In Situ Polymerization of Olefins with Nanoparticles by Metallocene-Catalysis

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Summary: Exceptionally strong materials could be synthesized by filled polyolefins with nanosized, regid particles or fibers. Metallocene catalysts are excellent tools in the production of tailored microstructures as well as tacticities of polypropylenes. They are soluble in hydrocarbons and therefore can cover perfectly the surface of nano particles. Here multi-walled carbon nanotubes (MWCNT) (diameter 15–25 nm, length up to 50 μm) were used as fillers. Before polymerization, the fillers were separated by ultra sound and then treated with methylaluminoxane (MAO). MAO reacts partially with defects and functional groups of oxidized MWCNT. Catalytically active centers are formed after adding the zirconocenes or other transition metal complexes directly on the CNT surface. The thickness of the polymer layer can be controlled by the monomer pressure and polymerization time. We obtained coatings of 5 to 100 nm. By this method carbon nanotubes can be covered also with isotactic or syndiotactic polypropylene, but also with polyethylene with any molecular mass. The nanocomposites obtained were especially investigated in regard to their crystallization behavior, which depended significantly on the matrix used.

Keywords: in-situ polymerization; MWCNT; nanocomposites; polyethene; polypropene

Introduction

Polyolefins are often filled with organic or inorganic components to increaase their strength, impact resistance, or conductivity and to reduce their permeability of gases.[1] Within the last years, much research in academic and industrial laboratories has focused on the field of polyolefin nanocomposites because of their high potential as materials with novel properties.[2,3] Exceptionally strong materials could be synthesized by the soft polyolefin matrix with nanosized, rigid filler particles. The properties of the nanocomposites are not only influenced by the kind of fillers, but also by the microstructure of the polyolefins and the preparation process. A lot of work has been carried out to use layered silica and metal oxides,[4] clay, self-assembled nano hoehmites,[5] or montmorillonite[6,7] as fillers to obtain composite materials which show a lower permeability for gases. In the past, most composites are commonly prepared by mechanical blending of the particles or fibers above the melting temperature of the matrix desired. Melt compounding of polyolefins with nanoparticles often led to insufficient filler dispersion, especially at high filler contents, what lead to aggregation and intercalation, which in turn decreases the mechanical properties.[8] The shear forces necessary for a good particle separation are often so high, that when applied they degraded the polymer itself.

Another commune method to prepare nanocomposites is mixing in solution, but the solubility of polyethene (HDPE) and polypropene is too little in most low boiling organic solvents. Another problem is the hydrophilic nature of most inorganic fillers and the hydrophobic nature of the polyolefins. The diverseness results in weak

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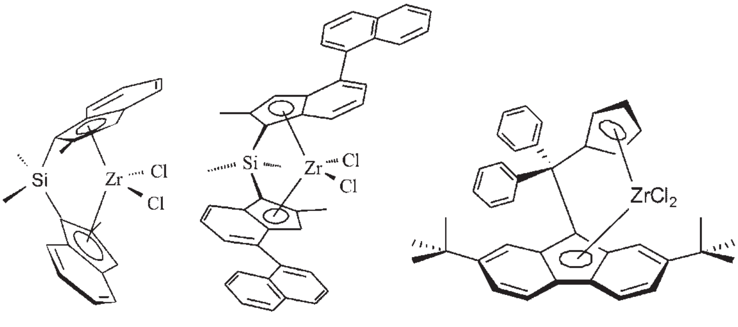
interfacial adhesion between filler and polymer matrix and low mechanical properties. Therefore fillers must be modified by surface active agents. Both disadvantages can be solved by in-situ polymerization where the cocatalyst (e. g. MAO) can be absorbed or anchored on the surface of the nanofillers, changing the surface to a hydrophobic one. As a second step, the activated fillers are used as some sort of heterogenous cocatalysts for olefin polymerization what leads to polymer encapsulated nanotubes.

Metallocene/MAO and other single site catalysts are soluble in hydrocarbons and therefore they can cover perfectly the surface of particles or they can permeate in the layers of layered silicates and oxides. Aluminum flake filled polyethylene was first prepared by this procedure showing high thermal but low electrical conductivity.[9,10]

Metallocene/methylaluminoxane catalysts are highly active for the production of precisely designed polyolefins and engineering plastics.[11–14] Especially zirconocene and half sandwich titanium complexes have opened a frontier in the area of new polymer synthesis and processing. The transition metal complexes can be activated by MAO but also by other bulkey cocatalysts such as perfluorochenylborate. By changing the ligand structure, these catalysts allow the synthesis of polymers with a tailored microstructure tacticity and stereo regularity as well as new copolymers with superior properties such as film clarity, tensile strength and lower extractables. With these single site catalysts the in-situ polymerization boosts in combination with an effective pre-treatment of the filler, the physical and chemical properties of the resulting composite materials. For example dramatically improved stiffness with a neglible loss of impact strength, high gas barrier properties, significant flame retardancy, better clarity and gloss as well as high crystallization rates were found. Even low nano particle contents are already sufficient to obtain new or modified material characteristics, especially on the Crystallization behavior. The crystallization behavior (crystallization temperature (T_c), the melting temperature (T_m), and the half-time of crystallization ($\tau_{0.5}$) of polymers plays an important role during the processing of these materials. By reduction of the cooling time required for part solidification, cycle times can be shortened. This can be accomplished by the incorporation of nucleating agents into the neat polymer which speed up the crystallization. The crystallization kinetic influences the morphology, which in turn affects the mechanical and physical properties of a semi-crystalline polymer like PP or PE.[15,16]

Preparation Method

The in-situ polymerization has been successfully used to incorporate a various number of nanofillers e.g. carbon black (CB), carbon nanofibers (CNF) and different types of carbon nanotubes (CNT). All



Cat. 1 **Cat.2** **Cat.3**

Figure 1.

Catalyst used. Cat 1: iPP (Mw ≈ 350 000 g/mol). Cat 2: iPP (Mw ≈ 1 400 000 g/mol). Cat 3: sPP (Mw ≈ 400 000 g/mol); PE (Mw = 800 000 g/mol).

incorporated fillers, neither the inorganic nor the organic, showed any deactivating effects on the catalysts. A further advantage of this method is the versatility of metallocene/MAO catalysts, which allow the tailoring of the polymer microstructure, and therefore of the composite matrix, by the utilization of a metallocene with a suitable structure.[17] Metallocene/methylaluminoxane catalysts are also excellent tools in the production of certain molecular masses and, in case of polypropylenes, tacticities. PP with an isotactic, syndiotactic or atactic configuration can be obtained by using C_2-, C_{2V}- or C_s-symmetric zirconocenes.[18,19]

The molecular weights were not influenced by the nanoparticles. For the production of an (ultra) high molecular mass matrix (UHMWiPP) *rac*-dimethylsilylbis (2-methyl-4-(1-naphthyl)indenyl)zirconium dichloride (**cat 2**) was used, but necessarily requires the pre-treatment described in Figure 2. The isotactic pentads were 97 ± 2% and the molecular mass about 1 400 000 g/mol. C_s-symmetric metallocenes, such as Di(paramethylphenyl)-methyl (cyclopentadienyl(2,7-bis-tert-butylfluorenyl)) zirconium dichloride (**cat 3**) can be used for sPP matrices.

In all cases, the polymerizations were performed in dry toluene at 30 °C. The first step of preparation was the absorbance of MAO onto the filler surface. The second step was the addition of a transition metal compound and the formation of catalytically active sites on the surface and the addition of monomere.[20] The gas pressures were about 2 bars.

The viscosimetric molar weights were determined by viscosimetry at 408 K using a Ubbelohde viscometer (capillary 0a, $K = 0.005\ mm^2/s^2$) as a 1 mg/ml solution in 50 ml decahydronaphthalin. Melting and crystallization temperatures (T_m/T_c) as well as the half-time of crystallization ($\tau_{0.5}$) were determined by differential scanning calorimetry (DSC) with a DSC 821e (Mettler Toledo) from the second heating cycle at a heating rate of 20 $K \cdot min^{-1}$. Electron microscopy was performed on a Leo 1530 FE-REM (SEM) and on a JEOL JEM-1011 (TEM).

A homogeneous distribution and a good interfacial adhesion are crucial for the successful preparation of nanocomposites but often difficult to achieve. Especially fillers with high aspect ratio like carbon nanotubes tend to stay aggregated during

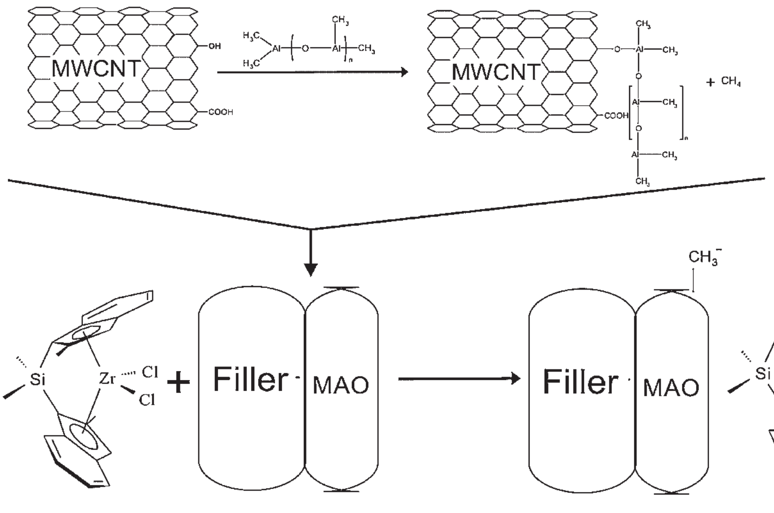


Figure 2.
Hydroxyl or carboxyl groups present on MWCNT can react with added MAO to form a heterogeneous cocatalyst. The MAO is now anchored, but still able to form an active complex with the metallocene. Therefore the polymer is growing directly from the surface.

the polymerization process because of their high surface energy and numerous π-π electron interactions between the tubes. The filler had to be pre-treated in a way to separate it, e.g. by ultrasound, and to prevent it from deactivating the catalysts. While spherical and particles with low aspect ratio could be separated quite well by simply sonication with ultrasound with low energy input in a low viscosity medium like toluene, the separation of high aspect filler particles is more difficult and required a much higher energy input. A too high energy input can lead to an irreversible damage of the tubes.[21]

After the ultra sonic forced separation of the particles we immobilized MAO by establishing a covalent bonding between MAO and hydroxyl- and carboxyl-functionalized filler surfaces, such as silica balls (monospheres®) or oxidized MWCNT, though impregnating the tubes for 24 h with MAO at rt. Purified and oxidized nanotubes are bearing functional groups such as hydroxyl or carboxyl on their surfaces, especially at their open caps. These groups can react with MAO by the formation of covalent oxygen aluminum bond, without deactivating effects for the catalysts. The MAO is now anchored, but still able to form a catalytically active complex with the metallocene (Figure 2).

Thus, a heterogeneous cocatalyst is formed. This method causes a lower activity during the coating process, because unreacted and dissolved MAO was removed by filtration which in turn caused low [Al]/[Zr] ratio, but it even allows an ultrasonic treatment of the impregnated nanotubes! And this ensures optimal pre-conditions for an extremely good filler dispersion within the finished material. After completion of the coating phase, the activity can be raised to a normal level by the addition of MAO. Especially for ultra high molecular mass matrices this method provided outstanding results.

Results and Discussion

The homogeneity of the MWCNT cover by polyolefins depended on the number of defects on the surface of the tubes. If there are only few defects as in the case of pristine MWCNT, only few active centers were formed after the addition of MAO and zirconocene. To increase the number of defects, the tubes are oxidized with HNO_3/H_2SO_4 for 90 minutes at 120 °C.[22,23] After this, they were washed and dried.

After this oxidation, there are many functional groups on the outer layer of the multi-walled carbon nanotubes. Most of them are concentrated at the caps of the tubes. From Figure 3 can be seen that the polymerization starts at the ends of the

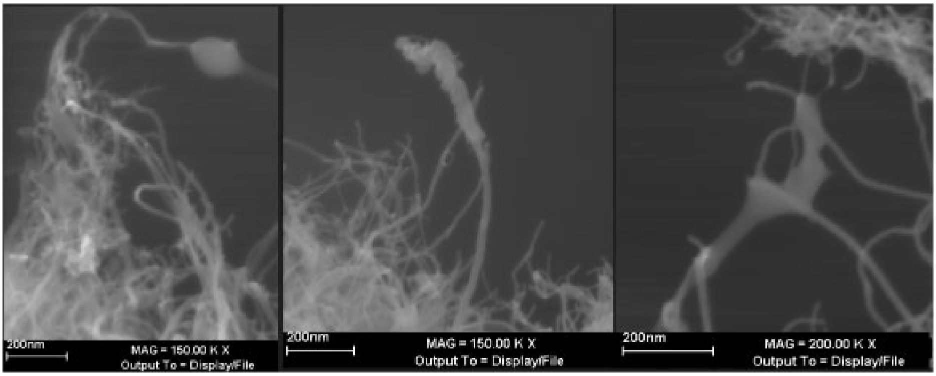


Figure 3.
SEM micrograph (magnification x 150 000–200 000) of ox. MWCNT after 15 – 20 min of coating. Polymer accumulated at the edges of the nanotubes, where MAO was anchored the most.

tubes. The layer thickness was controlled by the amount of anchored MAO and the polymerization time.

In Figure 4 CNT encapsulated by a high molecular weight isotactic polypropylene generated by **cat 2** can be seen. The detailed micrograph on the right shows the different layers (about 20) of the tube with a distance of 0.3 nm. The nanotube was covered with a HMWiPP-film of about 8 nm thickness. Even the open cap of the MWCNT was encapsulated too. This resulted in an excellent adhesion between tube and polymer.

The melting temperature of all Polyolefin/CNT nanocomposites was neither influenced by the presence or the type of nanotubes, nor their amount. The average melting temperature depended only on the matrix used. T_m was $160 \pm 1\,^\circ C$ for HMWiPP, $155 \pm 2\,^\circ C$ for conventional iPP, $143 \pm 1\,^\circ C$ for sPP and $137 \pm 1\,^\circ C$ for PE basing composites. All melting temperatures were in the range or marginal above of the particular Polyolefin.

In contrary to T_m the effect on the crystallization temperature was in all cases much more emphasized and since it is known that CNT act as nucleating agents, improvements on the crystallization behavior were expected.

Pure high molecular mass iPP had a T_c of about 117.8 °C. The addition of only 0.9 wt% MWCNT led to an increased crystallization temperature by 5 K (Figure 5). At higher filler contents the enhancement of the crystallization temperature raised rapidly to a certain extent of 7 to 8 K above pure iPP which was reached at a MWCNT content of about 3 wt%. The Tc's of higher filled composites were in the same range. Common iPP showed the same trend. The neat material had a Tc of 111 °C. The addition of only 0.1 wt% MWCNT led to an increased Tc by 4 to 5 K. The maximum enhancement of the crystallization temperature was 9 K above pure iPP and was reached at a nanotube content of 1.5 to 2 wt%. The effect on syndiotactic polypropene was even more emphasized.[24] It could be raised by 6 to 15 K at MWCNT contents of 0.1 to 0.9 wt%. The behaviour of PE/MWCNT nanocomposites was considerably different (Figure 5).

All incorporated amounts of CNT increased Tc of the resulted nanocomposites in comparison to neat PE. The reference PE had a Tc of about 114 °C; 0.6 wt% MWCNT led to an increase of about 1.5 K und a maximum was found at 5 wt% filler content, which caused an increase of 3.7 K.

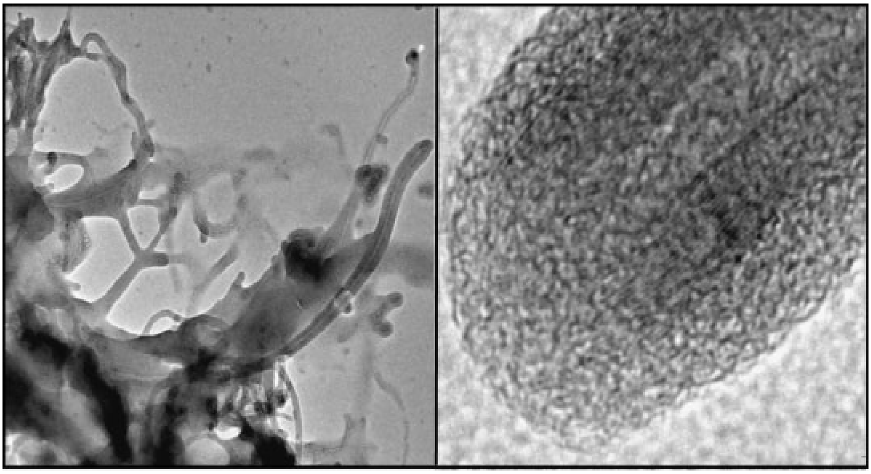


Figure 4.
TEM image of polymer encapsulated ox. MWCNT. Almost every nanotube is covered by a thin and homogenous in-situ grown HMWiPP film (left). On the right: TEM images (magnification x 400 000) of an ox. MWCNT, coated by a thin polymer film (≈8 nm).

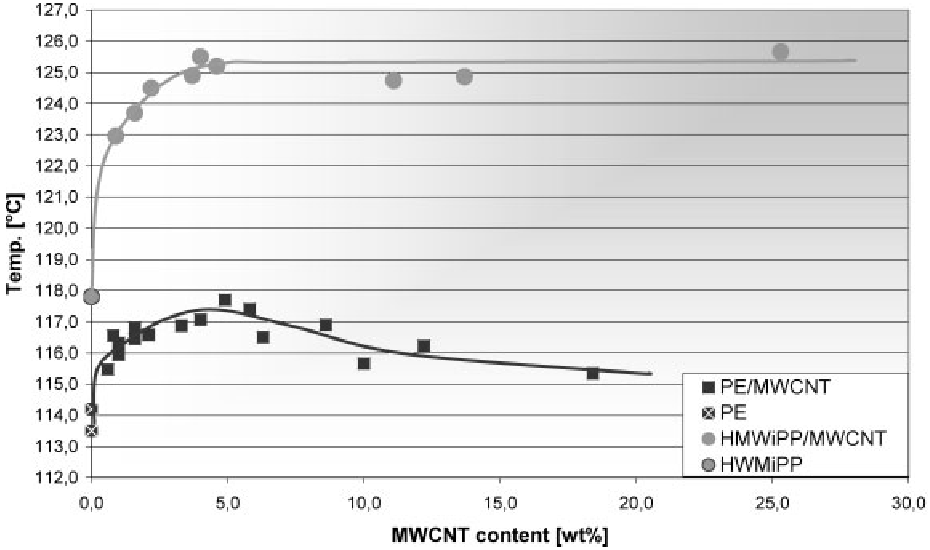


Figure 5.
Crystallization temperature in regard of the filler content for an iPP and PE based nanocomposite. All PP basing nanocomposites showed basically a similar developing of Tc values, independently neither of their tacticity nor their molecular mass, while the composites with a PE matrix showed a maximum in Tc at about 5 wt% incorporated nanotubes.

Higher filler loadings led to lower Tc's, but which were still leveled above as what was found for pure PE. For example a PE/MWCNT nanocomposite containing 18.0 wt% of CNT had a Tc of 115.4 °C. In comparison to PP/MWCNT composites the effect on the PE matrix was not a quarter as good distinctive (Figure 5).

The half-time of crystallization, representing the CNT nucleating effect, was for PE/MWCNT not as pronounced as for comparable PP based nanocomposites.

However in Figure 6a it can be seen that the half-time of crystallization was reduced significantly with low amounts of nanotubes at a temperature of 123 °C. There was a reduction of $\tau_{0.5}$ in the range of 0–6 wt% with a minimum at ca. 4 wt% filler content. At the minimum the solidification of 50% of the crystallizable material was about 2.5 times faster then neat PE. Larger amounts of MWCNT seemed to decelerate the crystallization until (MWCNT content >10 wt%) it was as slow as for pure PE. It can be said, that PE, which inherently crystallizes faster than PP was much more influenced by the presence of the nanotubes and their amount.

All types of PP basing nanocomposites showed basically a similar developing of $\tau_{0.5}$ values, independently of their tacticity or molecular weigh. It depended preliminary on the quality of the CNT dispersion in the matrix. At the temperatures shown pure iPP did not crystallize or it took too long to provide reliable results, on the other hand the crystallization of the obtained nanocomposites was too fast in the range of temperature where iPP gave adequate results.

The half-time of crystallization of all PP/MWCNT nanocomposites was reduced significantly with low amounts of CNT at a wide range of (isothermal) crystallization temperatures (Figure 6b). In contrast to that, PE based nanocomposites did not crystallize at higher temperatures than the pure polyethene.

However, at 130 °C, for instance, $\tau_{0.5}$ was 8 min for an iPP/ox.MWCNT composite with 0.1 wt% filler content, while 2.5 wt% reduced $\tau_{0.5}$ to only 1.5 min. When the percentage of MWCNT was raised to more

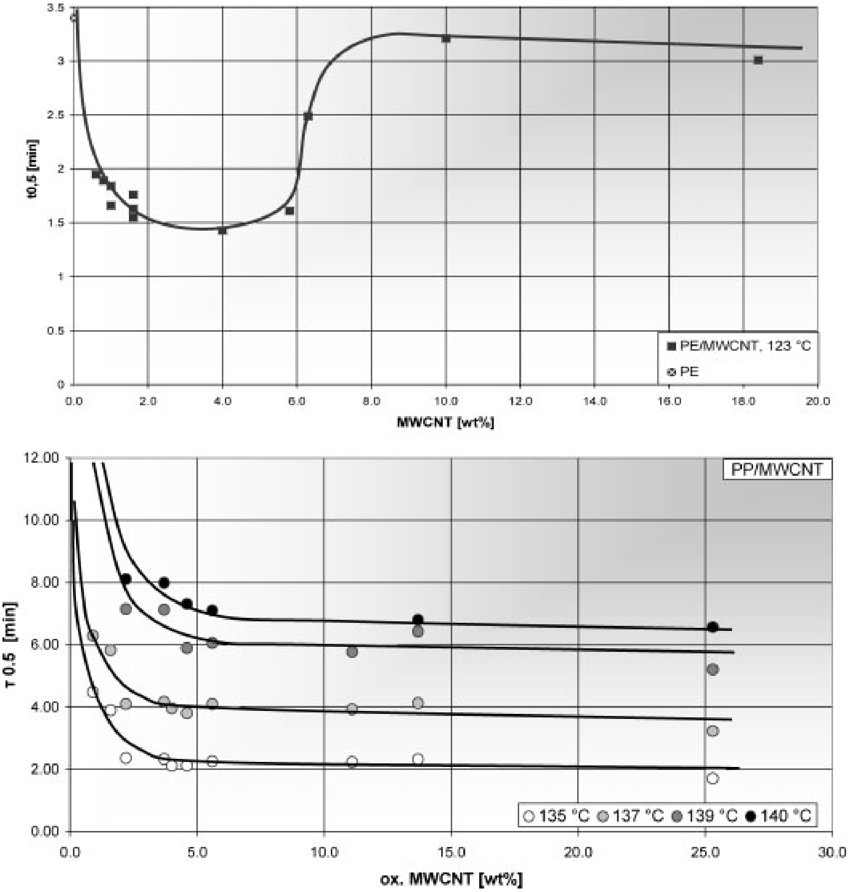


Figure 6.

Half-time of crystallization of PE/MWCNT and HMWiPP/ox.MWCNT nanocomposites in dependence on the filler content at different isothermal crystallization temperatures. PE and its composites crystallized only at 123 °C, while PP basing nanocomposites gave reliable results over a wide range of temperatures.

than 3 wt% no further reduction of $\tau_{0.5}$ was obtained anymore. The half-time of crystallization in regard of the filler content of HMWiPP/MWCNT also showed an exponential decrease until a saturation of the nucleant effect was reached and $\tau_{0.5}$ remained on a constant low level unattached by a further increment of the CNT content. It must be noted that the influence of CNT on $\tau_{0.5}$ is still controversy discussed in literature.[20,24–30] The half-time of crystallization of CNT nanocomposites was found to decrease in all cited references with regard to the pure polymers, independently of which polymerization technique was used. Wagner et al.[26] showed that MWCNT acted as α-nucleating agents in iPP. Valentini et al. also reported a reduction for PP/EPDM/SWCNT nanocomposites prepared by melt compounding. But in this case $\tau_{1/2}$ showed a minimum at 0.5 wt% SWCNT.[27] The authors attributed this to the fact that the SWCNT nucleate crystallite growth on one hand, but hinder the spherulite growth on the other hand.

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