Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Walter, Philipp , Mäder, Dietmar , Reichert, Peter and Mülhaupt, Rolf(1999) 'NOVEL POLYPROPYLENE MATERIALS', Journal of Macromolecular Science, Part A, 36: 11, 1613 — 1639

To link to this Article: DOI: 10.1081/MA-100101617

URL: http://dx.doi.org/10.1081/MA-100101617

J.M.S.—PURE APPL. CHEM., A36(11), pp. 1613–1639 (1999)

NOVEL POLYPROPYLENE MATERIALS

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Key Words: Polpropylene, Metallocene, Blend, Nanocomposite, Layered Silicate, Toughness

ABSTRACT

Recent progress in transition metal catalyzed propylene polymerization based upon single-site catalysts and melt compounding of polypropylene is stimulating the development of novel polypropylene materials with unconventional property combinations such as improved low temperature toughness, low haze, elasticity, and improved toughness/stiffness balance. As a function of metallocene architectures, polypropylene microstructures can be varied over a very wide range in order to produce thermoplastic elastomers and highly flexible polymers as well as stiff engineering thermoplastics and fibers. Control of polypropylene molecular architectures, especially random placement of steric irregularities in the polypropylene main chain, and the addition of clarifiers represents the key to producing novel transparent polypropylenes. Metallocene-based ethene/1-olefin copolymers such as poly(ethylene-co-1-butene) are attractive blend components to afford either single-phase flexible or two-phase rigid blends with improved low temperature impact strength as a func-

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tion of the 1-butene content. New families of polypropylene nanocomposites, containing nanowhiskers and anisotropic nanoparticles derived from organophilic layered silicates, exhibit effective matrix reinforcement at low filler content.

INTRODUCTION

Among thermoplastics polypropylene is outstanding with respect to its attractive combination of low cost, low weight, heat distortion temperature above 100°C, and extraordinary versatility in terms of properties and applications, ranging from molded parts to films and fibers. As hydrocarbon resin polypropylene is equivalent to a solid, high molecular weight modification of oil which can be shaped by molding and is converted back into liquid oil by thermal degradation occurring at temperatures exceeding 400°C. Therefore, polypropylene waste is readily recycled either by remolding, feedstock recovery, or preferably, by substituting oil in steel mills and power plants. Innovations in catalyst and process technologies have significantly simplified polypropylene production by eliminating removal of both catalyst residues and wax-like byproducts due to very high catalyst activities and stereoselectivities. Modern gas phase and liquid-pool propylene polymerization are energy-efficient and do not require the use of solvents. Today, polypropylene is a prime example of an environmentally friendly polymer which is easy to recycle and preserves oil-like energy content for future generations in accord with the demands for sustainable development. In contrast to expectations of the early 1970’s (cf. Figure 1), when R&D was focused on high performance polymers, polypropylene proved to be highly innovative with exceptional annual average growth rates of approx-imately 9% since 1980 and remarkable market expansions into engineering resin applications [1].

As a consequence of its high versatility and attractive price/performance ratio, polypropylene is competing very successfully with other, more expensive, less versatile, and environmentally less friendly polymers. An important objective in polypropylene engineering plastics development is to improve polypropylene’s heat distortion temperature/stiffness/toughness balance. The exciting prospects and achievements of polypropylene technology was reviewed by Moore [2] and also in a recent multi-authored reference book edited by Karger-Kocsis [3]. Here recent progress in the field of metallocene-catalyzed propylene polymerization and polypropylene melt compounding of isotactic polypropylene is illustrated by selected examples of research conducted at the Freiburg

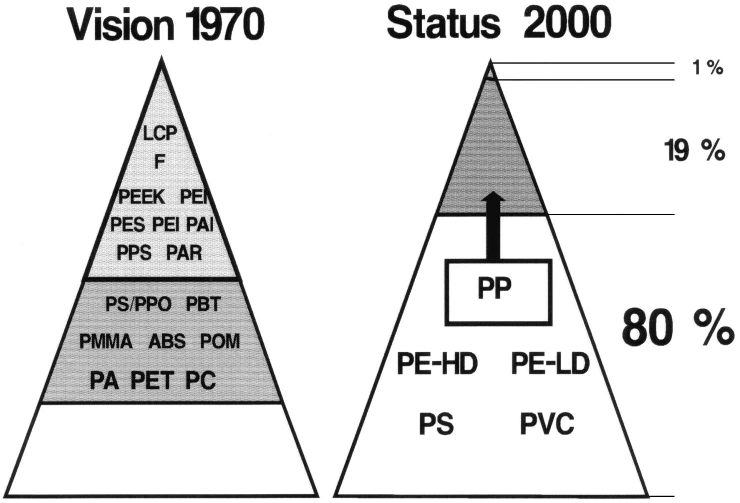

Figure 1. Polypropylene is competing very successfully with other thermoplastics and is entering the engineering resin market which was claimed by condensation polymers.

Materials Research Center. Special emphasis is placed upon correlations between polypropylene properties and metallocene architectures as well as formation of polypropylene blends and new polypropylene nanocomposites containing anisotropic layered silicates.

EXPERIMENTAL

Materials

All catalyst components, including toluene solvent and monomers, were handled and stored under dry argon atmosphere. *Rac*-$Me_2Si(Ind)_2ZrCl_2$, *rac*-$Me_2Si(2\text{-}MeInd)_2ZrCl_2$, and MAO (10 wt% in toluene, M_n= 1000g/mol) was supplied by Witco Co., Germany. *Rac*-$Me_2Si(Benz[e]Ind)_2ZrCl_2$ was obtained from Prof. Dr. H. H. Brintzinger, University of Konstanz, *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$, *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}PhenylInd)_2ZrCl_2$ as well as *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}NaphInd)_2ZrCl_2$ from BASF AG, $Me_2Si(Me_4Cp)(N\text{-}tert.\text{-}butyl)TiCl_2$ from Prof. Dr. J. Okuda, University of Mainz, zirconocenedichloride, toluene from Roth GmbH, ethene from Gerling Holz u. Co., propene (polymerization grade) and 1-butene (polymerization grade) from BASF AG. Toluene solvent was rectified over $LiAlH_4$ and refluxed and distilled over Na/K alloy prior to use. Ethene and MAO were used without further purification, 1-butene was purificated by passing through $NaAl(C_2H_5)_4$ filled columns. The synthetic clay used here to produce polypropylene nanocomposites is a fluorine containing mica, prepared from talcum and Na_2SiF_6, which was obtained from CO-OP Chemical Co., Japan (trade name of this material is SOMASIF®ME100, abbreviated as ME100). The ion exchange capacity of ME100 was between 0.7 and 0.8 meq/g. The d_{001} interlayer spacing of the virgin ME100 is 0.95 nm. It was cation exchanged with octadecylamin, protonated with HCl, to render the silicate organophilic (sample code is ME/ODA) and to increase interlayer distance to 1.98 nm. Details of this process were reported elsewhere in more detail [4]. Polypropylene P4 (PP HC 001 A-B1; MFI 3.2 g/10 min) was obtained from Borealis, Novolen M from BASF AG, and the maleic-anhydride-grafted polypropylene compatibilizer (PP-g-MA) was supplied by Hoechst AG (Hostaprime HC5; 4.2 wt% grafted maleic anhydride). For comparison, talcum-filled polypropylene was prepared using Prever M8® (3 µm talc; Lucenac), Prever® (10 µm talc; Lucenac) and polypropylene KY6100® (Shell). The blend studies with EB (obtained from J. Suhm, Freiburg) was performed using isotactic metallocene-polypropylene (Novolen M from Targor GmbH). Polypropylene filler blends contained microfillers (glass beads: Potters Ballotini 5000 CP-00 with 5 µm diameter, talc with 10 µm particle size and aspect ratio 5-10: Luzenac OOS, calcium carbonate cubes with 5.5 mm size: Plüss Staufer BL) and nanofillers (pyrogenic silica with 0.01 µm diameter: Aerosil P380 from Degussa, glass nanospheres with 0.25 µm diameter: Monospher 250 A from Merck AG, titandium dioxide whiskers with 0.35 mm diameter and aspect ratio of 50: Tismo D from Otsuka).

Metallocene-Catalyzed Olefin Homo- and Copolymerization

According to procedures reported by Suhm [5], propylene polymerization and ethene/1-olefin copoymerization were performed in a 1.6 I Buechi glass autoclave rinsed with 300 ml of a 0.03 mol/l $Al(iBu)_3$ solution in toluene prior to use. Typically, 480 ml toluene and 6.2 ml MAO-solution were fed into the glass reactor. The total volume of the reaction mixture was 0.5 I. After thermal equilibration of the reactor using two independent cooling systems for inner and outer cooling, ethene and 1-butene or propene, respecitvely, were continuously added by two mass-flow controller (F-201C-FA, Bronkhorst, Nl-7261 AK Ruurlo, Netherlands) combined with a digital readout and control system (E7000, Bronkhorst, Nl-7261 AK Ruurlo, Netherlands) using different mass ratios of gas flows. The reaction mixture was saturated with propene or ethene and 1-butene for 30 minutes by a continuous gas stream. The polymerization was started by injecting typically 2 μmol of metallocene catalyst in 10 ml toluene, equivalent to [Zr] = 4 μmol/l and [Al] = 80 mmol/l. The pressure of ethene/1-butene gas and propene gas feed respecitvely was kept constant during the polymerization by a pressure valve. Typically, after 60 minutes copolymerization was quenched by pouring the autoclave content in 3 L acidic methanol.

Blend and Nanocomposite Formation

Melt compounding was performed in a Haake Rheomix 90 twin-screw kneader equipped with a 60 ml mixing chamber that was preheated at 200°C. Then, i-PP (45 ml) together with 0.5 wt% Irganox 1010/Irgafos 168 (4:1) stabilizer were fed into the mixer and kneaded at 60 RPM After 1.5 minutes, EB was fed during 0.5 minutes. After 5 minutes total mixing time, the samples were quickly recovered and quenched between metal plates. Sheets of all samples of about 2 mm thickness were prepared by compression molding in a vacuum press for 15 minutes at 200°C and 10 bar pressure, followed by quenching at room temperature.

Polypropylene compounds containing micro- and nanofillers and blend thereof were prepared by melt compounding in a Haake Rheomix 90 kneader at 240°C, following procedures reported previously by Stricker [48]. To obtain the polypropylene nanocomposites, organophilic layerded silicate powder, obtained by milling, stabilizer (0.25 wt% of a 4:1 mixture of Irganox 1010/Irgafos 168 from Ciba, Basel) and the polypropylene were dry-mixed in tumble mixer. The PP-g-MA and the obtained mixture were fed separately. The components were melt-blended at 210°C by using a twin-screw extruder (WP ZSK-25) to yield the compounds. After pelletizing, the product was dried at 80°C. The dried pellets were injection-molded by means of a Ferromatic-Millacron K40 injection-molder.

Polymer Characterization

^{1}H-NMR spectra were recorded from solutions of 40 mg of polymer in 0.5 ml $C_2D_2Cl_4$ at 400K temperature by a Bruker ARX 300 at 300 MHz; ^{13}C-NMR spectra at 75.4 MHz, with a 90° pulse angle, inverse gated decoupling, 5 s delay and at least 8000 scans. The signals were referenced to $C_2D_2Cl_4$ (δ = 74.06 ppm). High temperature size exclusion chromatographic (SEC) analyses of molar mass and molar mass distribution were performed at BASF AG. Glass temperatures were determined by means of differential scanning calorimetry (DSC) with a Perkin Elmer Series 7 from the heating curve at a heating rate of 10K/min. Dynamic mechanical analysis (DMA) was performed by means of a Rheometrics Solid Analyzer (RSA II) with dual cantilver bending geometry using a dynamic temperature ramp with a heating rate of 2 K/min, 0.1% strain and a frequency of 6.28 rad/s. The test specimen (2mmx6mmx60mm) were compression molded in vacuum at 140°C and cooled down to room temperature within 30 minutes.

The interlayer distance of the layered silicate was studied by means of wide angle X-ray scattering (WAXS) using a Siemens D500 apparatus with the CuK_{α}radiation (λ = 1,5418 nm) and a scanning rate of 0.3°/min. The morphology of the samples was examined by transmission electron microscopy (TEM). For TEM measurements, ultrathin sections were prepared at -140°C with an Ultracut E, Reichert & Jung, ultramicrotome using a diamond knife. The measurements were carried out on a Zeiss CEM 912 (120 kV). The tensile modulus of the composites and nanocomposites was measured using an Instron 4202 (ISO/DP 527) and the impact strength with an impact tester Zwick, model 5102 (ISO 180/1A).

RESULTS AND DISCUSSION

Synthesis of Tailor-Made Polypropylenes

Since the early 1950‘s when Natta and his coworkers discovered isotactic polypropylene, it is well known that catalyst architectures are closely related to polypropylene stereochemistry [6]. Most of the initial catalyst research was focused on the production of highly isotactic polypropylene. A remarkable sequence of breakthroughs in catalyst research by Galli and his coworkers has led to the development of highly active and highly isoselective donor-modified, magnesium-chloride supported catalysts where catalyst particles serve as templates to control morphology development of polypropylene particles. In Montell’s reactor granule technology, porous polypropylene granules are being used as microreactors to incorporate other polymer phases into the continuous polypropylene martrix [7]. During the mid 1980’s, Brintzinger introduced chiral ansa-metallocenes such as bridged bisindenyl metallocenes, which upon activation with methylaluminoxanes produced the first homogeneous isoselective cat-

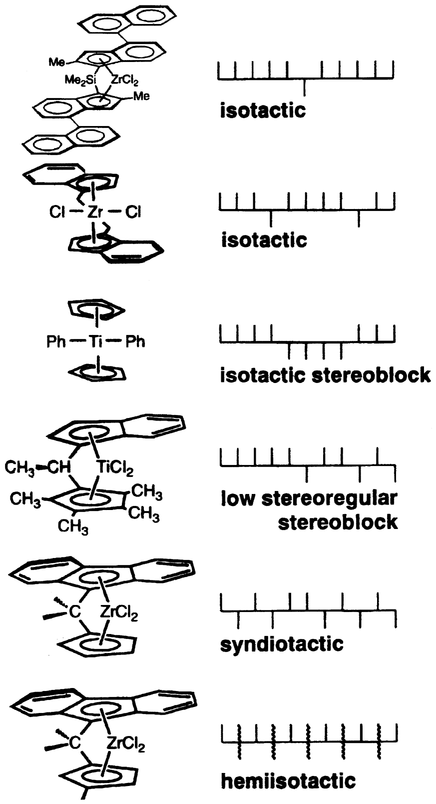

Figure 2. Correlations between metallocene architectures and polypropyene microstructures.

alysts [8-11]. Since then, several families of metallocenes have emerged and insight in basic reaction mechanisms has been achieved. As a function of the metallocene architectures it is possible to produce in industrial processes most of the stereoisomers originally proposed by Natta (cf. Figure 2). In addition to isotactic polypropylene also syndiotactic polypropylene [13], stereoblock elastomeric polypropylene [14, 15] and even high molecular weight atactic polypropylene are now available. According to a model proposed by Fink [16], stereochemical control can be attributed to the formation of the lowest-energy conformers of the cationic metallocene alkyls and positional changes of the polymer chains during insertion.

In comparison to most conventional catalysts, methylaluminoxane-activated as well as activator-free metallocene catalysts are composed of essentially one type of catalytically active center. Therefore this class of catalysts is also referred to as "single-site" catalysts. It should be noted, however, that the first isoselective metallocene generation, in spite of their single-site nature, did not meet the specifications of most industrial propylene polymerization processes. The homogeneous catalysts were heterogenized in order to prevent formation of dust-like particles and to afford stable operation in gas phase polymerization. Moreover, the performance of the initial metallocene generation with respect to stereoselectivity, catalyst activity, and also comonomer imcorporation was rather poor and required improvements. The groups of Spaleck [17, 18] and Brintzinger [19, 20] recognized during the early 1990's that the substituents of the bisindenyl ligand framework represented the key to circumventing most problems encountered with first generation of isoselective metallocene catalysts. The family of dimethylsilylene-bridged bisindenyl ziconocenes with substitution in 2- and 4-position is illustrated in Figure 3.

In Figure 4, bar charts display the performance of propylene homopolymerization and ethene/1-octene copolymerization using homogeneous catalysts derived from metallocenes in Figure 3 which were activated with methylaluminoxane (MAO). Typically polymerization was performed at 40°C and 2 bar propylene. For comparison Spaleck's data on propylene homopolymerization [17] was included. Clearly, the molar mass increases significantly when a methyl substituent is introduced in 2-position. Today the mechanistic view is accepted that this 2-methyl substitution prevents chain termination via β-hydride transfer to propylene monomer. When chain transfer takes place exclusively via β-hydride transfer to the transition metal, degree of polymerization increases with increasing propylene pressure [20]. The substitution in 4-position did not affect molar mass, but had a dramatic impact on catalyst activities and comonomer incorporation. It is apparent from Figure 4 that catalyst activity in propylene homopolymerization as well as 1-octene incorporation in ethene/1-octene copolymerization increases as a function of the ring substitution with 4-napthyl > 4-phenyl > benzannelation. Most likely, steric hindrance promotes formation of the catalytically active cationic alkylmetallocenes, whereas dimerization of cationic alkylmetollecenes with neutral metallocenes can produce inactive binuclear cationic complexes. In the case of ethene/1-octene copolymerization, molecular modeling was applied successfully to support that benzannelation promoted 1-octene incorporation in contrast to 2-methyl substitution [21]. Benzannelated and 4-phenyl and 4-naphthyl-substituted metallocenes with 2-

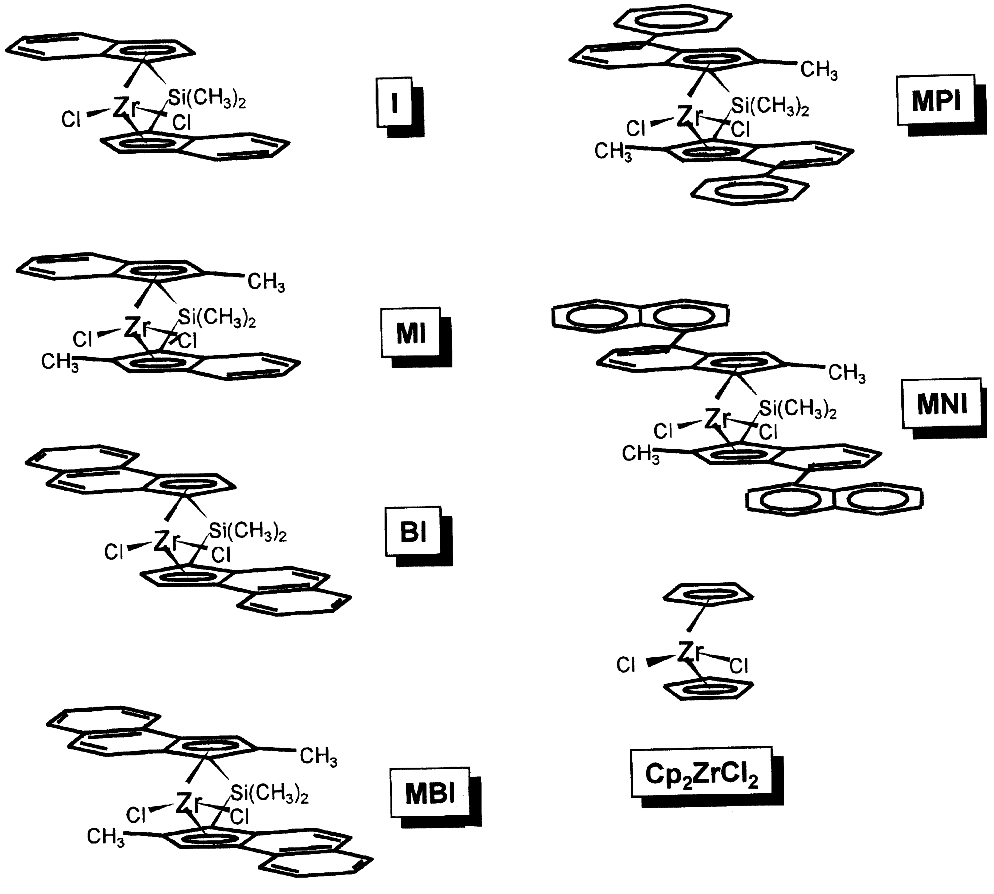

Figure 3. Isoselective metallocenes.

methyl-substitution meet the demands of modern propylene gas phase polymerization.

In contrast to most conventional highly isoselective catalysts, where low stereo- regular polymers are obtained exclusively as undesirable and frequently low-molecular weight by-products, tailor-made isoselective metallocenes can be used to achieve random placement of steric irregularities in the isotactic polypropylene chains without sacrificing narrow molecular weight distribution of the polymer and single-site nature of the catalyst. Typical steric irregularities are isolated inversions of the configuration of the stereogenic carbon atom in the repeat unit due to false insertion, and regioirregularities resulting in head-to-head propylene incorporation or formation of isolated ethene units via 1,3-insertion

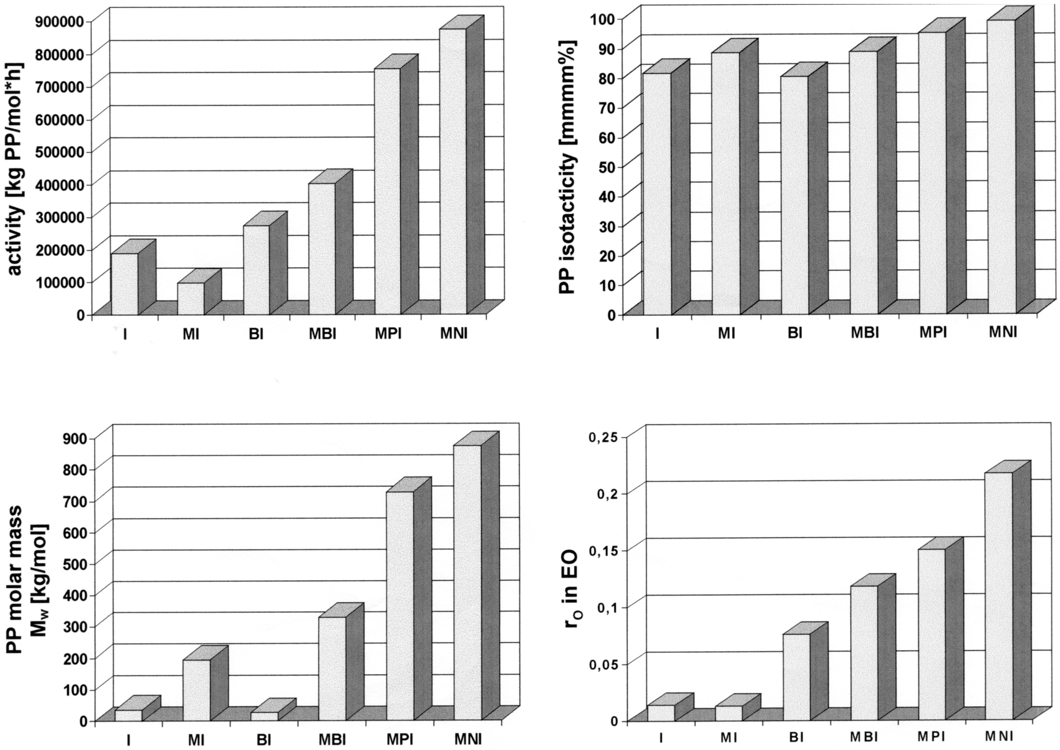

Figure 4. The role of bisindenyl ligand substitution patterns on catalyst activity, polypropylene molar mass, polypropylene stereoregularity, and copolymerization parameter r_O in ethene/1-octene copolymerization.

without requiring ethene as comonomer. It was Fischer who recognized that the isotactic segment length between two steric irregularities (cf. Figure 5) controls both melting temperature and crystal modification of polypropylene [22]. With decreasing isotactic segment length, the melting temperaturre can be lowered from 165 to 125°C and the content of γ-modification increased significantly. Lower melting temperature is of interest in packaging application with improved heat sealability. Moreover, metallocene-polypropylene gives much higher spinning speed and improved orientation in spinning processes [23].

As pointed out by Lotz [24] and Kressler [5, 25, 26], crystallization of the γ-modification does not form large spherulites. In accord with earlier observations by Brückner and Meille [27], the γ-modification of isotactic polypropylene the orthorombic unit cell is composed of bilayers of parallel helices with

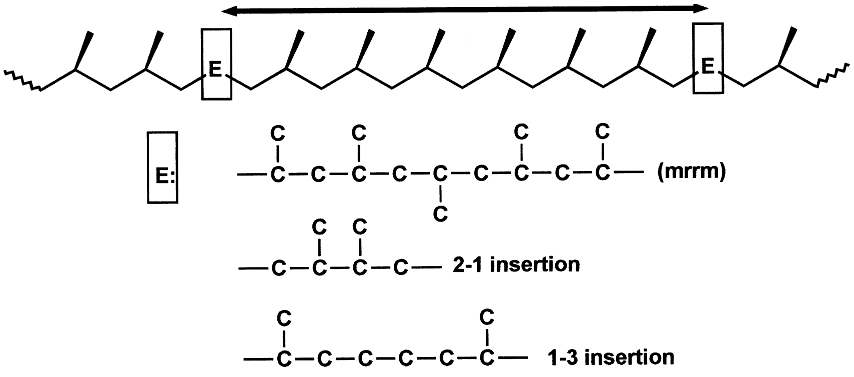

Figure 5. Steric irregularities placed randomly in the backbone of isotactic polypropylene produced with metallocene catalysts.

adjacent bilayers being tilted with an angle of 80° (cf. Figure 6). In the absence of spherulites, optical properties of polypropylene, assisted by the addition of nucleating agents such as substituted dibenzylidene sorbitols, can be improved substantially. Today, transparent polypropylenes are entering markets such as thinwall-molded food containers, bottles, drink cups, and packaging of CD-ROM [28]. New polypropylenes with low haze are starting to compete with conventional transparent polymers such as styrenics. Fine-tuning of polypropylene architectures and development of clarifier additives are likely to further improve optical properties and to enhance polypropylene's competitiveness in the field of transparent polymers.

Polypropylene Blends with Poly(ethene-co-1-butene)

Since Natta's discovery of isotactic polypropylene, an important objective was to improve low temperature impact strength without sacrificing stiffness. This can be achieved either by means of ethene/propene copolymerization or by blending polypropylene with elastomers [29-32]. Attempts to correlate blend properties with molecular architectures were hampered by the rather complex mixtures of polymer chains with molecular architectures obtained with conventional catalysts. The development of rubber-toughened polypropylene benefits from recent advances in metallocene catalyzed copolymerization. In contrast to most conventional catalysts, where comonomers are preferably incorporated in wax-like fractions, single-site metallocene catalysts give very uniform

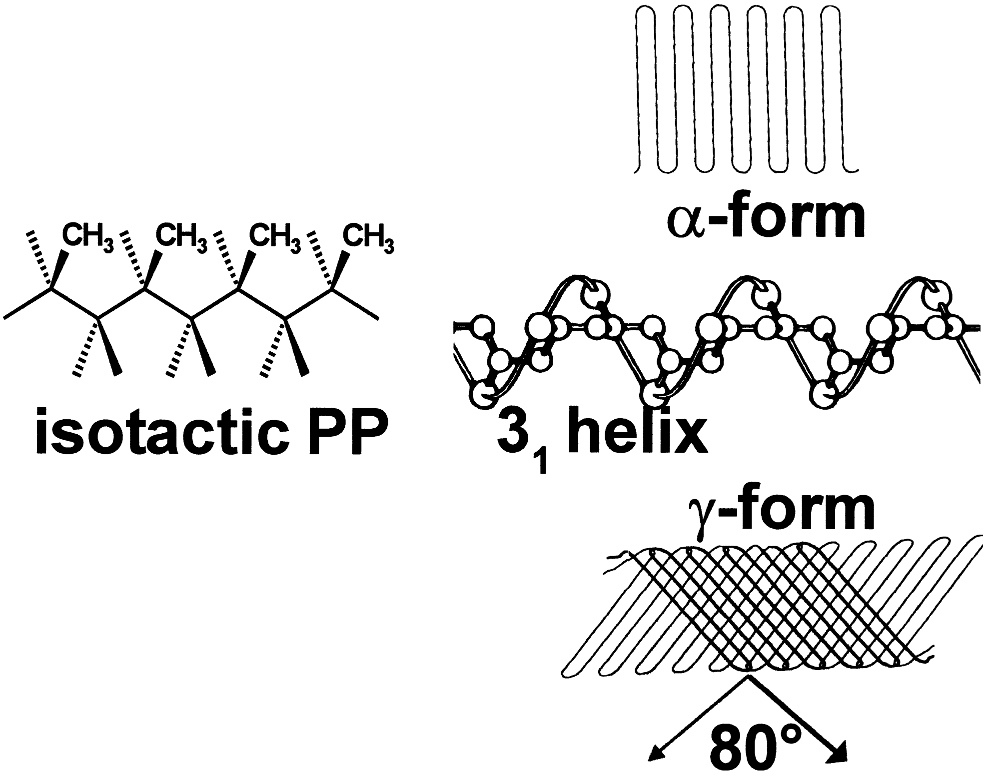

Figure 6. Crystallization of isotactic polypropylene in α- and γ-modification.

comonomer incorporation which is independent of molar mass. With metallocenes displayed in Figure 3, it is possible to produce the entire feasible composition range of ethene/1-olefin copolymers including copolymers with long-chain 1-olefins and olefinic macromonomers. Especially ethene copolymers with higher 1-olefins such as 1-butene and 1-octene are of interest because of their lower glass transition temperatures with respect to EPM. From model studies by Graessley and Fetters [33-35] on polypropylene/poly(ethene-co-1-butene), using hydrogenated polybutadiene with variable 1,2- and 1,4-units to obtain EB, and from investigations by Yamaguchi [36, 37] on metallocene copolymers, it was concluded that two-phase blends were formed at low 1-olefin content, whereas, 1-butene rich blends of EB containing just a few percent ethene were miscible with isotactic polypropylene (iPP). With MAO-activated metallocene-catalysts displayed in Figure 3, it was possible to produce EB copolymers with 10, 24, 48, 58, 62, 82, 90 wt% 1-butene incorporation and to examine their blends with iPP as a function of 1-butene content. With increasing 1-butene content, the compatibility between iPP and EB was gradually matched. For EB with 1-butene content >88 wt% Bar [38] confirmed the miscibility window by means of Atomic Force Microscopy which revealed the presence of a single phase blend morphology.

As apparent from Table 1, compatibility matching represents the key to controlling mechanical properties. In the miscibility region with 1-butene-rich EB highly highly flexible blends are formed, whereas at very low 1-butene content, the blends are rigid and brittle. Toughening of stiff polypropylene also responds to changes in EB molecular architectures. Only at 1-butene content varying between 48 and 58 wt% significant improvement of notched Izod impact

TABLE 1. Mechanical and Thermal Properties of iPP/EB (80 Vol%/20 Vol%) Blends as a Function of the 1-Butene Content of EB (Data Obtained from Maeder [39])[a)]

EB 1-butene content (wt.-%)	T_g^{EB} EB Bulk (°C)	T_g^{EB} EB in Blend (°C)	T_g^{iPP} IPP in Blend (°C)	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at break (MPa)	Notched Izod Impact Strength 20 °C (kJm^{-2})	Notched Izod Impact Strength -28 °C (kJm^{-2})
0 (iPP)	-	-	5	900	28	700	3.6	2.0
10	-26	-34	5	720	23	600	7.4	2.7
24	-33	-40	5	710	21	650	16	2.9
48	-55	-65	5	650	19	540	no break	7.9
58	-56	-62	4	610	18	620	no break	3.9
62	-52	-41	-4	450	18	640	20.4	2.6
82	-32	-10	-10	520	18	890	13	2.0
90	-27	-9	-9	540	18	960	10	2.0

a) glass temperatures were determined by means of dynamic mechanical analysis at 2 K min^{-1}

strength was achieved at room temperature and at –28°C. In contrast to all EP-based blends, only iPP/EB blends with EB containing 46 to 58 wt% 1-butene exhibited rubber glass temperatures below –50°C [39]. Maeder's systematic comparison of the glass temperatures of the bulk elastomer with those of the elastomer phase revealed pronounced glass temperature depression for the elastomer phase in the two-phase region with 1-butene content of EB < 50 wt% [40]. This glass temperature depression was attributed to thermally induced stresses resulting from differential volume contractions of the two phases during cooling. In conclusion, metallocene catalysis provides excellent model polymers which can be used to elucidate basic structure/property correlations and to predict polymer properties as a function of molecular architectures. Libraries compiling basic correlations between catalyst structure and polymer architectures as well as polymer properties can be established and may help in the future to facilitate materials development involving computer simulations.

Polypropylene Nanocomposites

In conventional injection molding, only few percent of polypropylene's ultimate strength of 16 GPa and PP's ultimate modulus of 50 Gpa [41] are reached, whereas fiber processing, drawing, and special solid state processing can give much higher strength due to better orientation. It is an important objective in polypropylene development, especially in engineering applications, to reinforce the polypropylene matrix during melt processing. Two approaches are being persued: (1) molecular reinforcement by means of improved polypropylene orientation in melt processing, and (2) fiber- and filler-reinforcement. According to Ehrenstein [42, 43] important parameters for self-reinforcement in injection molding are very high injection rate, high injection pressures, and melt temperature of 160-190°C, which is slightly above polypropylene's melting temperature and much lower with respect to conventional injection molding. Under those reaction conditions, high injection rates of 180 mm/s with respect to 30 mm/s in conventional molding account for alignment of the polypropylene chains as well as flow- and pressure- induced crystallization, thus forming shishkebab structure and no spherulites. Typically, 2.5-fold increases of tensile strength and modulus combined with up to 7-fold toughness, improved heat distortion temperature, better wear resistance, and reduced creep were reported for such injection-molded self-reinforced polypropylenes [43]. It will be interesting to learn more about the performance of metallocene polypropylenes, in particular highly syndiotactic polypropylene which forms 2_1 helix and could give improved orientation.

Production of polypropylene composites based upon fiber and fiber mat reinforcement requires special processing technology involving fiber impregnation and prepreg formation [44-47]. Therefore, special emphasis is being placed upon the development of filled polypropylene which can be produced by means of conventional melt processing. Traditional fillers for polypropylene are calcium carbonate, talc, glass fibers, wollastonite, mica, glass beads and wood flour. It is well known that filler anisotropy, i.e, large length/diameter ratio ("aspect ratio"), is especially favorable in matrix reinforcement [47]. The use of stress-concentrating nanofillers offers attractive potential for promoting energy dissipation at the crack tip involving the entire sample volume in plastic deformation processes. Stricker has compared anisotropic and isotropic fillers with micro- and nanometer dimensions [48].

In Figure 7, the toughness/stiffness-balance of polypropylene compounds containing 0, 0.5, 1, 2.5, and 5 vol% filler is displayed and reflects the

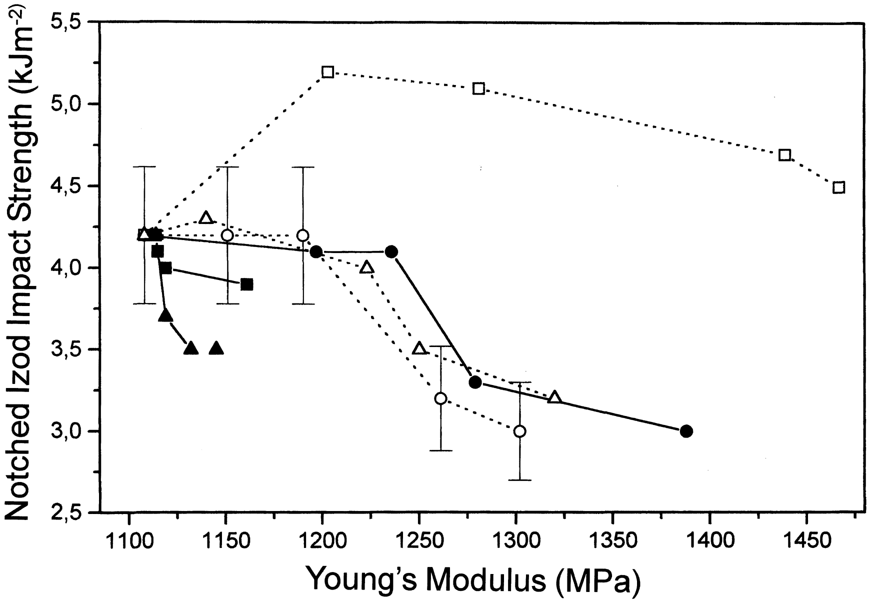

Figure 7. Toughness/stiffness balance of polypropylene compounds containing (from left to right) 0, 0.5, 1, 2.5 and 5 vol% filler such as talc (●), calcium carbonate (▲), glass beads (■), pyrogenic silica as nanosilicates (O), glass nanospheres (Δ), and titanium dioxide nanowhiskers (□). Data was taken from Stricker [48] with permission from Kunststoffe, Hanser Verlag.

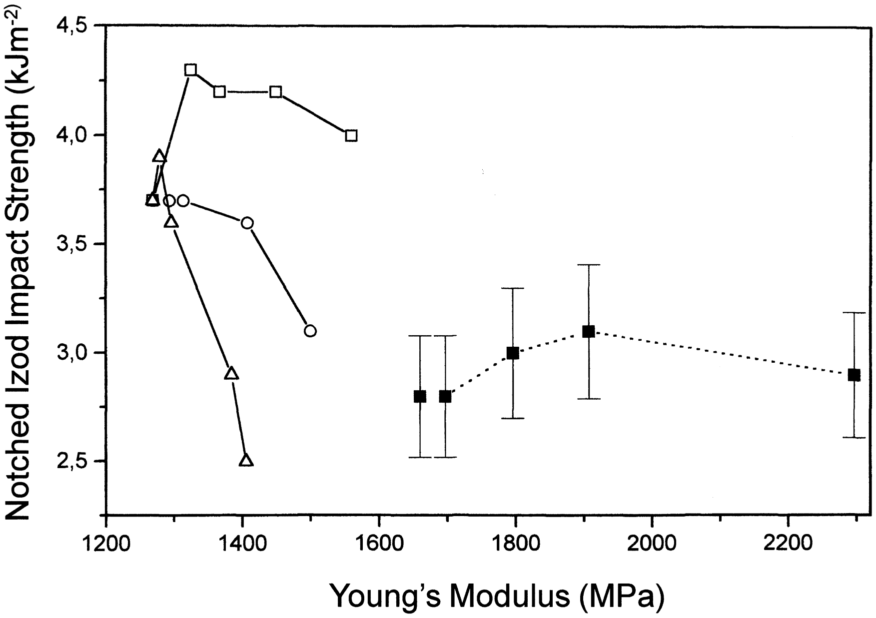

Figure 8. Toughness/stiffness balance of polypropylene compounds containing 10 vol% of a filler blend comprising a mixture of micro- and nanofillers with mixing ratio varying from 100/0, 95/5, 90/10, 75,25, 50/50 (left to right) for glass beads combined with pyrogenic silica nanoparticles (○), glass beads combined with glass nanospheres (□), glass beads combined with titanium dioxide nanowhiskers (Δ), and talc combined with titanium dioxide nanowhiskers (■). Data was taken from Stricker [48] with permission from Kunststoffe, Hanser Verlag,

influence of filler size and shape. Only anisotropic fillers such as talc give substantial improvement of stiffness. In comparison to talc with 10 μm average particle size, titanium dioxide nanowhiskers with 350 μm length and aspect ratio of 50 gave much higher toughness without sacrificing high stiffness, in spite of dispersion problems. Unusual property synergisms were discovered when nano- and microfiller were blended together. As shown in Figure 8, at 10 vol% total filler content micro- and nanofillers were blended toegther at volume mixing ratios of 100/0, 95/5, 90/10, 75/25, and 50/50. In sharp contrast to filler blends of isotropic fillers such as glass beads and pyrogenic nanosilicates, the addition of nanowhiskers together with talc gave much higher Young's modulus with respect to those of the polypropylene compounds containing 10 vol% of the corresponding individual filler blend components. In spite of attractive property combinations, the use of nanofillers is limited. On one hand, this is due to limited availability and handling problems associated with potential health hazards relating to inhalation of nanowhiskers. On the other hand, strong interparticle interactions hamper effective filler dispersion, as reflected by formation of large clusters which can initiate mechanical failure upon exposure to small mechanical stresses. Recent advances have been successful to generate anisotropic nanoparticles during processing using organophilic layered silicates.

As illustrated in Figure 9, key intermediates of nanocomposites are water-swellable clay minerals and synthetic layered silicates, which are rendered organophilic by means of ion exchange with protonated alkylamines or alkyl ammonium cations containing at least one n-alkyl chain with more than six methylene units. Key component of natural clay (bentonite) is montomorillonite which contains aluminosilicate layers where individual sheets of octahedral alumina are sandwiched in between two sheets of tetrahedral silica. Since part of the three-valent aluminium cations are exchanged by two-valent magnesium cations, the individual layers possess anionic charges. In order to compensate such charges, sodium., calcium, and magnesium cations are incorporated in the inter-

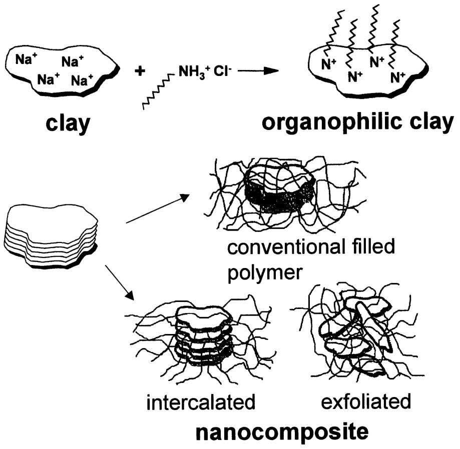

Figure 9. Formation of nanocomposites based upon layered silicates: layered silicates are rendered organophilic by means of ion exchange with alkyl ammonium ions such as protonated octadecyl amine. Upon exposure to shear stresses during processing individual layeres are dispersed within the polypropylene matrix.

layer galleries. Especially when sodium cations are present in the interlayer galleries, the corresponding layered silicates such as sodium bentonite are able to swell in water. When protonated octadecyl amine (ODA) is added, ion exchange takes place and renders the individual layers organophilic thus improving compatibility with polymeric materials. During melt compounding or polymerization, polymer can be inserted in between the layers or individual layers which are dispersed in the polymer matrix. Increasing interlayer distance is monitored by means of wide angle X-ray scattering and transmission electron microscopy. Polymer nanocomposite development is stimulated by research at Toyota where polyamide 6 nanocomposites with improved toughness/stiffness/heat distortion temperature balance became available during the late 1980's [49-51]. However, it should be noted that the basic chemistry of organophilic clays was established more than fifty years ago by Hofmann and Weiss [52, 53]. Today nanocomposite formation represents an attractive route to upgrade and diversify well-known polymeric materials and to afford unique property profiles [54-57]. Recently, polyamide 6 nanocomposite films with improved barrier properties, e.g., reduced oxygen permeability, have been introduced [58].

According to Okada and coworkers [59-62], polypropylene nanocomposites are obtained when organophilic clay such as montmorillonite, obtained by means of ion exchange of sodium cations for protonated octadecylamine (ODA), was melt compounded with PP in the presence of propylene oligomers, preferably maleic-anhydride grafted polypropylene. Although TEM images and investigations by means of dynamic mechanical analysis supported matrix reinforcement and formation of nanocomposites, limited information was available concerning the toughness/stiffness balance of such polypropylene nanocomposites. In our research [63], we have used Okada's route to *in situ* generate and disperse nanosilicates with high aspect ratio derived from organophilic fluoromica, abbreviated as ME100 and obtained by chemical conversion of talc with Na_2SiF_6 , which is rendered organophilic by means of ion exchange of sodium ions for n-octadecylammonium (ODA) cations. Melt compounding of such organophilic fluoromica with polypropylene was performed at 240°C in the presence and absence of maleic-anhydride-grafted polypropoylene (PP-g-MA) containing 4.2 wt% maleic anhydride grafts, using a Werner & Pfleiderer ZSK25 twin-screw extruder. Mechanical properties of nanocomposites (NC samples) are listed in Table 2 and compared with those of conventional talc-filled polypropylene (T samples) using talc with average diameter of 3 and 10 μm, respectively.

In accordance with earlier observations by Okada and coworkers, the presence of considerable amounts of the PP-g-MA as compatibilizer was impor-

TABLE 2. Polypropylene Nanocomposites Containing Organophilic Layered Silicates in Comparison to Conventional Talcum-Filled Polypropylene

Sample	PP		PP-g-MA		layered silicate[a)]		Young's Modulus [MPa]	Yield stress [MPa]	Elongation at break [%]	Impact strength [kJ/m²]
	type	[wt.-%]	type	[wt.-%]	type	[wt.-%]				
PP/PP-g-MA	P4	80	HC5	20	-		1680	33	8	1.9
NC5	P4	75	HC5	20	ME/ODA	5	2542	39	4	1.8
NC10	P4	70	HC5	20	ME/ODA	10	3370	44	3	1.4
PP	KM6100	100	-		-		1410	31	74	2.7
T3-12	KM6100	88	-		talc T3	12	2510	32	36	3.1
T3-23	KM6100	77	-		talc T3	23	3110	32	13	3.1
T3-32	KM6100	68	-		talc T3	32	3610	31	9	2.9
T10-12	KM6100	88	-		talc T10	12	2300	31	28	3.3
T10-23	KM6100	77	-		talc T10	23	2940	31	9	3.4
T10-32	KM6100	68	-		talc T10	32	3310	30	7	3.1
T10-40	KM6100	60	-		talc T10	60	4250	30	5	2.7

a) T3: talc with average particle size of 3 μm (Prever M8 from Lucenac), T10: talc with average particle size of 10 μm (Prever from Lucenac)

Figure 10. Transmission electron microscopic image of polypropylene compound containing 10 vol% organophilic fluoromica (ME100/ODA) without addition of PP-g-MA compatibilizer (A, left) and the corresponding ME100/ODA nanocomposite obtained in the presence of 20 wt% PP-g-MA compatibilizer.

tant to achieve adequate dispersion and interfacial adhesion of the silicate layers (cf. Figures 10 and Figure 11). In the absence of PP-g-MA the shape of the fairly large initial ME/ODA particles is retained during processing, while PP-g-MA affords much larger interlayer distances and dispersion. As will be reported elsewhere in more detail, also the length of the n-alkyl substituent of the alkylamine plays an important role [63]. Although the mechanisms require further clarification by means of spectroscopy, it is obvious that the anhydride group attached to polypropylene promotes interfacial adhesion. Most likely, anhydride groups react with octadecylamine, which is present in acid/base equilibria, to yield N-octadecyl-succinimide-grafted polypropylene and silanol groups at the silicate surface which form strong hydrogen bridges to N-alkyl-substituted succinimide attached to iPP. Moreover, the octadecyl group attached to the polypropylene via imide coupling promotes hydrophobic interactions between octadecyl side

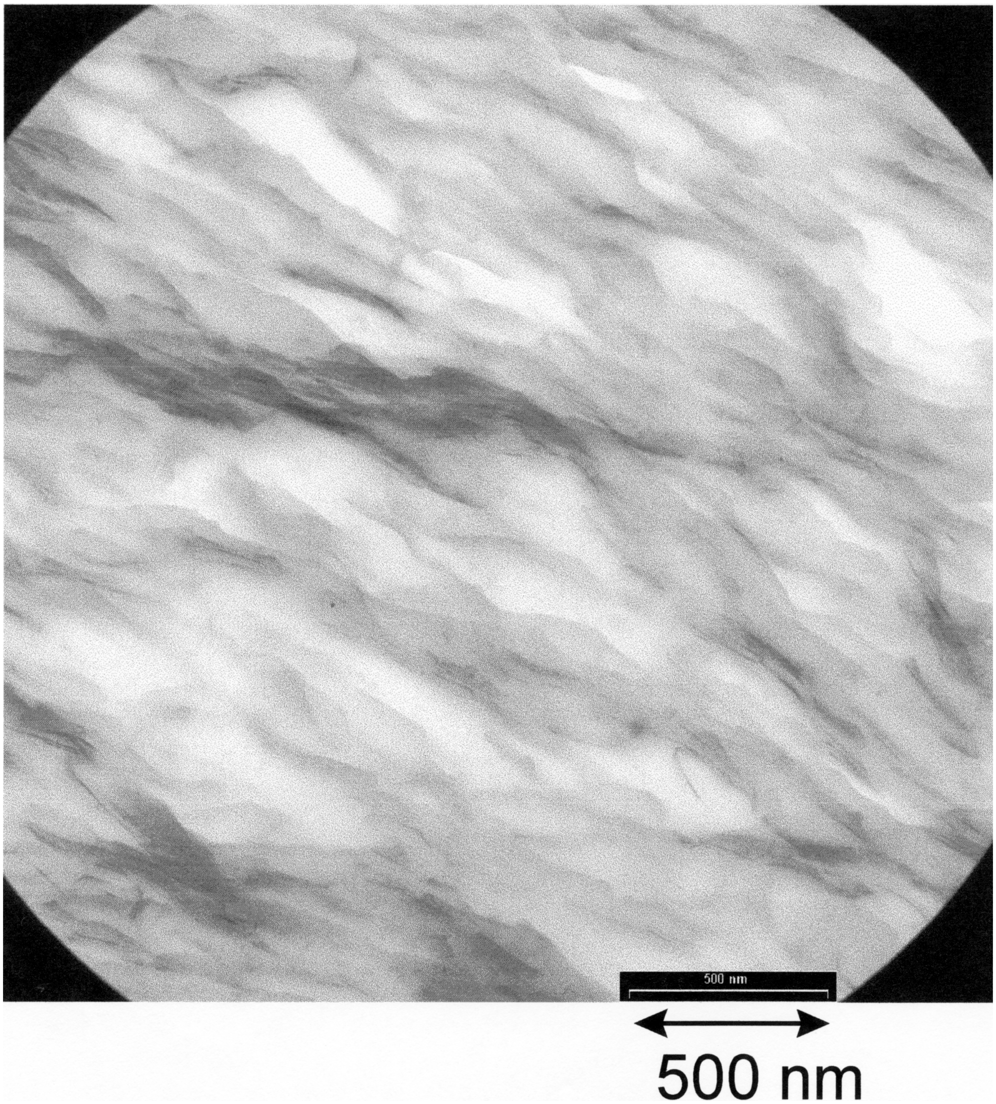

Figure 11. Transmission electron microscopic image of polypropylene nanocomposite containing 10 vol% organophilic fluoromica (ME100/ODA) and 20 vol% PP-g-MA as compatibilizer.

chains and octadecylammonium cations located at the silicate interface. Good interfacial adhesion via hydrogen bridges and strong hydrophobic interactions favors stress transfer during processing and affords steric stabilization of the silicate nanoparticles.

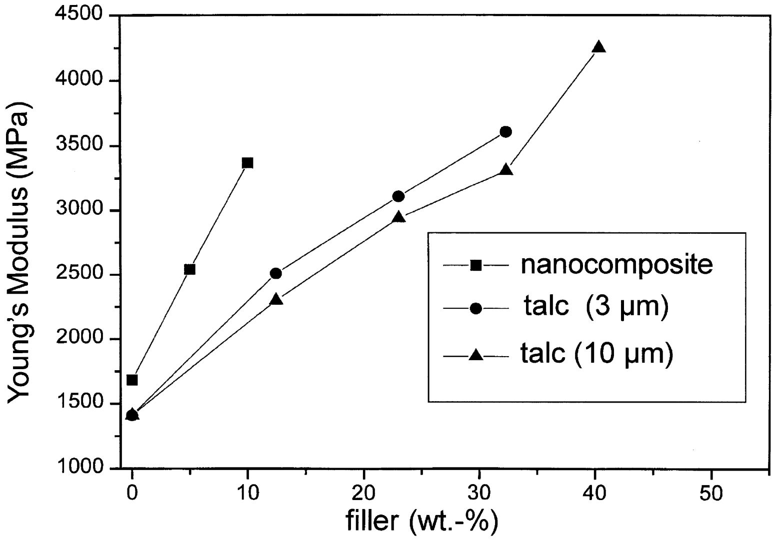

Figure 12. Young's modulus of polypropylene compounds, prepared by melt compounding, as a function of filler content using organophilic fluoromica and talc with 3 μm and 10 μm average particle diameter.

As apparent from Figure 12, an important feature of polypropylene nanocomposites with respect to conventional talc-filled polyprolylene is the possibility to achieve matrix reinforcement with much lower silicate content. In fact, 10 wt% organophilic ME/ODA, which corresponds to less than 7 wt% silicate when account is taken of the organic ODA content of ME/ODA, is sufficient to increase the Young's modulus to 3300 MPa. More than 30 wt% talc is needed to achieve similar stiffness. Clearly, the addition of 20 vol% PP-g-MA, which has lower molecular weight with respect to the iPP matrix, accounts for low toughness of both iPP/PP-g-MA blends and the corresponding nanocomposites (cf. Table 2). Therefore, it is obvious that both the selection of compatibilizers and optimization of processing conditions play an important role in polypropylene nanocomposite formation in order to achieve simultaneous improvements of stiffness and toughness. Are more detailed study addresses the role of such components [63]. In a recent disclosure, Montell North America and General Motors Research and Development announced the development of thermoplastic olefin elastomer-based polypropylene nanocomposites which are considered to compete with PC/ABS blends and other traditional thermoplastics. Since a few percent of organophilic layered silicates are sufficient to achieve reinforcement, nanocomposites are up to 30% lighter than competitive resins. Moreover, due to low filler content, painted parts were claimed to exhibit better surface appearance [64].

Although mechanical properties of PP nanocomposites do not yet match those of glass mat reinforced iPP, nanocomposite formation holds attractive potential beyond improvement of mechanical properties. In addition to matrix reinforcement, it is possible to enhance dimensional stability, reduce creep, improve interfacial adhesion, reduce gas permeation, reduce coefficient of thermal expansion, and promote flame retardency. In the future, a wide range of tailor-made organophilic clays will emerge as new additives of polypropylene, propylene copolymers, and poylpropylene compounds in order to achieve unique property combination and to upgrade and diversify polypropylene.

CONCLUSION

Although polypropylene has been discovered more than forty five years ago, polypropylene development will continue to represent one of the most innovative fields in chemistry with exciting potential for industrial applications. On one hand, new generations of single-site catalysts will facilitate tailor-making of novel polypropylene materials including polypropylene stereoisomers, propylene copolymers, and polypropylene compounds produced either by melt processing or reactor granule technology. An important challenge in catalyst development is to explore new systems which incorporate polar comonomers in order to overcome property limitations associated with the hydrocarbon nature of the polyolefin backbone, e.g. poor dyeability and paintability, which require surface pretreatments and compatibilizer addition. On the other hand, propylene polymers will be used extensively as raw materials in melt compounding. Blends and compounds with well-defined nanoscale-architectures will be the key to a wide range of materials with unusual property combinations and expansion of low-weight polypropylene materials in engineering applications. At the beginning of the 21st century the extraordinary versatility of polypropylene offers attractive potential for the development of materials which meet the demands of sustainable development.

ACKNOWLEDGEMENTS

The authors thank the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie (BMBF) for financial support as part of the BMBF project no. 03D00551. Furthermore, the authors thank BASF AG for supporting this research and appreciate many helpful advises by Dr. Thomas Engelhardt form Süd-Chemie AG concerning clay and nanocomposite chemistry.

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