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- [3] A. Reicharz, A. Demarmels, 'Damage characterization in silica filled epoxy resins', to be presented at EPF '90, 3rd Eur. Fed. Symp. on Polym. Mat., Sorrento, Italy, Sept. 24–28, 1990.
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- [5] 'Interfacial Phenomena in Composite Materials '89', Proc. Conf. from Sept. 5–7, 1989, Sheffield, UK, Ed. F. R. Jones, Butterworths, London, 1989.
- [6] E. P. Plueddemann, 'Silane Coupling Agents', Plenum Press, New York, 1982.
- [7] E. P. Plueddemann, 'Present status and research needs in silane coupling', in 'Interfaces in Polymer, Ceramic, and Metal Matrix Composites', Ed. H. Ishida, Elsevier Science Publishing Co., Inc., New York, 1988, p. 17.
- [8] J. E. Castle, J. F. Watts, 'Surface analytical techniques for studying interfacial phenomena in composite materials', in 'Interfacial Phenomena in Composite Materials '89', Ed. F. R. Jones, Butterworths, London, 1989, p. 3.
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- [12] F. R. Jones, 'Interfacial aspects of glass fibre reinforced plastics', in 'Interfacial Phenomena in Composite Materials '89', Ed. F. R. Jones, Butterworths, London, 1989, p. 25.
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- [16] D. Skudely, 'Silanisierter Füllstoffe und ihre Einsatzgebiete', *Kunststoffe* **1987**, *77*, 1153.
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- [18] A. C. Moloney, H. H. Kausch, H. R. Stieger, 'The fracture of particulate-filled epoxide resins', *J. Mater. Sci.* **1983**, *18*, 208.
- [19] J. Lilley, 'The fracture of filled epoxy resins', Ph.D. Thesis, University of Keel, 1973.
- [20] J. Spanoudakis, R. J. Young, 'Crack propagation in glass particle-filled epoxy resin', Part 2: 'Effect of particle-matrix adhesion', *J. Mater. Sci.* **1984**, *19*, 487.
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- [24] W. J. Cantwell, A. C. Roulin-Moloney, T. Kaiser, 'Fractography of unfilled and particulate filled epoxy resins', *J. Mater. Sci.* **1988**, *23*, 1615.
- [25] H. R. Beer, T. Kaiser, A. C. Roulin-Moloney, H. H. Kausch, 'Static fatigue and time to failure predictions of particulate filled epoxide resin composites', *J. Mater. Sci.* **1986**, *21*, 3661.
- [26] J. W. Smith, 'Deformation induced failure mechanisms in particulate filled epoxy resins', Ph.D. Thesis No. 792 EPFL, Lausanne, 1989.
- [27] A. Reicharz, A. Demarmels, T. Kaiser, ABB Corporate Research, internal reports.

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Hans-Peter Schlumpf*

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termed as fillers or extenders. In thermoplastics, both fillers (excluding air) and reinforcing additives have only four things in common: they increase the volume, enhance stiffness, decrease the elongation and thermal expansion, and improve the dimensional stability of the finished parts.

2. Market Situation

Filled polypropylene is one of the fastest growing thermoplastic material in Western

Europe and the USA. Talc is the leading filler for polypropylene followed by natural CaCO₃. A low consumption for all other mineral fillers with the exception of glass fibres can be foreseen for the next years. Main applications for mineral filled polypropylene are automotive parts like heating systems, air intake or lamp housings. Injection-moulded garden furniture is actually the hottest item for talc or carbonate filled polypropylene. Electrical, business, and domestic appliances (kitchen and washing-machine parts) have a good potential too. Not to forget the application of fine carbonates in oriented polypropylene film (OPP) weaving tapes or strappings.

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3. Mineral Fillers in Polypropylene

The classification of fillers according to their chemical composition makes, due to the resulting complexity, this frequently unfamiliar field very difficult on the part of the processors. A substantial clearer picture of the influence of the fillers is obtained, when they are classified according to their mode of action. In this case, the most important selection factors are: 1) aspect ratio or shape, 2) coarsest particles (top cut), 3) specific surface area, 4) surface energy or surface tension, and 5) surface treatment.

3.1. Aspect Ratio (Shape of the Particles)

The so-called aspect ratio or shape of fillers, meaning the length of the particles divided by their thickness, determines in polymers with medium-to-low polarity like polypropylene, whether they act as a filler or reinforcing additive. The technical literature defines five different filler shapes: 1) sphere (glass and silicate spheres), 2) cube (CaCO_3), 3) block (silica, BaSO_4), 4) platelets (talc, mica, kaolin, graphite), and 5) fibres (glass, carbon or cellulose fibres, wollastonite, whiskers).

All main mechanical properties of mineral filled polypropylene are very much influenced by the aspect ratio of the fillers involved.

Reinforcing fibres (glass fibres, wollastonite) increase in polypropylene the tensile strength, the stiffness (modulus), and the impact strength of the composite. Negative factors are the decreased three-dimensional tension distribution and shrinking behaviour.

Platelets like talc or mica act mainly by increasing the stiffness of filled polypropylene. Plate-like fillers decrease important properties like tensile strength, impact strength, and the three-dimensional shrinking. From the composite behaviour, the reduced impact strength (brittleness) is the limiting factor for many applications.

Spherical fillers like CaCO_3 , glass or silicate spheres lead in polypropylene to a medium stiffness only which is, at the same filler level, lower than the stiffness when adding platelets or fibres. In contrast to plate-like fillers, the impact strength of homo-polypropylene filled with spherical additives like CaCO_3 up to a filler level of 30 wt.-% is practically unchanged.

3.2. Coarsest Filler Particles (top cut)

Modern air classification technology used by the filler producer allows a very sharp top cut of the filler distribution curve

to be made. This top cut markedly influences the mechanical properties of filled polypropylene. The coarsest foreign particles are the places of the highest stress concentration at which cracking or fracture occur upon the application of stress. Moreover the top cut affects the following parameters:

- impact strength (increased)
- surface finish (higher gloss)
- burst strength of films (increased)
- abrasion of screws and barrels (reduced)

3.3. Specific Surface Area of the Filler

The specific surface area of fillers (m^2/g) is measured with the BET method using N_2 as adsorbent. The filler surface area determines the number of possible adsorption places between the polymer chains and the additive. A large filler surface area gives rise to an important number of possible adsorption sites and, thus, to better mechanical values than a smaller surface area. Increasing the specific surface area of a filler means producing an increased amount of very fine particles. Very fine particles lead, in relationship to the gravitational forces, to much higher *van der Waal's* interaction forces than coarse particles. This can be demonstrated by the well known filler agglomeration leading sometimes to feeding problems in the compounding equipment, therefore, increasing considerably the dispersion problems of polar fillers in unpolar polymers like polyolefins. However, in the processing or compounding with insufficient shearing forces, a too large filler surface area can lead to dispersion problems in polypropylene. If non-divided filler agglomerates are thereby formed, they act like a coarser top cut. Therefore, filler level and filler surface area should always be adjusted to the shearing conditions of the compounding equipment so that the additive can be dispersed without problems.

3.4. Surface Energy or Surface Tension

The surface energy (mJ/m^2) of fillers can not be determined directly, but mathematically the surface energy is the same as the surface tension (mN/m) which can be measured even of powders. The surface energy is determined by the outmost atomic layer of the filler surface. The surface energy or surface tension determines the magnitude of the interaction forces between plastic molecules and the filler surface, and, thus, decisively effects the mechanical properties of the polypropylene compounds. The values of surface energies for fillers, reinforcements and polymers vary very much:

mica	2400 to 5400 mJ/m^2
glass fibres	1200
kaolin	500–600
CaCO_3	65–70
talc	60–70
polypropylene	31
Teflon	18

Also in this case as with the surface area, too high surface energies, e.g. mica or kaolin, may cause dispersion problems in polypropylene. Like this, the advantage of the high interaction forces between filler and polymer is removed. The filler producer can change the surface energy up to a certain degree by surface coating of the products. To obtain a better susceptibility to dispersion, attempts to decrease the surface energy are, therefore, usually made.

3.5. Surface Coating

Many discussions among the users of fillers and reinforcing materials for polypropylene are circling around surface coatings, coupling agents, or similar additives. The chemicals offered on the market may include: silanes, titanates, zirconaluminates, Cr complexes, fatty acids or esters, fatty metal soaps, esters or waxes.

The possibilities of surface coatings for mineral fillers for polypropylene can best be explained taking mica, talc, and CaCO_3 as samples:

Talc: no chemical coupling possible; coating with lubricants like metal stearates, esters or waxes

Mica: chemical coupling possible; silanes (azido silanes), organic silicones

CaCO_3 : coupling with acids possible; chemisorbed dispersing agents, specialized surface coating for rapid filler dispersion.

A good surface treatment covering most of the filler surface and having a good chemical or physical bond with the filler surface is an important asset for a mineral filler leading to the following advantages in polypropylene: 1) hydrophobicity, 2) decrease of surface energy, 3) better dispersion, 4) easier compoundability, 5) better flowability, 6) reduction in stabilizers and lubricants, and 7) better surface finish.

The main function of most surface coatings is to decrease the surface energy of the filler. In this way, the attraction forces between the mostly polar filler particles, especially in unpolar plastics like polyolefins, are greatly reduced. In contrast to uncoated fillers, less agglomerates are formed which can cause negative effects as mentioned above. Moreover, surface coatings of fillers decrease the adsorption of phenolic-type stabilizers on the filler surface and, thus, improve the thermo-oxidative stability of filled polypropylene considerably.