMT content based on Fe and Al ICP-OES intensity. A Cone Calorimeter (Cone, Fire Testing Technology, East Grinstead, United Kingdom), operating at 35 kW/m<sup>2</sup>, was used. The experiments were conducted on (10.2 cm by 10.2 cm by 5.1 cm)  $\pm$  0.1 cm samples with an aluminum-foil pan. All values are reported with a 2 $\sigma$  uncertainty of  $\pm$  5 % in HRR and  $\pm$  2 s in time.

## Results and Discussion

The physical characteristics of the nanoparticle coated substrates are provided in Table 1. The increase in substrate mass due to the coating (coating mass fraction %) was measured using a laboratory microbalance. The amount of nanoparticles in the coating (nanoparticles mass fraction % in coating) and on the substrate (nanoparticles mass fraction % on substrate) was calculated from TGA and microbalance values. The average coating thickness was estimated by SEM of freeze fractured samples (based on 10 measurements of five different samples). The MMT coatings on PUF were significantly thicker (1.00  $\pm$  0.45)  $\mu$ m with a higher nanoparticle concentration in the coating and on the substrate.

Figure 1 shows the SEM micrographs of a CNF coated (top), a MWCNT coated (middle) and a MMT coated (bottom) foam. For each sample, the left image is

showing a pristine sample at low magnification and the right image the same sample after cryo-fracturing at higher magnification.

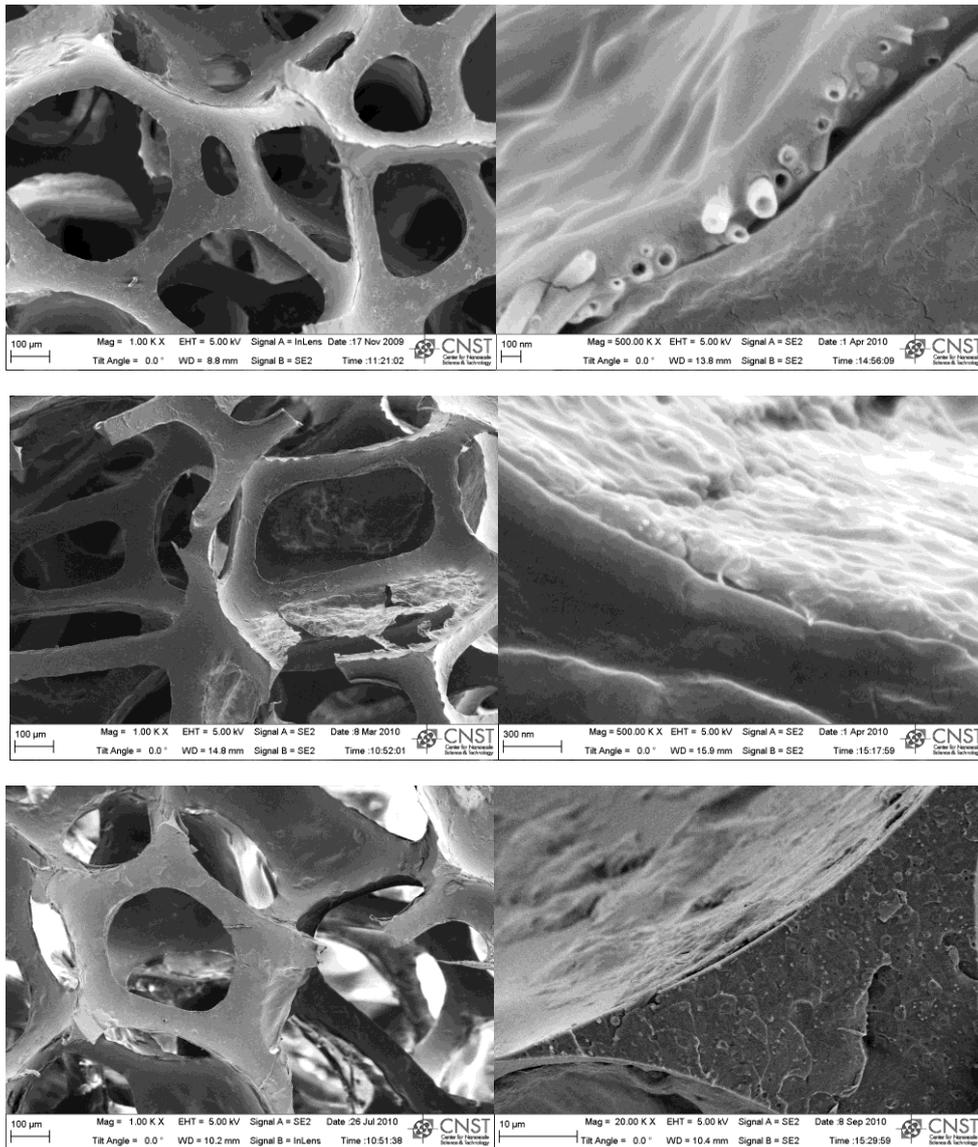


Figure 1. SEM micrographs of a CNFs coated (top), a MWCNTs coated (middle) and a MMT coated (bottom) foam. For each sample, the left image is showing a pristine sample at low magnification and the right image the same sample after cryo-fracturing at higher magnification.

At low magnification, all three samples appear to be homogeneously coated. There is no evidence of residual macroscopic agglomerates detached from the PUF substrate. At higher magnification, the MMT coating appears to be thicker and more heterogeneous with “islands” of clay of few microns in size. The irregular structure of the MMT coated samples is confirmed by the standard deviation values for thickness reported in Table 1 (45 % relative standard deviation for MMT, 11 % for MWCNT and 10% for CNFs).

Table 1. Average physical characteristics of nanoparticle coated PUFs.

	Coating mass fraction (%)	Nanoparticle mass fraction (%)		Coating thickness ( $\mu\text{m}$ )
		on substrate	in coating	
MMT	$3.2 \pm 0.6$	$2.1 \pm 0.2$	$66 \pm 13$	$1.00 \pm 0.45$
MWCNT	$3.4 \pm 0.4$	$1.7 \pm 0.1$	$50 \pm 3$	$0.44 \pm 0.05$
CNF	$3.2 \pm 0.4$	$1.6 \pm 0.1$	$51 \pm 3$	$0.36 \pm 0.04$

These data indicate that CNFs produce the most homogeneous coating in spite of their large diameter (CNF’s diameter is at least one order of magnitude bigger than MWCNT’s diameter or MMT’s thickness).

The cone calorimeter data for the coated and uncoated PUFs are reported in Table 2 and Figure 2. All data are normalized assuming a constant burning area, equal to the initial top surface of the samples. This is a fair assumption for the uncoated PUF, which “melts” and collapses quickly during the cone test, but overestimates the peak of heat release rate (PHRR) in the non-collapsing coated samples. Indeed, the burning surface area in MWCNTs and CNFs coated PUFs at the time to peak (TTP) was higher (at least twice) due to flame spread over the side of the samples. In spite of this artifact, MWCNT and CNF coated samples still had the lowest PHRR. We estimate an additional reduction in the PHRR of at least 50 % for MWCNT and CNF coated samples if this burning surface area effect is accounted for.

Table 2. Cone calorimeter data of the uncoated and coated PUFs.

PUF Sample	PHRR ( $\text{kW}/\text{m}^2$ )	TTP (s)	THR ( $\text{MJ}/\text{m}^2$ )	Residue (% by mass)
PUF	$620 \pm 26$	$75 \pm 3$	$33 \pm 2$	$2.2 \pm 0.1$
CNF	$371 \pm 10$	$27 \pm 2$	$26 \pm 1$	$11.0 \pm 0.4$
MWCNT	$403 \pm 10$	$78 \pm 2$	$26 \pm 1$	$11.1 \pm 0.4$
MMT	$515 \pm 15$	$86 \pm 2$	$31 \pm 2$	$2.6 \pm 0.3$

The carbon-nanofiber-coated foam showed the highest reduction in flammability (40 % reduction in PHRR with 1.6 % by mass of nanoparticle). It exhibited lower flammability than the PUF where CNFs were homogeneously dispersed throughout the matrix (35 % reduction with 4 % by mass of nanoparticle) [5], and the PUFs with any of 17 other flame retardants (halogenated and non-halogenated) commonly used in polyurethane foams (31 % reduction with 20 % mass fraction additive in the best formulation) [15]. These preliminary data indicate that LbL/nanoparticle technologies can be effectively used for developing cost-effective fire safe polyurethane foams.

Fiber-like nanoparticles (i.e., CNFs and MWCNT) appeared to be more effective than platelet-like nanoparticles (i.e., MMT). At a given loading of CNFs, LbL techniques showed an improved performance compared to homogeneous dispersion of the same nanoparticle throughout the polymer matrix. These findings suggest that both the segregation of nanoparticles at the substrate surface and the use of fibers (subject to entanglement) promote the formation of a protective entangled nanoparticle network [6].

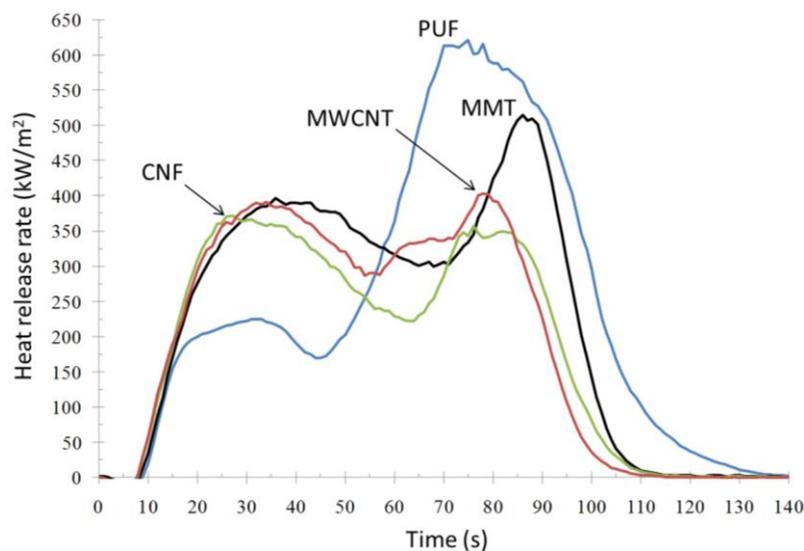


Figure 2. HRR curves for coated and uncoated foams. All data are normalized by assuming a constant burning surface equal to the initial top surface of the samples. The  $2\sigma$  uncertainty is  $\pm 5\%$  in HRR and  $\pm 2$  s in time.

Stress induced release was investigated by simulated “wear and tear” or “chewing” experiments. CNFs and MWCNTs release was quantified by UV-VIS on a Beer’s

law calibration curve constructed from the measured absorbance, at the maximum absorbance band (267 nm), of five prepared nanoparticle calibration suspensions. Clay released during stressing was quantified using a Beer's law calibration curve based on Fe and Al ICP-OES intensity of three MMT calibration standards in diluted nitric acid and DI water.

Table 3 reports the stress induced release data by simulated "wear and tear" and "chewing" experiments. Chewing release was always higher than wear and tear release. MWCNT release in chewing condition was approximately one order of magnitude higher than CNF and MMT release. MMT showed the lowest release in all conditions. No released material collected contained free nanoparticles. The nanoparticles were always encased in the polymer coating matrix.

Table 3. Stress induced release data by simulated "wear and tear" and "chewing" experiments.

	Release by simulated chewing (%) <sup>*</sup>	Release by simulated wear and tear (%) <sup>*</sup>
CNF	0.053 ± 0.005	0.010 ± 0.001
MWCNT	0.46 ± 0.04	0.0085 ± 0.0008
MMT	0.043 ± 0.004	0.00028 ± 0.00002

<sup>\*</sup>Expressed as mass fraction % of the total nanoparticle content in the sample.

## Conclusions

The data collected here indicate that LbL/nanoparticle technologies deserve serious consideration for developing cost-effective fire safe polyurethane foams. This approach offers two advantages as compared to the direct incorporation of nanoparticles into the PUF: first, it is a post-manufacturing process that does not affect foaming and does not require a re-tuning of the formulation; second, the nanoparticles segregation at the surface of the substrate, rather than a homogeneous dispersion throughout the polymer, promotes the formation of a continuous percolated network with reduced flammability at a lower nanofiller content.

Stress-induced nanoparticle-release studies indicated that simulated chewing release was always higher than wear-and-tear release, independently of the type of nanoparticle. MWCNT release in chewing condition was approximately one order magnitude higher than CNF and MMT release. The nanoparticles were always encased in the polymer coating matrix and no released material collected contained free nanoparticles.

Until risk models are developed it is unclear if these exposure values are sufficient to warrant EHS concerns. Ongoing toxicity studies on the extracted solutions are being carried out at Duke University.

## References

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- [1] Certain commercial entities, equipment, or materials may be identified in this document in order to describe an experimental procedure or concept adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the entities, materials, or equipment are necessarily the best available for the purpose.
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