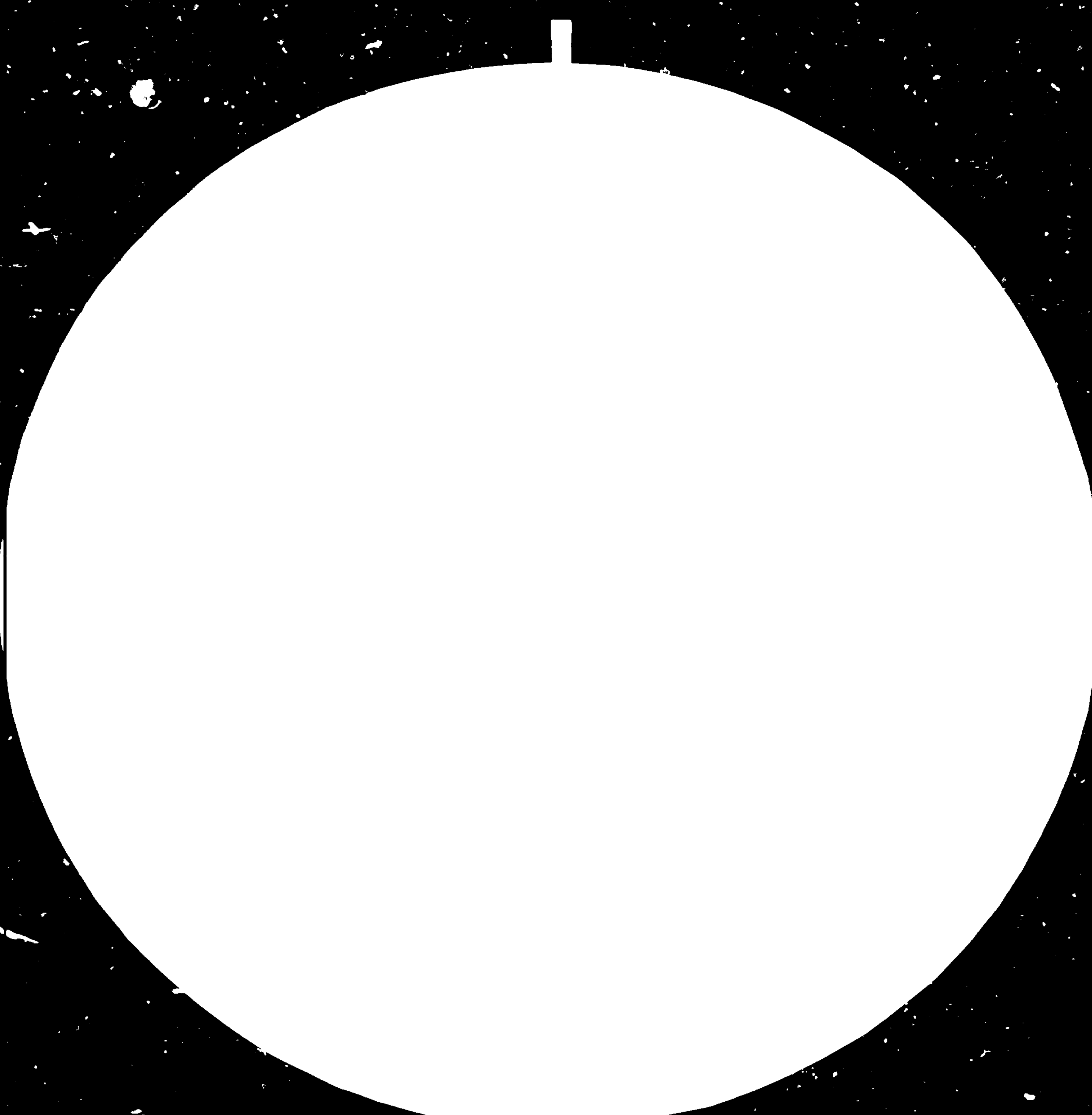
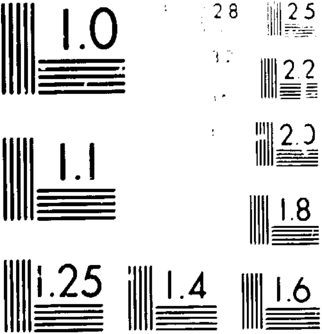
UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org




1.0
2.8
2.5
2.2
1.1
1.8
1.25
1.4
1.6

→ Maria Dietrich

UNIDO - Czechoslovakia Joint Programme
for International Co-operation in the Field of Ceramics,
Building Materials and Non-metallic Minerals Based Industries
Pilsen, Czechoslovakia

Distr
LIMITED

JP/58/80
September 1980

ORIGINAL: English

12140

SPECIFICATION OF LIMESTONE AND KAOLIN PROPERTIES FOR THEIR USE AS FILLERS FOR PLASTICS.

By: Jiří Babůrek +

Special Consultant: Z. A. Engelthaler

35

+ Research Institute for Ceramics, Refractories and Raw Materials, Horní Bříza, Czechoslovakia

ABSTRACT

The study deals with the significance of mineral fillers - especially aimed at the application of calcium carbonate and kaolin - for the production of plastics.

The most important requirements on the initial raw materials are specified and explained. The problem of special dressing methods of these materials, however, is extraordinarily complicated and it is the subject of an intensive research in all the industrially developed countries of the world.

CONTENTS

INTRODUCTION

Plastic composite materials are formed by an intimate mixture of a thermoplast or resin and a filler. In compliance with the terminology suggested by an American company for material testing a filler is defined as a relatively inert material added into the plastics with the aim to modify their strength, toughness, processability and other qualitative parameters or to cut production costs. Against that plastics with mineral fillers are usually defined as synthetic materials the strength of which exceeds considerably the strength of the basic organic material. In this case, however, mainly materials of fibrous nature are used as fillers.

The strength of a large number of natural materials depends to considerable extent on a mutual relation of the so called countinuous and discontinuous phase of a mixture. For instance the stiffening effect of straw added into bricks was known to the Egyptians as early as more than 2000 years ago.

Practically all thermosetting plastics are of a composite nature but some thermoplastics were applied with fillers many years ago. For instance phenolic plastics were successfully filled with wood saw dust as early as at about the year 1900; the strength of polystyrene was successfully doubled by adding glass fibres about 50 years later.

At present we live in the age of so called composites. Composite materials are becoming ever more significant to be applied in the processing industrial branches where high quality of products must be ensured at ever decreasing sources of labour and at minimum energy consumption.

It may be said that the following properties will be a decisive criterion for the choice of materials:

mechanical properties:	modulus of elasticity and toughness
chemical properties:	atmospheric stability incombustibility chemical resistance
economical parameters:	high productivity in processing cheap raw materials cheap production technology

INFLUENCE OF FILLERS ON THE PROPERTIES OF PLASTICS

1. Modulus of elasticity and toughness

The modulus of elasticity is incidental to the strength of intermolecular bonds which are comparatively weak in amorphous organic materials.

For great many products, first of all for those being transported or which are used as structural materials for the building of transport means (airplanes, motor cars, ships and subjects of daily use), it is important that the material could not only be loaded with maximum force but, at the same time, weight of the material should also be as low as possible. Therefore, it is useful to compare also the specific moduluses of elasticity of the individual materials. The two values of some selected materials are shown in Table No. 1.

It is obvious that, from the point of view of specific modulus of elasticity, glass is equivalent to steel but its well known deficiency is its low toughness caused by a very slow dissipation of elastic energy when supplied to it by an impact. The energy is consumed by breaking of chemical bonds in the neighbourhood of the impact.

From the values shown in Table No. 1 it is evident that even the implementation of transverse bonds in polar amorphous resins (phenolics, polyesters, etc.) could not increase the modulus of elasticity above 4 GPa and that these materials cannot compete with iron, glass or cellulose fibres from the hardness point of view. Therefore, a development of so called reinforced plastics is being quickly widespread recently. The tough inorganic phase in them forms a component of high modulus of elasticity whereas the organic polymer serves the purpose of bonding agent rendering high toughness to it.

Laminates - material possessing a high modulus of elasticity forms the continuous phase (fabric, etc.) and a thermosetting plastic or a thermoplast is the bonding agent. Thereby high moduluses of elasticity are achieved but processing is rather difficult and expensive.

Filled thermoplasts - filler, i. e. a component with a high modulus of elasticity forms the dispersion phase in the continuous thermoplastic matrix. It is an advantage that the thermoplastic processability of the filled thermoplasts is preserved. From the point of view of increasing the modulus of elasticity the most effective known fillers are short glass fibres. Less effective are fillers in the shape of particles though e. g. when 60% of kaolin was used as a filler in the mixture of a linear polyethylene the modulus of elasticity was increased 7 times against a polyethylene without any filler (Table No. 1). Non-modified particle fillers cannot be dispersed well in organic polymers and they usually cannot form a strong enough bond with the surrounding polymer matrix that results in a low toughness of composite materials made this way. Therefore, the main point of research should be a creation of such boundary layers between the fillers and the polymer matrix which can provide for an effective transfer of forces

Table No. 1 Moduluses of elasticity and specific moduluses of elasticity of some materials

Material	Modulus of elasticity GPa	Specific modulus of elasticity MPa.m3.kg-1
carbon fibre	210 - 420	85 - 170
steel	210	27
glass fibre	70 - 110	28 - 44
hemp, flax	50 - 80	30 - 50
spruce wood -		
longitudinally	16,6	33
radially	0,85	1,7
tangencially	0,70	1.4
polyethyleneterephta-		
late fibre	12	8.7
phenolic resin	2,7 - 4,2	1.9 - 3.2
hard PVC	3	2.1
l - polyethylene	0.9 - 1.2	1.0 - 1.3
r - polyethylene	0.2	0.2
rubber	0.01	0.01
Polyester laminate	7 - 21	5.4 - 11
l - polyethylene - kaolin		
40% of weight	2.5	2.0
60% of weight	4.7	3.1

that is a condition for the achievement of high modulus of elasticity as well as of high toughness.

2. Atmospheric stability

When compared with iron the plastics are advantageous because they cannot be attacked with corrosion but their atmospheric stability ranges in a very broad interval from materials quickly degradable up to materials of a long-time stability. The influence of filler on the photooxidation stability of polymers is mostly very complicated. Briefly said there are two overlapping influences - a photofiltration one and a catalytic one. A purposeful modification of fillers is a very prospective way how to increase or intentionally reduce the life of polymers.

3. Incombustibility

Combustibility is one of the main deficiencies of the majority of plastics, It is obviously impossible to achieve incombustibility of organic materials. However, it is necessary to pay attention to the justified fire safety requirements. Furthermore, it is also essential to point out to the required unintoxicability and corrosion resistance of the combustion products as is the case of phosgene and hydrogen chloride arising from burning PVC. A great advantage in using inorganic fillers to increase the fire safety may be seen in the fact that in case of mixtures with fillers the polymers do not drip.

It is quite known, e. g. when ceilings are clad with foamed polystyrene the burning material drips down on the floor whereby the whole room becomes a fireplace.

4. Chemical resistance

For application in a corrosive environment it is necessary to use fillers being themselves chemically resistant. For this reason a possible use of calcium carbonate is to be limited.

Another more complicated problem is constituted by the influence of filler on the velocity of diffusion of various chemicals. It is connected first of all with a creation of a suitable structure of intermediate phases at the boundaries between the filler and polymer resulting in a reduced movability of macromolecular segments.

5. Easy processability

Particularly the high productivity in processing is the main reason for the quick spreading of practical applications of plastics in the processing industrial branches. Savings achieved especially in the series production of engineering products due to the high productivity are so large when compared with metals that the cost of a polymer is not decisive.

Generally, it may be stated that in case of precise demanding products mechanical properties and processability will be the most significant properties whereas in case of less demanding products for wide use the cost of a polymer will become decisive.

The effect of fillers on the rheological properties by melting of thermoplastics is much complicated. It is necessary to realize that the melt of a polymer represents a non-Newton suspension in a non-Newton matrix. When the conditions have been chosen properly then thermoplastics with high content of fillers can be worked at high speeds without difficulties. Another unquestionable advantage of using filled mixtures is the possibility of quicker cooling which is a decisive criterion for the duration of injection cycle especially in case of large products.

As aforesaid, it is useful to use expensive fillers chiefly for the precise and demanding products; a comparatively expensive polymer matrix is mostly applied, too. An example of such a new reinforced thermoplastic may be given by polybutylene - a terephtalate filled with short glass fibres, its softening point being 214°C (at 1.82 MPa stress and 9.0 GPa modulus of elasticity). To the contrary, however, in case of serially produced cheap polymers - mainly polyolefins and PVC - it is useful to apply first of all cheap fillers in the highest possible concentration.

Out of a number of applicable inorganic fillers further attention will be paid here to the specification of two most perspective types - fillers on the basic of calcium carbonate and kaolin.

CALCIUM CARBONATE FILLERS

Calcium carbonate ($CaCO_3$) belongs to those inorganic fillers being used for the filling of plastics in ever increasing volumes especially owing to the following reasons:

- Their price is one of the lowest when compared with other quality fillers.
- Fillers of this type are non-poisonous, non-irritant and odourless.
- They are white and have significantly low index of refraction, they can be easily dyed to any shade.
- They are soft - the third degree of the Mohs scale.
- They do not contain water of crystallization.
- The raw material for them occurs in a very large number of deposits.
- Their particle size can be easily influenced in the widest range from among all the inorganic fillers.
- Their grain size classification can be controlled with great accuracy in compliance with the respective type of the polymer.
- Fillers of this type may be comparatively easily surface finished and dressed in dry state.
- These fillers can be blended with the majority of plastics without any technological difficulties.

- Their significant feature is that they are able to bind acids in the case of a secondary stabilization of polyvinylchloride - they neutralize chloride ions.

- They reduce shr nkage during the processes of casting and injecting of the composites.

- They are stable within a relatively wide temperature range - dissociation with calcium oxide (CaO) and carbon dioxide takes place at 800 to 900°C temperatures.

Calcium carbonate is a polar, reactive compound which has also some defficiencies from the point of view of its use as a filler into the plastics:

- Under the action of some stronger acids it releases a carbon dioxide while soluble salts are formed at the same time.

- Trigonal crystalline habitus of limestone (calcite) particles causes a lower reinforcing effect when compared with inorganic fillers of fibrous shape.

Calcium carbonate differs considerably from other inorganic fillers used in large scale such as e. g. kaolin, talc, quartz, etc. mainly by its whiteness, absence of water of crystallization and easy processing ability.

Basic criterions are shown in Table Nos. 2 and 3 being important for the assessment of suitability of various carbonate raw materials intended for the production of fillers for plastics. The tables also cover the most important parameters of the produced fillers. Carbonate raw materials must be of high mineralogical purity particularly because the presence of hard minerals (especially quartz) would affect adversely the abrasivity of the filled plastic that would result unfavourably in a quick wear of the forming machinery. The mineralogical purity of the initial raw material is also a very important factor influencing the whiteness of the final product.

Since fillers of this type are applied in a series of industrial uses such as in thermoplastics, thermosetting plastics, epoxy resins, rubber, coatings, insecticide carrier, etc. the applied raw material must be of high mineralogical purity, especially with extremely low content of compositions of iron, manganese, copper and sulphur.

Basic tests of suitability of a certain type of carbonate raw material for the production of fillers are as follows:

a) Chemical analysis including the determination of iron, manganese and copper contents extractible in nitric acid and of rest insoluble in nitric acid.

b) Mineralogical analysis aimed at the determination of structure and heterogenous admixtures, sizes of primary grains or particles.

c) Determination of whiteness and light reflectability under blue, green or red filters.

d) Grindability tests in various types of mills.

e) Practical tests of application of fillers into plastics including testing of products.

Table No. 2

Chemical composition of limestones (calcium carbonate) for the production of fillers for plastics (% weight)

Components	1	2	3
$CaCO_3$	98.2	98.1	97.95
$MgCO_3$	1.2	0.8	1.43
SiO_2	0.25	0.48	0.35
Al_2O_3	0.12	0.26	0.21
Fe_2O_3	0.06	0.11	0.08
H_2O	< 0.10	< 0.21	< 0.18
MnO_2	0.0035	0.004	0.0038
Cu	0	0.0006	0.0003
heavy metals	< 20 ppm	< 32 ppm	< 26 ppm

1 - refined limestone - USA

2 - reinforced chalk - France

3 - crystalline paleozoic limestone - ČSSR

Table No. 2a   Chemical composition of selected types of carbonate fillers for plastics (% weight)

Components	1	2	3
$CaCO_3$	98.70	99.75	99.0
insoluble rest in HCl	0.90	0.20	0.98
SiO_2	0.80	0.1	0.32
Fe_2O_3	0.20	0.02	0.07
Al_2O_3	0.15	traces	0.29
MgO	traces	traces	0.15
Mn	0.02 max.	traces	0.01
loss by drying at 110°C	0.10 max.	0.10	0.2 max.
So_4	0.15	0.06	0.08

1 - filler made of chalk - Champagne, France

2 - filler made of crystalline limestone (marble) - Spain

3 - filler made of crystalline limestor - Yugoslavia

Table No. 3 **Physical properties of different carbonate raw materials applicable <u>in the production of fillers</u>**

	Calcite	Aragonite	Dolomite
Specific weight	2.60-2.75	2.92-2.94	2.80-2.90
Hardness (MOHS)	3.0	3.5 - 4.0	3.5 - 4.0
Solubility in 100 parts of water at 18°C temperature	0.0013	0.0019	0.032
melting point	1339°C	it is changed into calcite at 825°C temperature	decomposition at 730--760°C temp.
formation and occurrence	limestone marble calcite chalk	cells of lamellibranches and corals, mineral forms are formed within 30-400°C temp.	rock complexes usually of Mesozoic age

Table No. 4 Testing of calcium carbonate for plastics by an ASTM method

	Standards
Particle size determination (sediment)	D 422
Particle size determination (sieves)	E 161, D 546
Bulk density	C 128, D 1895
Electric resistance (in water)	D 2448
Reflectability	E 97, D 2244
Oil absorption	D 281
Moisture content	D 280 (A method)
Specific weight	D 153
pH in water (5% $CaCO_3$ at 23°C temperature)	D 1208

Table No. 5 Properties of carbonate fillers intended for plastics used in food industry

	% microground limestone	% precipitated limestone
Content of $CaCO_3$ after drying (minim.)	94.0	98.0
Alkalis and magnesia salts	3.5	1.0
Loss by drying (max.) ASTM D 1199	2.0	2.0
Insoluble rest in acids ASTM D 1199	2.5	0.2
Fluorine content (max.)	0.005	0.004
Content of heavy metals (max.)	0.004	0.003
Lead content (max.)	0.0003	0.001
Arsenic content (max.)	0.0003	0.0003
Mercury content (max.)	0.00005 (0.5 ppm)	

Table No. 6 Typical physical properties of micronized carbonate fillers

	-325 mesh limestone of high purity	-325 mesh limestone of high purity	-325 mesh dolomitic limestone
PLA specification	P1	A1	A2
particle size %			
less than 0,5 µ	4	-	-
1	18	4	-
2	38	14	5
4	65		
5		31	
6	80	45	18
8	90	52	33
10	96	68	47
20		79	62
25		91	76
30		96	
35			90
40			96
% of particles exceeding 44 microns, ASTM-E 161 D 546	0.01	0.5	
light reflectability % ASTM-E 97 D 2244			
green filter	96.6	91.7	
blue filter	95.6	89.4	
pH in water 5% suspension at 23°C temp. ASTM D 1208	9-9.5%	9.5	9.0-10.0
water soluble salts at 23°C	0.06	0.06	
electric resistance in water - in ohms at 23°C temp. ASTM D 2448	17000-25000	17000-25000	3000-5000

KAOLIN FILLERS

The industry producing polymers shows ever increasing consumption of specially treated kaolins. The research in the dressing of kaolins for paper and ceramic industries has shown very good results in the recent decades many of which, concerning especially the refinement of kaolin, can be applied even in the production of plastics to a considerable extent.

Kaolins have a very important position among white fillers used in the production of rubber and, along with the calcium carbonate, they show the largest consumption trends even in the production of thermoplastics. The reason is quite obvious - specially dressed kaolin fillers influence significantly positively some physical properties of the plastics at a relatively low cost.

Suitable types of kaolins may be approximately classified into three groups. Two of these groups include kaolins according to the size and/or shape of particles the third group includes specially modified kaolins. According to the terminology being currently used in English (especially in America) professional literature the kaolins in the first two groups are classified as per their plasticity, i. e. whether they are "soft" or "hard".

It is difficult to define exactly the two types from the point of view of chemical or mineralogical composition. So called non-plastic kaolins, however, have finer particles and are more suitable to be used in the production of fillers. This viewpoint, however, does not apply to the most of the European kaolins the genesis of which is considerably different from that of the kaolins from Georgia and Florida - USA.

The third group includes calcined kaolins of low grade surface dressing method. Favourable dielectric properties of these materials which they keep for long periods even under unfavourable climatic conditions are their significant features.

In Table Nos. 7 and 8 there are shown basic properties important for the application of kaolin fillers in the production of plastics. To judge the raw materials usable in the production of special fillers for plastics the following properties are of a particular importance:

a) high mineralogical purity more closely specified especially by a low contents of abrasive admixtures (particularly of quartz and mica)

b) high chemical purity, especially low contents of iron, copper, manganese compositions and organic matters

c) high degree of whiteness and light reflectivity (particularly while using blue filter - after drying as well as after calcination).

Table No. 7 Properties of kaolin fillers for plastics

Properties	Kaolin dressed by wet method			Kaolin dressed by dry method	
	coarse grained	medium	fine grained	coarse grained	fine grained
Specific weight ASTM D 152	2.58	2.58	2.58	2.58	2.58
pH (20% suspension in water)	2.8-7.5	3.8-7.5	3.8-7.5	3.8-5.5	3.8-5.5
hardness (MOHS)	2	2	2	2	2
surface square area (m2/g - BET)	6-10	14-16	18-22	10-12	12-24
oil absorption (ASTM D 281)	28-32	32-40	40-48	28-32	34.40
"free" water content (% max.) ASTM D 280	1.0	1.0	1.0	1.0	1.0
whiteness (G.E. %-MgO)	79-85	85-87	87-90	74-84	74-80
ø particle size in microns ASTM D 422	4-9	1.8-0.7	0.7-0.2	1.5-1.8	0.3

Table No. 8 Properties of kaolin fillers for plastics - continuation

Properties	Calcined kaolin		Surface dressed kaolin		
	partially	completely	silane	resin	cation dressing
Specific weight ASTM D 153	2.50	2.63	2.58	2.58	2.58
pH (20% suspension in water)	4.2-6.0	4.2-6.0	4.0-9.0	6.5-7.5	7.0-8.0
hardness (MOHS)	4-6	6-8	2-8	2	2
surface square area (m2/g) BET	5-12	5-12	8-24	14-16	14-16
oil absorption (ASTM D 281)	45-60	45-90	28-60	28-31	24-33
"free"water content ASTM D 280	0.5	0.5	0.5-1.0	0.5-1.0	0.2-0.5
whiteness (G.E. %-MgO)	85-90	90-96	74-92	85-87	80-87
average particle size in microns ASTM D 422	1.5-1.8	0.9-3	0.3-3.0	0.7	0.6-4.5

Table No. 9 Optimum chemical and mineralogical composition of kaolins applicable for the production of fillers for plastics

Components	High quality filler, % by weight	Medium quality filler, % by weight
SiO_2	45.4	48.9
Al_2O_3	38.8	35.5
Fe_2O_3	0.3	0.6
TiO_2	1.0	0.8
CaO	0.1	0.3
Na_2O	0.1	0.1
K_2O	0.5	1.2
loss by ignition	13.8	12.7
kaolinite	95	88
quartz	1	5
mica and other accessory minerals	3	7

Table No. 10

Characteristic values of trace elements contents in kaolins intended for the production of fillers for plastics

Element	ppm
mercury	less than 3
arsenic	less than 10
barium	10 - 50
copper	1 - 9
(at fillers for rubber materials)	max. 3
lead	1 - 9
zinc	10 - 90
manganese	50 - 150
cadmium	10
antimony	10
nickel	10
cobalt	15
molybdenum	15

LIST OF TABLES