Physicochemical Problems of Mineral Processing, 42 (2008), 165-176
Fizykochemiczne Problemy Mineralurgii, 42 (2008), 165-176

Suzan S. Ibrahim*, Ayman A. El-Midany*

EFFECT OF TRIBLOCK-COPOLYMERIC COMPATIBILIZING ADDIDTIVES ON IMPROVING THE MECHANICAL PROPERTIES OF SILICA FLOUR -FILLED POLYPROPYLENE COMPOSITES

Received May 15, 2008; reviewed; accepted July 31, 2008

Minerals are introduced during the compounding processes into the polymeric host matrix in most thermoplastics industries to accomplish a variety of modified physical characteristics to the new-born composites. The introduction of well-dispersed silica flour particulates; tailored with respect to grade and fineness; into the virgin polypropylene matrix has shown an extreme improvement in the performance characteristics of the end-product. This could be attributed to the relatively low thermal expansion coefficient of silica. In this study, purified silica flour was blended with polypropylene to produce the finished masterbatch formulation for plastics industry. The flour was added during compounding stage with different loading levels from 1.5% to 15% by volume. Results showed substantial improving in many physical properties, i.e., increase in Young's modulus, impact strength, and yield stress measures. Moreover, silica addition resulted drop in all strain measures of the end products with various loading levels. On the other-hand, the addition of styrene-ethylene/butylene-styrene block SEBS and its grafted maleic anhydride surface compatibilizers was extra added during the blend digestion process to enhance silica/ PP wettability. After the addition of SEBS compatible reagent, results did not show improving in both Young's modulus and yield strength measures. Yet, remarkable improvement in impact strength and strain characters was noticed.

key words: silica, polymers, properties, Young's modulus, impact strength, yield stress, polypropylene

INTRODUCTION

Minerals as fillers have wide applications in different industries. Their addition advantages are twofold either performance enhancing and/or cost reduction. In the

* Central Metallurgical R&D Institute (CMRDI), P. O. Box 87, Helwan, Cairo, Egypt

first case, the mineral is called the functional filler because the mineral addition is incorporated to achieve a specific performance attribute to the end-product. Among these properties are the particle shape, the particle size and size distribution, purity, chemical and thermal inertness, (Table 1), (O'Driscoll, M., 1994). Whilst in the second case where the reduction of total formulation cost is being the principle driving force, the mineral represents merely the bulk filler or the extender for the costly polymer base matrix (Trivedi, N.C., Hagemeyer, R.W., 1994; Lee S., 2000; Dearmitt, C., 2000).

Table 1. Different plastic requirement needed to certain filler characteristics (O'Driscoll, M., 1994)

Compounding/plastic requirements	Filler requirements
Optimum compounding	Mean particle size, good wettability, good dispersion, no static charge
Low viscosity during compounding	Particles round as possible, small specific surface, low absorpitivity
High compounding speed	Low specific heat, high thermal conductivity
Low shrinkage, low internal stresses, no cracks	Low specific heat, high thermal conductivity, low thermal expansion, uniform filler distribution, good adhesion between filler and plastic
No abrasion in processing machines	Low hardness, small round particles, good thermal stability of any surface treatment used
High tensile strength & elongation, flextural strength	superior strength to matrix, high aspect ratio, good fiber/matrix adhesion, good distribution,
High stiffness	high aspect ratio in fiber, high modulus of elasticity
Good impact strength	Long fibers, adhesion to polymer matrix should not be perfect

Table 2. Effect of different mineral fillers with certain loading % on the properties of standard news prints (Johnston, J. H., 1997)

Property of 48.4 g/m^2 standard newsprint	Filled with type I silica at 1.8 wt% addition level	Filled with calcined clay at 1.7wt% addition level
Brightness change (points)	+1.7	+1.4
Opacity change (points)	+1.7	+1.1
L* change (points)	+0.9	+0.8
Porosity	+15%	0%
Top side roughness	-10%	0%
Burst strength	-10%	-9%
Tensile strength	-6%	0%
Coefficient of friction	+41	Not measured
Print through reduction	30-36%	20%

Silica is one of the most extensively and cheapest mineral commodity used in filler applications. When silica flour is embedded in a polymer matrix, it is constrained by its siliceous surface properties and its high degree of hydrophilicity in polymeric matrices (Lofthouse, C.H., 1997). Silica application ranges from using as an extender to a functional filler, Table 2 (Johnston, J.H., 1997). In plastics, it is used to increase abrasion, heat and scratch resistance in thermoset kitchen sinks. In electrical end-uses, it improves compressive, flexural strength, and dielectric properties. It is often used in corrosion protection systems, due to its superior resistance to corrosion, (Bryk, M.T., 1991; Scherbakoff, N., 1993; Payne, H. F., 1985; Zhang, Y.; Cameron, J., 1993;Shang, S. W.; Williams, J. W.; Soderholm, K-J. M., 1994; Leempoel, P., 1997; Sahnoune, F.; Karad, S.; Lopez Cuesta, J.-M. Crespy, A., 1997; Kauly, T.; Karen, B.; Siegmann, A., Narkis, M., 1997; Lyman, M.J., 1991; Krysztafkiewicz, A.; Maik, M.; Rager, B., 1992; Stricker, F., Friedrich, C., Mulhaupt, R., 1998).

EXPERIMENTAL

A representative white silica sand sample was supplied from high quality Edfo deposit. Microscopic evaluation as well as chemical investigation of the original sample was carried out. The sample was subjected to different steps of dry beneficiation process. At first, sieve classification was carried out to reject both +0.60mm and –0.10 mm fractions. The rejection of these two size fractions is mostly applied to remove most of the iron oxides inclusions especially in the coarser fraction as well as removing most of the ferroginatd clayey fines below 0.10 mm. The classified sand sample was directed to dry high intensity magnetic separation using Magnaroll separator to remove coloring impurities such as iron and titanium oxides. The clean sample was ground in a porcelain Fritsch ball mill to produce silica flour. Particle size distribution of the ground sample as well as the some physical measures were measured.

Fig. 1. ZK 25 T COLLIN Tischcompounder Extruder

Pure polypropylene powder of 0.91g/cm^3 in density, as the host matrix of the blend was prepared with different silica flour additions from 1.5% to 15% by volume. Sometimes, surface compatibilizers like styrene-ethylene/butylene-styrene block and its grafted maleic anhydride form of 0.90 g/cm^3 in density. They were added in two additions 2.5% and 5% by volume. These loading percentages were chosen according to literature survey. The components of each batch were dried separately for 2 hours at 110°C. They were thoroughly mixed together for 15 min in a plastic tumbling mixer. The final weight of each batch was 600 gm. The blends were subjected to compounding process using "Collin Twin Screw" Extruder at 200°C (Figure 1). Different operations were illustrated in Figure 2 (O'Driscoll, M., 1994).

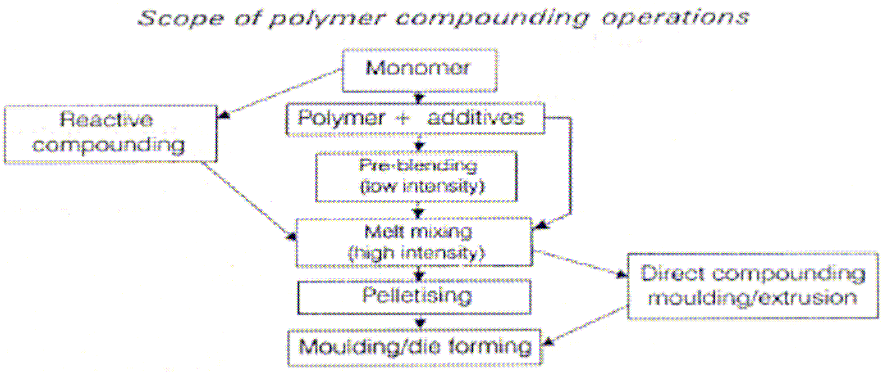

Fig. 2. Scope of Various Compounding Operations (O'Driscoll, M., 1994)

The materials were then fed by a horizontal metering screw hopper with 2 kg/hr feeding rate. The Chilled Rolls Take-off unit with a water bath was added to the system. A Collin Granulator (Figure 3). It was connected to cut the compounded film samples into short specimens of 1 cm length.

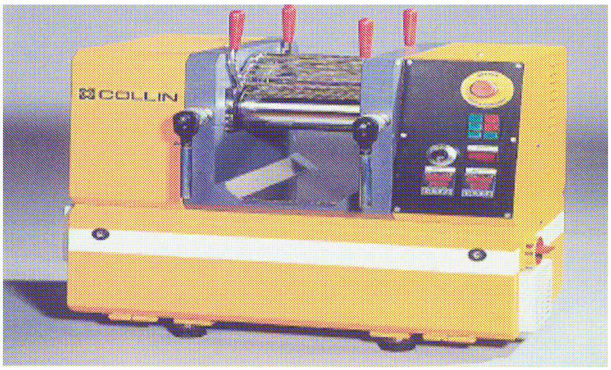

Fig. 3. W 100 T COLLIN Tischwalzwerk Granulator

The samples were subjected to a Milacron K-TEC 40 injection moulder to be prepared as 60mmx 10mmx 4mm rectangular bars for mechanical measures (Figure 4). Meanwhile, 10mm × 6mm × 2mm rectangular bars samples were shaped for impact strength measures. At least six readings were taken for each test, where the average measure was reported. Tests were performed at ambient temperature around 25^{o}C and constant humidity around 55%. The measures were plotted versus silica content.

Fig. 4. FERROMATIK MILACORN Shaping Unit

RESULTS AND DISCUSSION

Microscopic examination of the original white sand sample showed the presence of some reddish brown inclusions contaminated coarse particles. Traces of colored particulates in finer sizes was detected (Table 3). Sieve classification followed by the rejection of both +0.6mm and -0.1mm fractions removed most of these undesirables. The magnaroll dry high intensity magnetic separator succeeded to reject trace particles of various magnetic nature. Chemical analysis of beneficiated sample was illustrated in Table 4.

Table 3. Chemical composition of original silica sample

Constituent, %	Wt.%
SiO_2	99.32
Al_2O_3	0.04
Fe_2O_3	0.02
TiO_2	0.003
Na_2O	<0.01
K_2O	<0.01
CaO	0.06
MgO	0.02
L.O.I.	0.30

Table 4. Chemical composition of ground refined silica sample

Constituent	Wt.%
SiO_2	99.85
Al_2O_3	0.020
Fe_2O_3	0.016
TiO_2	0.017
Na_2O	---
CaO	0.026
MgO	---

Table 4 shows the high a quality of the prepared sample under investigation, where as Table 5 shows the physical properties of the ground refined silica sample.

Table 5. Some physical properties of the ground refined silica sample

Property	Measure
Refractive Index	1.55
Specific Gravity	2.65
Hardness	7.0
Oil Absorption	35
Surface Area	4.75
Dry Brightness	88
D_{98} D_{50}	20 10

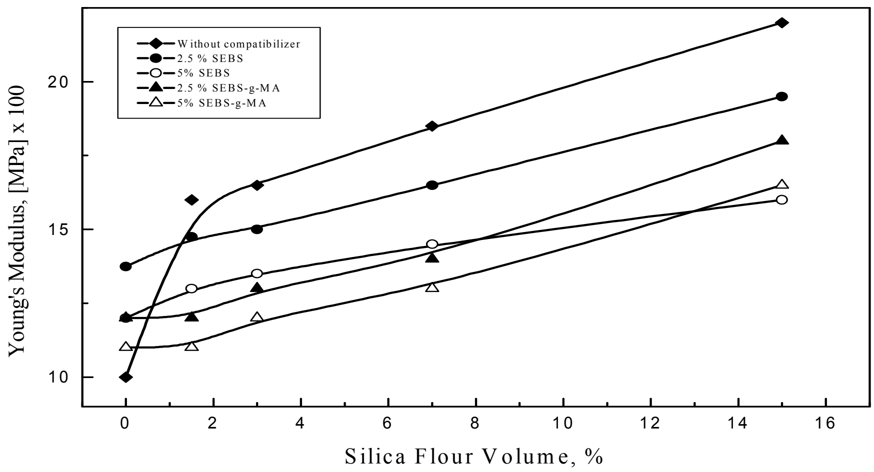

Fig. 5. Influence of silica content on the modulus of filled-PP blends

Figure 5 illustrates the effect of silica content on Young's modulus measures. It was noticed that the effect of silica content followed two stages. The first stage from 0% (without silica) up to 3% silica content and the second stage was above 3% to 15% silica content. In the first stage, the Young's modulus increased rapidly from 1000 to 1600 MPa by increasing the silica content. While in the second stage a gradual increase in the modulus, from 1600 to 2200 MPa, was noticed with increasing the silica content from 3 to 15%. The rate of change in the modulus with varaitation of silica content was 200 MPa per each 1% silica content in the first stage and 50MPa per each 1% silica content in the second stage. In other words, the rate of change in the modulus in the first stage is 4-fold the second stage. The addition of styrene-ethylene/butylene-styrene block and its grafted maleic anhydride as silica/PP surface compatibilizers was negatively affected the modulus character of end-product as shown in Figure 5. This could be explained after the high dispersion of hydrophilic silica particulates in the polymeric system.

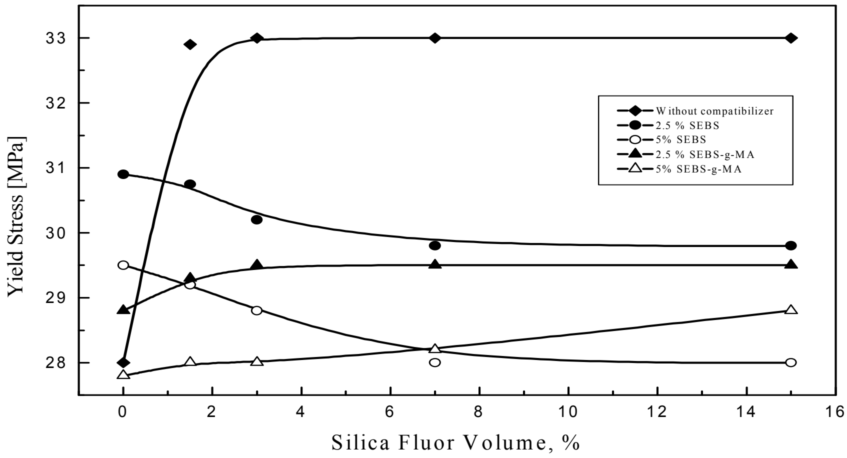

Fig. 6. Influence of silica content on the yield stress of filled-PP blends

Figure 6 illustrates the effect of silica loading level on yield strength measures. The same behaviour was noticed in case of yield strength. An increase reached 32.9 MPa in the 3 % silica content from 28 MPa in the pure sample with an achievement of 17.5%. The yield strength measure was then kept constant at higher silica levels, as shown in Figure 6. The addition of the both surface compatibilizers to the silica/PP system was inversely affected the yield strength. The yield strength was lower in case of additives. Additionally, for each compatibilizer, it was clear that no difference in yield strength measures with variation in silica content as shown in Figure 6.

Figure 7 depicts the Izod impact strength measures versus silica content in filled-PP. Gradual increase in impact measures from 1.6 kJ/m^2 in the neat system to 2.15 kJ/m^2 in the 15% silica filled system. An improvement reached 34.4% in the impact measures was remarked, as shown in Figure 7. It is well known that the presence of large particles and agglomerates >10-30 micron diameter, dramatically reduces impact strength measures of polypropylene masterbatch. These large particles acted as flaws where cracks can initiate. On the other hand, the inclusion of small well dispersed particles can have a very positive influence on the impact strength of PP systems (Valji, S.E., 1999). The incorporation of surface compatibilizers on fine products enhanced dispersion by reducing the interfacial strength (Hawley, G.C., 2000; Fellahi, S.; Boukobbal, F., 1993; Gaskell, P., 1997). This has been found to give a further improvement in impact performance This idea was confirmed to a great extent where the addition of both compatibilizers improved the impact strength measures of end-products as shown in Figure 7. At low silica content levels, 1.5% and 3%, addition of

2.5% SEBS-g-MA increased the impact strength from 1.8 kJ/m^2 to 2.6 kJ/m^2 with an improvement reached about 44%. At higher silica containing systems, 7% and 15% the addition of 5% SEBS-g-MA increased impact strength values from 2.10 kJ/m^2 to 2.70 kJ/m^2 with an improvement ratio of 28.6%.

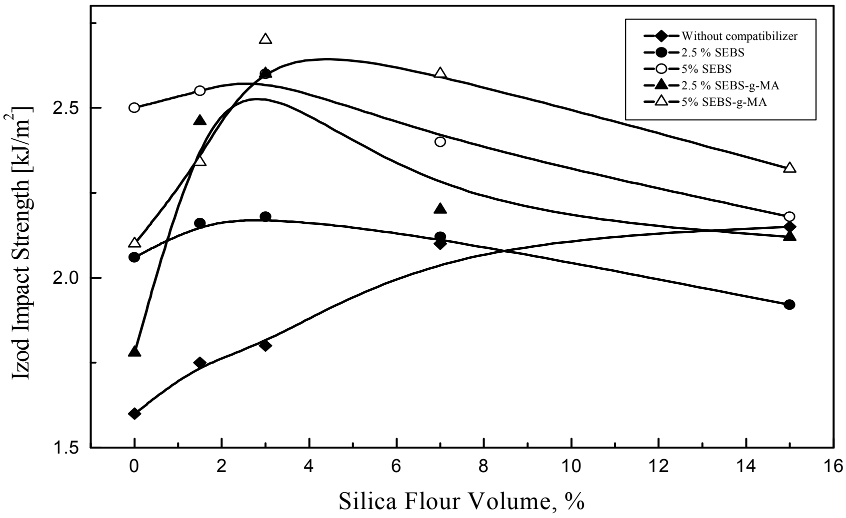

Fig. 7. Influence of silica content on izod impact strength of filled-PP blends

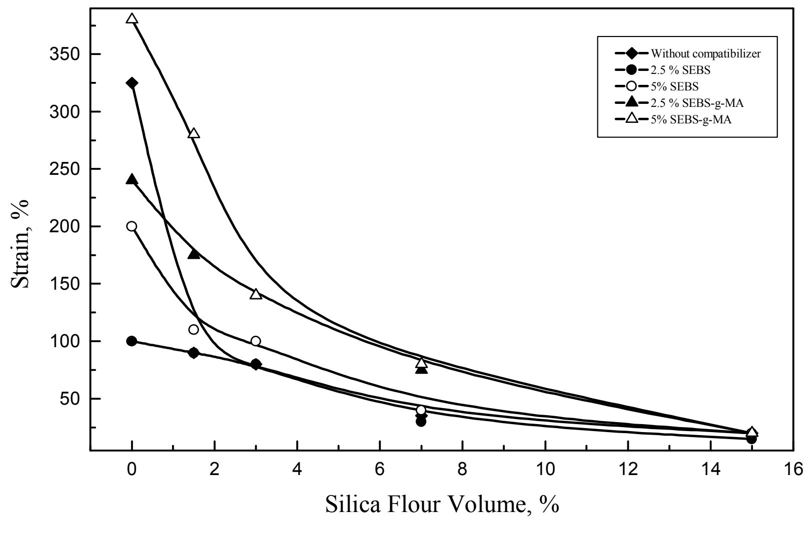

Fig. 8. Influence of silica content on the strain% of the filled-PP blends

The effect of silica addition on strain of filled/PP blends is shown in Figure 8. It was obvious that silica addition with any ratio negatively affected the strain%. In case of neat sample, strain measure reached 325%. After that, it showed dramatic decrease and reached 90% by adding 1.5% silica. It continued its decreasing to 20% at silica content of 15%. Yet some studies followed the influence of processing behavior of the mineral/polymer inside the extruder on the strain. This was carried out by controlling sample stretching during the process (Fourty, G., 1997). It was concluded that the increase in the orientation of the blend during melting i.e. the extrusion stage, could improve the strain. Morever, it was supposed that a better mineral filler orientation in injection molded parts could also improve not only the strain, but also the end-product impact strength (Fourty, G., 1997).

CONCLUSIONS

1. Minerals deposits are considered commercially viable for filler applications when the mineral could be applied without special treatment. However, dry beneficiation is preferable than wet operations to avoid extra operations like filtration and dryness of fine and ultrafine ranges.
2. High grade white sand sample was subjected to dry beneficiation including sieve classification and RE high gradient magnetic separation. The clean sample was ground to prepare pure silica flour.
3. Silica flour was applied in polypropylene masterbatch formulation with various additions. Results showed gradual improvement in Young’s modulus as well as the impact strength with increasing silica content in the blend. An increase in the yield stress was taken place at silica content of 3%. All silica filled blends showed dramatic drop in the strain measures. Yet some studies concluded that sample orientation controlling during extrusion could improve strain property as well as impact strength.
4. The addition of some surface modifiers e.g. SEBS and SEBS-g-MA was shown to improve some physical properties of silica filled/PP blends due to the increase in the mineral/ polymer interfacial wettability

ACKNOWLEDGMENT

The authors would like to express their great gratitude to Prof. Friedrich, C. ; Dr. Nitz, H., and all the assistance staff of Freibrger Materialforschungzentrum, der Albert-Ludwigs-Universitat, Germany for supporting this work through the DFG programms.

REFERENCES

O'DRISCOLL, M., "Plastic Compounding, Where Mineral Meets Polymer", Industrial Minerals, pp 35-43, December 1994

TRIVEDI, N.C., HAGEMEYER, R.W., "Fillers and Coatings", Industrial Minerals and Rocks, 6 th Edition, Senior Editor Donald D. Carr, 1994

LEE, S.,"Thermal, Mechanical and Morphological Characterization of Highly Filled Polyethylene Film", International Conference of Alternative White Pigments and TiO_2 Extenders for Coatings, Paper and Plastics, Orlando, USA, 2000

DEARMITT, C., "Filled-PP Possibilities and Optimization", International Conference of Alternative White Pigments and TiO_2 Extenders for Coatings, Paper and Plastics, Orlando, USA, 2000

LOFTHOUSE, C.H., "Production of Mineral Fillers", International Conference of Filled Polymers and Fillers "Eurofillers 97" Manchester, UK, 1997

JOHNSTON, J. H., "High Performance Natural Amorphous Silicas and Silicates for the Paper Industry", Advancing Papermaking 97, Frankfurt, Germany, Oct. 1997

BRYK, M.T., "Degradation of Filled Polymers" Ellis Horwood, London, 1991

SCHERBAKOFF, N., "Rheological, Interfacial and Morphological Changes Produced By Fillers in Immiscible blends", Diss. Abstr. Int., Vol. 54, No. 4, pp.257, Oct. 1993

PAYNE, H. F., "Organic Coating Technology", John Willey and Sons Publications, New York, 1985

ZHANG, Y.; CAMERON, J., "Silica Particle/Glass Fibre-Reinforced Polyester Resin", Journal of Composite Materials,USA, Vol. 27, No. 11, pp. 1114-1127, 1993

SHANG, S. W.; WILLIAMS, J. W.; SODERHOLM, K-J. M., "How the Work of Adhesion Affects the Mechanical Properties of Silica-Filled Polymer Composites", Journal of Material Science, UK, Vol. 29, No. 9, pp. 2406-2416, May 1994

LEEMPOEL, P., "Filler/Polymer Interface and Performance of Silicon Elastomers", Filled Polymers and Fillers Conference, Manchester, UK, 1997

SAHNOUNE, F.; KARAD, S.; LOPEZ CUESTA, J.-M. CRESPY, A., "Effect of Fillers and Interfacial Agents on the Mechanical and Morphological Properties of HDPE/PS Blends", International Conference of Filled Polymers and Fillers, Manchester, UK, 1997

KAULY, T.; KAREN, B.; SIEGMANN, A., NARKIS, M., "Highly Filled Particulate Thermoplastic Composites", Journal of Material Science, Vol. 32, Iss 3, 1997

LYMAN, M.J., "Silica Improves Thermoset Properties", Plastic Compounding , USA, Vol. 14, No. 7, pp. 61-63, Nov.-Dec., 1991

KRYSZTAFKIEWICZ, A.; MAIK, M.; RAGER, B., "Comparison of Waste Silica Fillers Modified With Various Proadhesive Compounds", Journal of Material Science ,UK, Vol. 27, No. 13, pp. 3581-3588, July 1992

STRICKER, F., FRIEDRICH, C., MULHAUPT, R., "Influence of Morphology on Rheological and Mechanical Properties of SEBS-Toughened, Glass-Bead-Filled Isotactic Polypropene", Journal of Applied Polymer Science, Vol.69, pp 2499-2506, 1998

VALJI, S.E., "Processing Technology, Increasing Profits in Industrial Minerals", Industrial Mineral Journal, Sept., 1999

HAWLEY, G.C., "Opacifiers in Paint & Plastics - An Overview", International Conference of Alternative White Pigments and TiO2 Extenders for Coatings, Paper and Plastics, Orlando, USA, 2000

FELLAHI, S.; BOUKOBBAL, F., "Study of the Effect of Fumed Silica on Rigid PVC Properties", Journal of Vinyl Technology, USA, Vol. 15, No. 1, pp. 17-21, Mar., 1993

GASKELL, P., "Mineral Fillers For Polypropylene", International Conference of Filled Polymers and Fillers, 8-11 Sept. Manchester, UK, pp 281-284, 1997

FOURTY, G., "Talc in Polypropylene", International Conference of Filled Polymers and Fillers, Manchester, UK, 1997

Ibrahim S. S., El-Midany A. A.,*Wpływ trójblokowych polimerów na poprawę mechanicznych właściwości materiałów kompozytowych wykonanych z polipropylenu z dodatkiem mączki kwarcowej.* Physicochemical Problems of Mineral Processing, 42 (2008), 165-176 (w jęz. ang)

Proszki mineralne są dodawane w trakcie tworzenia polimerowych matryc w przemysle termoplastycznych tworzyw sztucznych, dla modyfikacji cech fizycznych nowopowstałych materiałów kompozytowych. Przykładowo, dodanie dobrze rozdrobnionej mączki kwarcowej do czystej matrycy polipropylenowej (PP) powoduje korzystne zmiany w cechach produktu finalnego. Można to tłumaczyć względnie niski przewodnictwem cieplnym kwarcu. W badaniach, czysta mączka kwarcowa była mieszana z polipropylenem w celu przygotowania odpowiedniej receptury dla przemysłu tworzyw sztucznych. Dodatek mączki kwarcowej był różny i wynosił: od 1,5 do 15 % objętościowych. Otrzymane wyniki wskazują na poprawę cech fizycznych produktu końcowego takich jak: moduł Younga, wytrzymałość plastyczna i mechaniczna. Co więcej, dodatek warcu powodował obniżenie odkształcenia produktu końcowego, który został otrzymany przy wprowadzeniu różnych ilości mączki kwarcowej. Odwrotnie, dodane blokowego polimeru SEBS (styren-etylen/butylen-styren) i jego szczepionej formy przy użyciu bezwodnika maleinowego, spowodowało podwyższenie zwilżalności powierzchni kompozytu kwarc/PP. Dodanie SEBS nie spowodowało poprawę modułu Younga ani wytrzymałości plastycznej. Jednakże, wyraźna poprawa nastąpiła w odporności na uderzenie i wytrzymałości mechanizcnej materiału.

słowa kluczowe: krzemionka, polimery, właściwości, moduł Younga, odporność na udar, polipropylen