Properties of in-situ filled Polyethylene*

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Summary: Polyethylene-filler composites (kaolin, $BaSO_4$, and TiO_2) have been prepared by in-situ polymerization using a metallocene catalyst and by extrusion mixing in the melt. TiO_2 influences the polymerization process. In-situ polymerization was found to be advantageous with respect to encapsulation, dispersion of the filler particles leading to improved mechanical properties, except for TiO_2 containing composites. No significant influence on crystallization was observed.

Introduction

Engineering plastics are frequently modified by filling with inorganic particles. These solid additives can act as colorant, stabilizer, diluent, or mechanical reinforcement depending on their chemical nature, size, shape, and concentration. A frequently used technique to prepare these composites is melt-mixing. Agglomeration of the particles, insufficient encapsulation by the polymer or weak adhesion of filler and matrix can be observed resulting in a composite which does not show the desired material's properties. Alternatively, the composite can be formed *in-situ* when the polymerization of the organic matrix is carried out in the presence of filler dispersed in the polymerizing phase. This is possible, for example, using (homogeneous) metallocene catalysts[1)] in an organic solvent. Expected improvements are a more homogeneous distribution of the

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filler particles within the polymer matrix and a stronger polymer/filler adhesion because of a better wetting of short, growing chains compared with a high-molar mass, highly viscous polymer melt. A certain fraction of the dissolved catalyst is adsorbed by the filler surface. The fraction of residual catalyst in solution depends on the amount of filler and its activity. Consequently, most of the polymer chains will start growing from the surface of the filler, in particular at high filler concentrations, so that a good encapsulation of the particles by the polymer can be expected. Even in the interior of filler clusters, in their voids, fissures and cracks, a good polymer surface coverage can be expected, which will contribute to the mechanical stability of the clusters. There is no wetting of the filler surface by polymer when in-situ techniques are used since the polymer chains start growing already from the surface. Interaction of the filler with the chemistry of chain growth, however, could become a problem.

Early attempts of in-situ polymerization using Ziegler-Natta-type catalysts[2,3] were reported by Hider and Marchessault[4], Herman et al.[5], Donnet et al.[6], Kruse[7], Howard[8], Speakman et al.[9], and Dyachkowskii[10]. However, the obtained yields were rather low, there was not enough polymer volume and insufficient encapsulation of the filler by the polymer was observed. A two-catalyst system was introduced by Reichert et al.[11], the break through, however, was obtained after introduction of metallocene catalysts[1], as proven by Kaminsky and Zielonka[12,13]

We have prepared composites of polyethylene (PE), $BaSO_4$, TiO_2, and kaolin by melt-mixing and in-situ polymerization and have analyzed their properties calorimetrically (DSC), dynamic-mechanically (DMTA), and with nuclear magnetic resonance techniques (NMR) to investigate possible advantages and disadvantages of the methods. Some results of the NMR investigations have been published by Hillebrand et al.[14]

Materials and Methods

The following filler types were used:

Table 1: characteristics of the filler

filler type	average filler diameter/μm	specific surface m^2/g	density g/cm^3	producer
Kaolin	≤2	≅ 21	2.62	Thiele Kaolin Company
$BaSO_4$	0.1	> 25	4.4	Sachtleben Chemie GmbH
TiO_2	0.1	≅ 50	4.0	Sachtleben Chemie GmbH

The TiO_2 contained 99% rutil and was surface-modified with Al_2O_3 and ZrO_2. A previously organic surface modification had been removed thermally before use. All fillers were dried and degassed thermally under vacuum conditions and stored under Ar until used.

The solvent toluene was distilled from $NaAlEt_4$ in an Ar-atmosphere. The catalyst used was bis(cyclopentadienyl)zirconiumdichloride (STREM), and a 10% Methylaluminoxan solution in toluene (Witco) was used as delivered (4.6%-5.6% Al, average molar mass 800 g/mol – 1,200 g/mol).

Polymerization was performed[‡] at 25°C and 1,000 hPa ethylene pressure. The filler was dispersed in toluene under protective gas and methylaluminoxan was added. After a pre-reaction time the solution was further diluted and the catalyst – a pre-reacted solution of the metallocene and methyaluminoxan in toluene – was added. Polymerization was finally started after an additional pre-reaction time, degassing and increase of stirring to 1,400 rpm. The product was washed with CH_3OH and HCl and vacuum dried. With a density ρ (25°C) = 0.94 g/cm^3 the polymers are at the lower limit of high density polyethylene (HDPE).

[‡] We are indepted Prof. Fink and his team at the Max-Planck-Institut für Kohlenforschung, Mülheim, Germany for providing laboratory equipment and support.

Extrusion-mixed samples were mixed in a twin-screw extruder[§] with conical, co-rotating screws at 190°C/200 rpm under N_2 after addition of stabilizer Rgafos 168 (Ciba-Geigy), and PE was used that had been synthesized as described above but without filler. All mixtures were compression-moulded at 165°C/14,000 hPa/5 min and cooled down at 10°C/min.

Calorimetric analysis (DSC) were performed on a Perkin-Elmer DSC-2, heating rate and cooling rate 10°/min. A ISI 60 (International Scientific Instruments) microscope was used for **scanning electron microscopy**[**] (SEM) after vapour deposition of W on fracture surfaces. **Dynamic-mechanical analysis** (DMTA) was done on a ATM 3 torsional pendulum (Fa. Myrenne, Germany) at a constant frequency of 1 Hz, monitoring the free decay of the oscillation caused by a 1° deflection of the specimen over a temperature range from –180°C...100°C at a heating rate 1°C/min. The filler content of the samples was determined thermogravimetrically on a Perkin-Elmer TGA 2. The following samples were prepared:

Table 2: composition of the samples

Sample	In-situ polymerized Filler content %(v/v)	Extrusion mixed Filler content %(v/v)
PE/kaolin	5.0	5.1
	12.0	-
	35.4	35.2
PE/$BaSO_4$	5.2	-
	11.3	-
	35.1	34.2
PE/TiO_2	5.2	-
	12.1	-
	35.2	-

[§] The compounding was kindly performed with the assistence of Dr. Klaas Remerie, DSM, Geleen, NL.

[**] We thank Mr. Bongard, Max-Plank-Institute für Kohleforschung, Mülheim, Germany, for conducting the SEM investigations and the photographic pictures.

The average composition is accurate to +/- 0.4%(v/v), determined from 4 independent analysis of the batches.

Results and Discussion

Melting and crystallization of the composites were analyzed calorimetrically characterizing the transition temperature at the onset of the specific heat capacity peak. Although the produced PE can be addressed as a high density PE (HDPE) the degree of crystallization calculated from DSC using the specific heat of fusion for entirely crystalline PE $\Delta_m H$ = 293 J/g was rather low: 73% for freshly synthesized pure PE prepared material and 55% after a heating and cooling cycle with 10°/min. The crystallinity of the fresh reactor composites were almost the same for all samples around 70%. Second and third measurements of the samples showed a lower degree ranging from 61% to 42%. Crystallinity usually was found to decrease with increasing filler content. There were, however, no significant differences between the samples taking into account the experimental error of +/- 5%. The only exception was the highly filled TiO_2 composite. These preparations showed the same high crystallinity of about 70% for the reactor powder but only 46% for the melt extruded composite. After the first melting however, crystallinity of all TiO_2 composites was usually as low as 42%. The high crystallinity of the virgin reactor powder is caused by stress-induced crystallization and additional amounts of moncline PE[15]. Melting (onset of the DSC trace) started at about 127°C for the in-situ preparations and melt mixed samples regardless type and amount of filler except highly filled TiO_2 preparations (120°C, second heating). The crystallization does not show significant nucleating activities by any of the fillers. The low crystallinity of TiO_2 containing in-situ preparations can be caused by interaction of the TiO_2 surface with the polymerization process, and the synthesis of branched PE chains, see also below.

Dynamic mechanical analysis of the pure PE in principle shows 3 dispersion processes - α, β, and γ, see Fig. 1. With decreasing temperature the strongest process (α-process) has been attributed to a longitudinal chain transport in the crystalline phase caused by 180° rotations[16]. The glass transition has been identified by Illers as the β-process[17] which commonly is nearly invisible in linear, highly crystalline PE but can be forced by

swelling the sample. The γ-process is composite in structure and can be attributed to kink inversions[18] or molecular motions in longer loops caused by local reorientations of short methylene units in crystalline phases, motions near crystalline defects[17]. α- and γ-process are clearly activated Arrhenius processes while the β-process shows a WLF-behaviour (WLF ≡ Williams-Landel-Ferry) and has a highly cooperative character, so that steric hindrances can affect the β-process considerably. The branched low density PEs (LDPE) do show the β-process but it is absent in linear PE (LPE) of sufficiently high crystallinity indicating that state of order and molecular dynamics in these disordered phases of LPE and HDPE is qualitatively different from the behaviour of common amorphous polymer phases. The transition from the glassy state - with its predominantly localized molecular motions - to the melt with its large segmental motions can be described by almost one group of relaxation modes. The presence of crystallites extends this to a broader range resulting in a more continuous character of the transition.

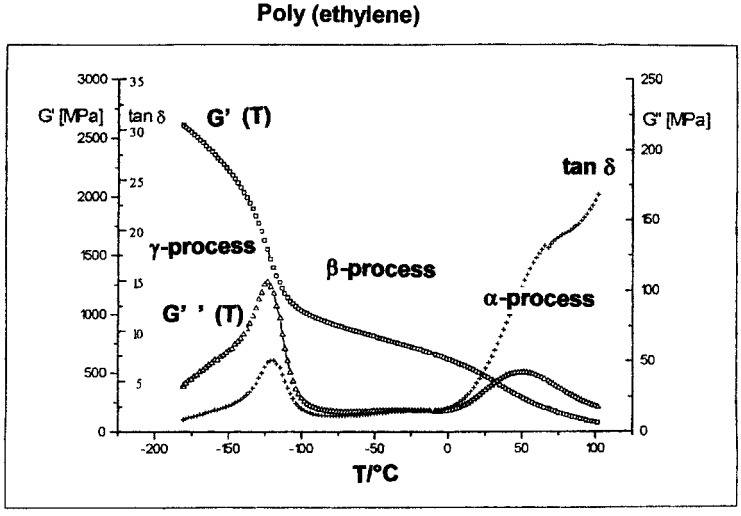


Fig. 1: relaxation processes in pure PE as revealed by a dynamic-mechanical experiment at a frequency of 1Hz. G' is the storage (shear) modulus, G" is the loss modulus and tan δ is the loss factor with the loss angle δ, i. e., the phase shift between shear stress and

shear deformation. The β-process at about –40°C is relatively weak. For further explanations see text.

The most important effects of filler on the visco-elastic properties of polymers are caused by occupation of a volume fraction of the composite by the rigid inflexible particles. Surface near polymer-filler interactions can result in a layer of bound polymer around the filler with properties different from those of the undisturbed matrix polymer[19, 20]. The filler can be fine disperse or can form clusters. High deformation forces below the glass transition of the polymer can cause a relative displacement of filler particles in a cluster resulting in friction and less energy elastically stored. Beyond the glass transition temperature the whole cluster now appears to be entirely rigid and can therefor increase the modulus by immobilization of neighbouring polymer chains[21]. The same type of mechanism can act at the γ-transition and thus explain the step observed in the relative storage modulus $G'_{composite}/G'_{polymer}$ near –125°C, see Fig. 2.

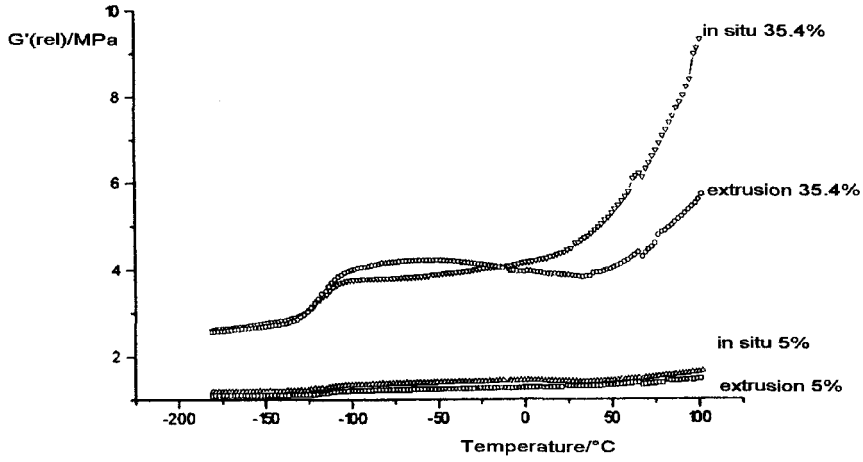


Fig. 2: relative storage modulus $G'_{composite}/G'_{polymer}$ for low and high kaolin content prepared by the different techniques as indicated. The decrease of the curve of the highly filled melt mixed material beyond –50°C is probably caused by increased filler-filler friction.

The decrease of the modulus caused by the onset of the γ-relaxation process therefor appears stronger compared with an unfilled system. The strong increase of $G'_{composite}/G'_{polymer}$ with temperature observed in highly filled (kaolin and $BaSO_4$) composites – Fig. 2 – is caused a) by the fact that the modulus of the polymer decreases in the molten state while that of the filler remains rather constant[22], and b) by the stresses caused by differences in expansivity between polymer and filler[23]. The effects of kaolin content and preparation method on the storage and loss modulus are shown in Fig. 3 and Fig. 4. Low filler content shows a higher storage modulus for the in-situ preparation up to 100°C, while the highly filled composite shows a markedly higher storage modulus at temperatures beyond the γ-process. This indicates a better encapsulation of the filler particles for the in-situ preparation in general as well as for agglomerations and a stabilization of the clusters at higher temperatures. NMR-experiments showed[14] that high concentrations of the active filler kaolin support a certain defect motion in the orthorhombic crystalline phase of PE that is already working at room temperature. In contrast to the γ-process this molecular motion is not associated with a transport of matter.

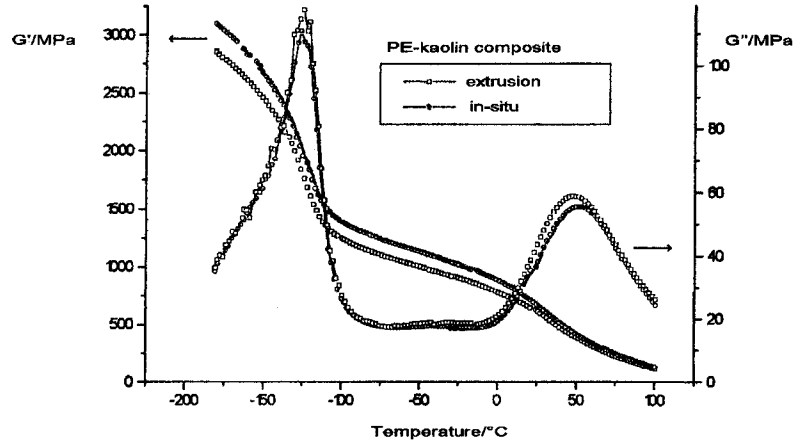


Fig. 3: in-situ and melt mixed PE-kaolin composites, 5% filler.

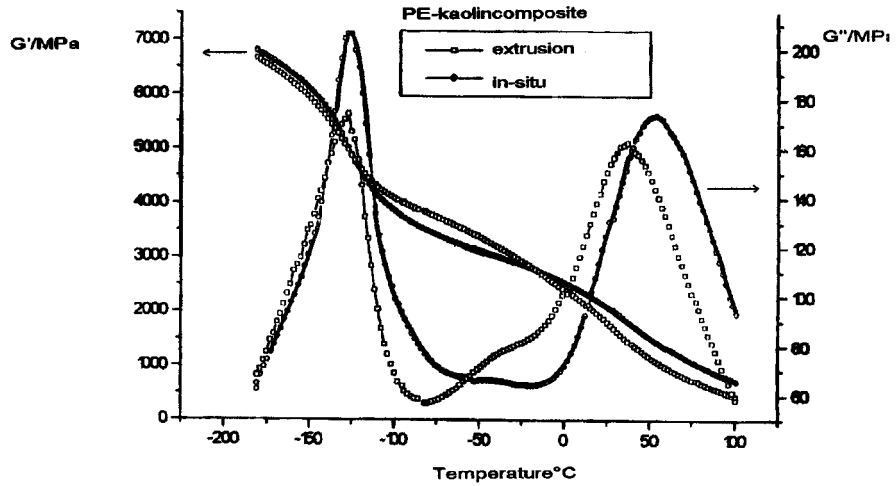
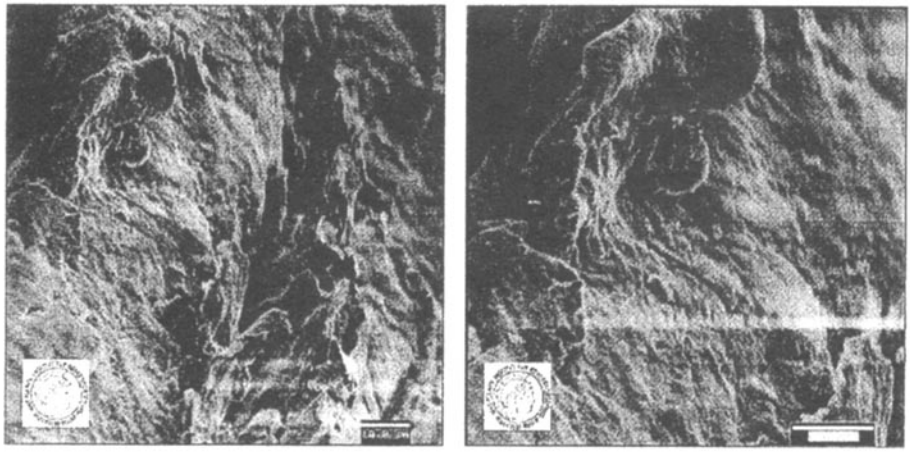
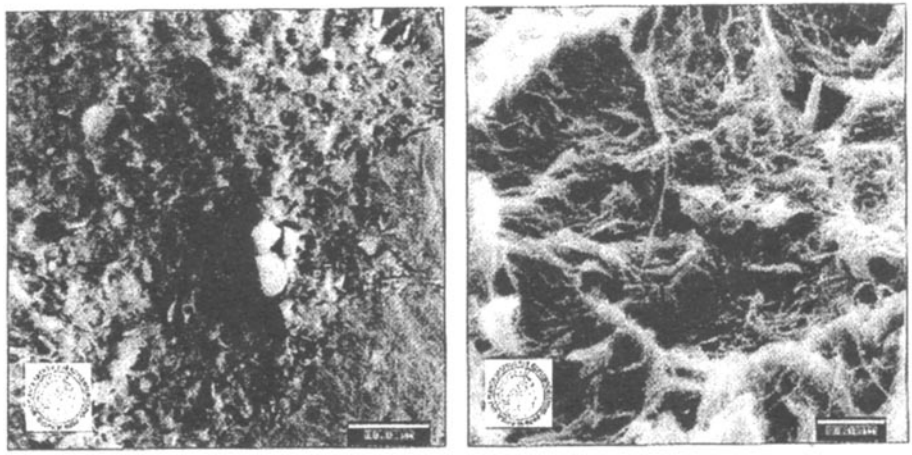


Fig. 4: in-situ and melt mixed PE-kaolin composites, 35% filler.

Fig. 3 reflects the stronger adhesion between filler and polymer in in-situ composites and no indication of cluster formation: the storage modulus of the in-situ composite is higher. The differences between the two preparation techniques becomes more obvious at high filler concentration. Fig. 4. indicates cluster formation in the melt mixed composite and a highly disordered glassy phase of the melt mixed composite showing a clear β-relaxation. The in-situ prepared composite indicates strong polymer-filler interactions since the γ-relaxation process is stronger, and the α-process is shifted to higher temperatures compared with the melt mixed composite. These interpretations are supported by SEM as shown in Fig. 5. Qualitatively the same is observed with $BaSO_4$, although on a lower level of the modulus, indicating a much less effective reinforcement by this type of a spheric, rather inert filler, see finally a comparison of the different systems in Fig. 9. Filler encapsulation is very effective and cluster formation is suppressed after in-situ preparation even in highly filled samples. The melt mixed composites, however, show insufficient encapsulation with a low polymer-filler adhesion and cluster formation, Fig. 7. The microscopic picture of $Ti0_2$-filled samples shows a striking difference compared with kaolin-and $BaSO_4$-composites, see Fig. 8.



PE 5.0% kaolin in-situ magnif. 1.500x magnif. 3.000x



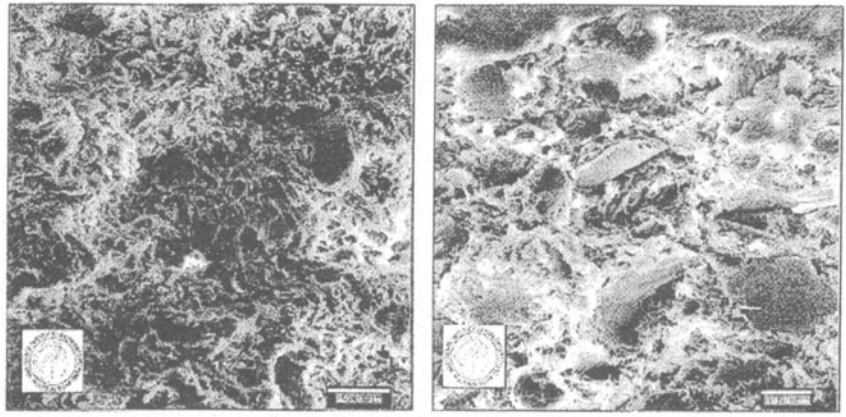
PE 5.1% kaolin extrusion magnif. 3.000x magnif. 5.000x

Fig. 5: SEM pictures of low filled PE-kaolin composites fracture surfaces in-situ polymerized (top) and melt-mixed (bottom). The bar is 10µm on the first three pictures and 5 µm on the bottom right picture.

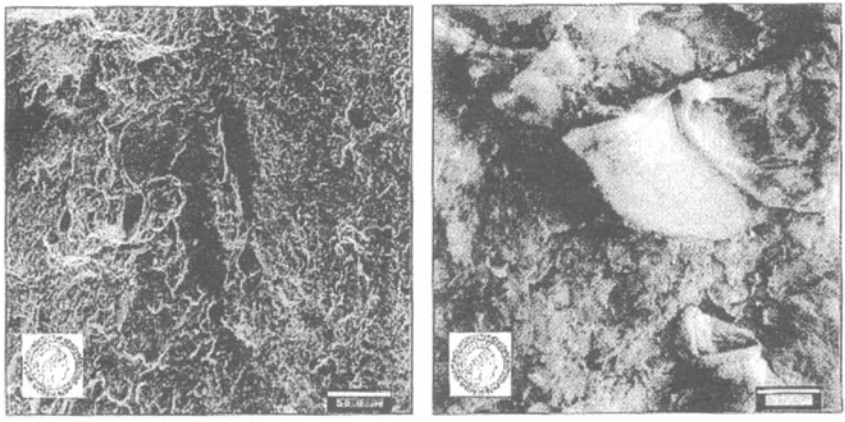
The fracture surface is more rugged and shows cracks, voids and a rather discontinuous morphology – even at low TiO_2 concentrations. The highly filled TiO_2 composites show

spherical agglomerated filler structures up to 30μm in diameter with large voids. The polymer morphology is inhomogeneous with a crude, granular morphology.

The poor microscopic appearance of the TiO_2 filled composites correlates with the dynamic-mechanical behaviour and the low degree of crystallinity. The β-relaxation becomes pronounced at 35% TiO_2, which – together with the low crystallinity – indicates the presence of branched polyethylene chains. The reinforcement caused by TiO_2 is not as strong as in the other composites, and the highly filled composite shows the lowest modulus, even lower than the unfilled PE. Compared with the other filler types, a low-temperature shift of the γ-process is caused by TiO_2. The α-process is down shifted by about 20°C, and all relaxation processes are decreased at high filler concentration revealing a considerably reduced molecular mobility of the polymer chains. The occurrence of a strong β-relaxation and the low intensity of the relaxation processes indicates a modification of the polymerization resulting in a fairly high degree of branching of the PE polymerized in the presence of high amounts of TiO_2 that cause a low cristallinity[24]). The decrease of the γ-relaxation, on the contrary, has to be attributed to the presence of the filler since a lower degree of crystallinity would result in a stronger low-temperature relaxation[24]. This indicates that polymer and filler are fairly separated in these composites. The filler is predominantly concentrated in the spherical aggregates visible on the fracture surfaces. The weak mechanical interaction between filler an polymer neither allows a high storage nor strong dissipative processes. Comparable results were not detected in melt mixed composites from TiO_2.

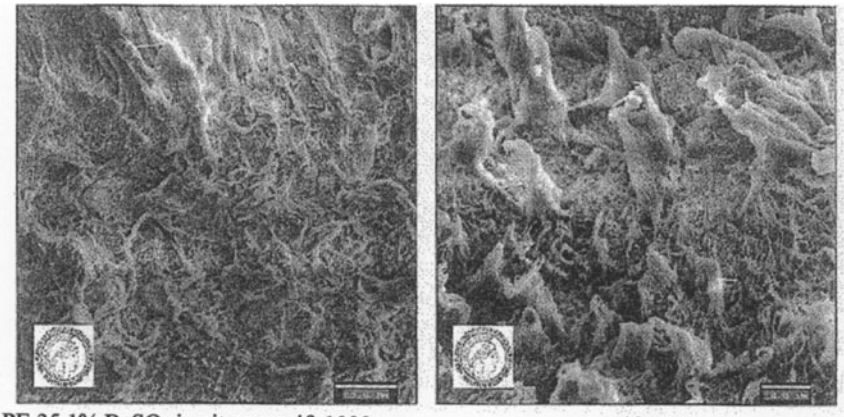


PE 35.4% kaolin in-situ magnif. 1000x magnif. 2000x

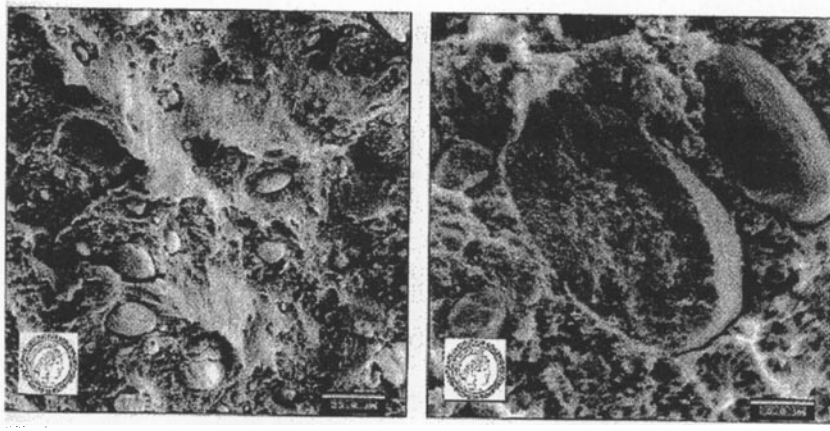


PE kaolin 35.2% extrusion magnif. 500x magnif. 5.000x

Fig. 6: SEM pictures of low filled PE-kaolin composites fracture surfaces surfaces in-situ polymerized (top) and melt-mixed (bottom). The bars indicate 25 μm, 10 μm, 50 μm and 5 μm, respectively (top left to bottom right).



PE 35.1% $BaSO_4$ in-situ magnif. 1000x magnif. 2000



PE 34.2% $BaSO_4$ magnif. 1000x magnif. 5000x

Fig. 7: SEM pictures of highly filled PE-$BaSO_4$ composites fracture surfaces surfaces in-situ polymerized (top) and melt-mixed (bottom). The bars indicate 25 µm, 10 µm, 25 µm and 5 µm, respectively (top left to bottom right).

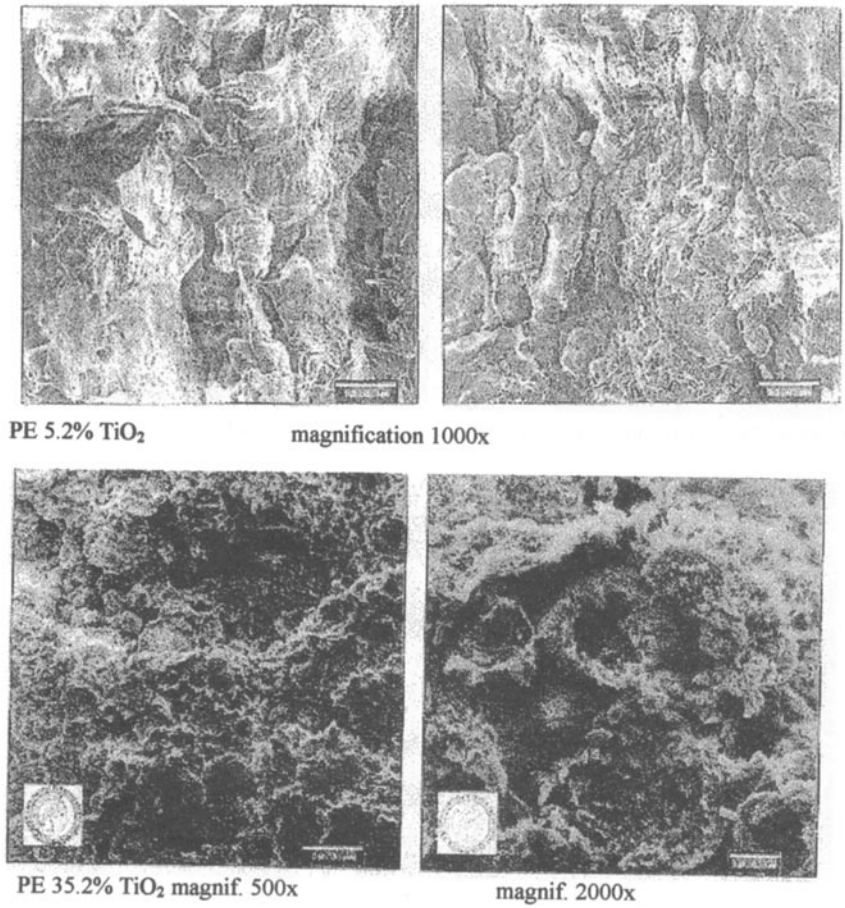


Fig. 8: SEM pictures of highly filled PE-$BaSO_4$ composites fracture surfaces in-situ polymerized (top) and melt-mixed (bottom). The bars indicate 25 µm (top), 50 µm (bottom left) and 10 µm (bottom right), respectively).

The still rather high storage modulus at low TiO_2 concentrations is due to the high specific surface of this filler type. A comparison of all in-situ polymerized composites is shown in Fig. 9.

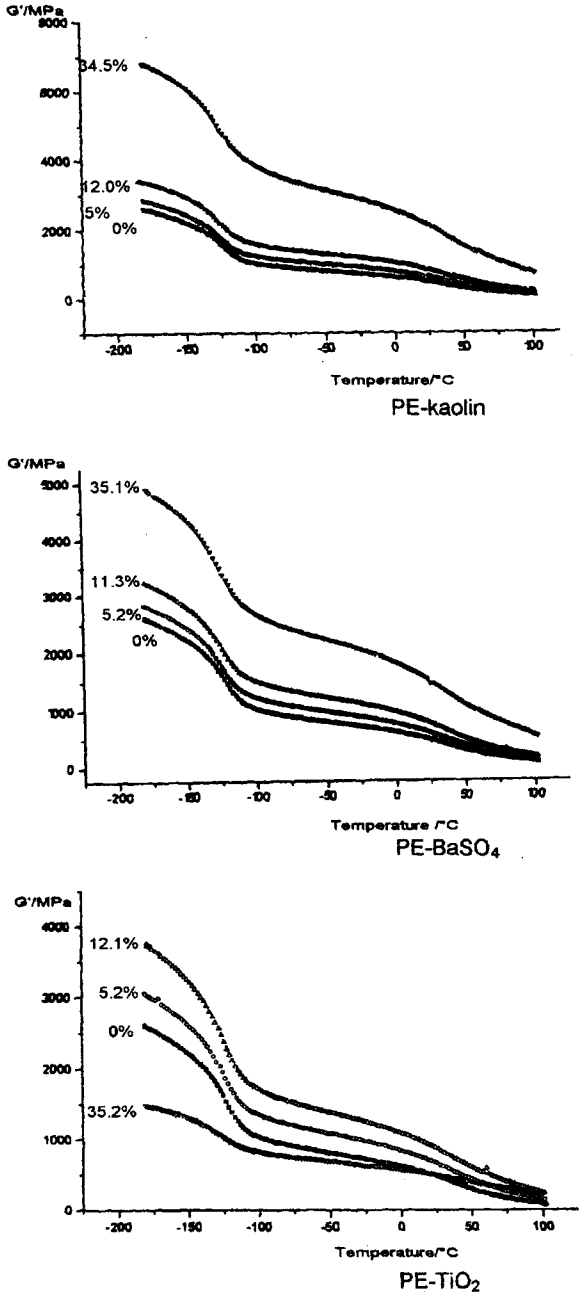


Fig. 9: comparison of the temperature dependence of the storage modulus G' for the three different PE-filler systems all prepared by in-situ polymerization.

Conclusion

Metallocene-catalyzed polymerization of PE in the presence of filler can be influenced. This was evident in particular at filler concentrations of TiO_2 as high as 35 %(v/v). In this case branching of the polymer was observed. The composite showed low crystallinity and many structural defects. In all the other systems under investigation a good encapsulation and a better dispersion of the filler particles (in particular at low filler concentrations) was observed after in-situ polymerization compared with melt-mixed composites. In general, improved mechanical properties were observed in in-situ prepared composites, mainly caused by stronger polymer-filler interactions, reduced agglomeration of particles, and stronger clusters. The reduced mechanical stress during in-situ polymerization is another advantage of this technique. Except for the systems polymerized in the presence of TiO_2 no significant effects on crystallinity or crystallization was observed for "in-situ systems". Physisorption of the catalyst by the filler with residual amounts of free catalyst left in the solution depends on the filler activity. Therefor, polymer forms only around the filler particles at higher filler concentrations when the amount of free catalyst in the solution is almost negligable, and kaolin, a highly surface active filler, seems to support a special type of defect transport in the orthorhombic PE-phase at room temperature and in particular at high filler concentrations[14].

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