



16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

Research of surface properties of fillers for polymers

O.K. Semakina ^a *, A.N. Phomenko ^b, A.A. Leonteva ^a, I.E. Rymanova ^a

^a Tomsk Polytechnic University, Lenina avenue, 30, Tomsk, 634050, Russia

^b LLC "NC "Rosneft" RTC, Krasnaya st., 54, Krasnodar, 353000, Russia

Abstract

The behavior of filler particles in the polymer matrix on a physical model representing the suspension of solid particles in the apolar liquid has been studied. Relative sedimentation volumes of powder components included in the polymer composition for the cable insulation in liquids of different polarity have been identified. The dependence of the effect of hygroscopic powder fillers on the relative sedimentation volume of powders and a ratio of wetting has been studied. It has been found that hydrophobic interactions are not observed at the surface of completely dry materials placed in liquids of different polarity. Consequently, the role of the filler is actually to prevent adsorption of moisture from the air on the surface of the particles, to reduce their hygroscopicity. It is proposed to assess the degree of water-repellency of the particles of powdered fillers by the measurement of their maximum hygroscopicity.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: polymer composition, lyophobic interactions, hygroscopicity, sedimentation volume

1. Introduction

The production technology development of new composite plastics is connected to necessity of looking for new environmental safety solutions.

Introduction of filler in polyolefin disturbs the polymer matrix uniformity, leading in some cases to physico-mechanical deterioration of composite materials. Interaction of fine-dispersed solid particles with a polymer is estimated by homogeneity degree of particles and polymer adhesion to their surface¹. Basically, homogeneity

* Corresponding author Olga K. Semakina. Tel.: 8-960-973-0081

E-mail address: SOK @tpu.ru

degree of particles and polymer adhesion depend on physico-mechanical properties of filler particle surface^{2,3}. Solid particles are modified for property change.

The surface of the most mineral fillers is polar, and organic modifier surfacing is necessary for its hydrophobization. Filler wettability with a polymer improves after the surfacing, particle tendency to aggregation reduces, absorption of plasticizers decreases, water resistance and polymer dielectric properties get better.

Fine-dispersed mineral fillers, like other loose materials, are characterized by effect of aggregation. Aggregate is a formation consisting of a large number of particles connected with autoadhesion power, and they form a single whole. In this regard, mixing of fine-dispersed fillers with aggregates and a polymer are very difficult tasks. Getting in a liquid medium, the aggregates segregate into separate particles in case of equality of polar medium and solids. The more the difference of polarities between dispersed phase and disperse medium, the more tendency of dispersoid particles to aggregation must be. A lack of intensive interaction between a polymer and particle surface leads to the fact that their dispersion in the polymer becomes less than dispersion of the original filler. For this reason, surface modification of the filler is an important way to increase filler particle wetting with a polymer disperse medium, to improve particle distribution in matrix and allows loading the maximum amount of filler in the polymer.

Water adsorbed on the surface of fine-dispersed particles of the filler influences the aggregation process. Behavior of particles with different amount of adsorbed water in a polymer matrix was studied using a physical model corresponding to a suspension of solid particles in apolar liquid.

The detailed study of sedimentation volume of fine-dispersed particles with a hydrophilic surface in heptane and water revealed the effect of relative air humidity on the results of the experiment⁴.

The concept of hydrophobic interactions was originally developed for molecular-disperse systems. The papers⁵⁻⁹ show that hydrophobic interactions can be applied to particulates: graphite, teflon. Hydrophobic interactions in water suspension of hydrophobic particles and a number of natural hydrophilic minerals with a surface hydrophobized using flotation reagent were studied in the papers¹⁰⁻¹². Hydrophobic interactions refer to a group of weak interactions and act independently from Van der Waal's forces as being an additional factor of promoting aggregation of non-polar groups and molecules in a water medium.

2. Experimental

This work is devoted to the study of surface properties of the components in the polymer composition obtained by injection molding and intended for manufacturing of cable insulation. Compatibility of individual substances with a polymer matrix was investigated.

The object of the study was a polymer composition based on polypropylene used for cable insulation. It was proposed to improve ways of stabilizer introduction, fillers and flame retardants in polyolefins by creating their concentrates. The compatibility of physico-chemical properties of the input component surface with a surface of the polymer granules was necessary to determine.

The aim of the study was to determine the wettability of powder materials that make up the composition. As stabilizers preventing or retarding thermal oxidative and photo-oxidative degradation Irganox 1010 and calcium stearate were used. As flame retardants, preventing degradation of the material with the release of combustible gases and their inflammation, antimony oxide (III) and decabromodiphenyl oxide (DBDPO) were used; as fillers – talc, chalk or microcalcite – to improve hardness, rigidity, heat resistance, cold and wear resistance.

A method for assessing the compatibility of fine-dispersed materials by a wettability coefficient obtained from a ratio of the measured relative sedimentation volumes of the investigated powders in liquids of different polarity was developed. Distilled water was used as polar liquid; octane was used as apolar one.

When the particle surface is polar, their relative sedimentation volume due to the aggregation is significantly greater than a relative sedimentation volume of the particles with a hydrophobic surface when they are in peptizing condition. Thus, in the system with a polar surface of solid particles of the filler in a polymer matrix apolar medium particle aggregation is observed resulting in increasing their relative sedimentation volume in static conditions.

The magnitude of the volume occupied by the same sample weight in liquids of different polarity allows evaluating their wettability based on the ratio of wetting K ¹³⁻¹⁵:

$$K = V_p / V_{ap} , \quad (1)$$

where V_p – relative sedimentation volume in polar liquid, cm^3/g ;

V_{ap} – relative sedimentation volume in apolar liquid cm^3/g .

With values $K > 1$ – the surface of the test material is hydrophobic; $K < 1$ – the surface is hydrophilic. The larger the value K is different from a unit the more hydrophobic or hydrophilic a test material is.

The relative sedimentation volume of the components in liquids of different polarity shown in Figure 1 was determined. The diagram shows that the maximum hydrophobic component is calcium stearate, which relative volume of sedimentation in water is $20 \text{ cm}^3/\text{g}$. A less hydrophobic component is Irganox 1010 which volume of sedimentation in water slightly exceeds the volume of the precipitate in octane. Other components – decabromodiphenyl oxide, talc and antimony oxide – are hydrophilic materials as the values of their sedimentation volumes in an aqueous medium are smaller than the volume of sedimentation in octane.

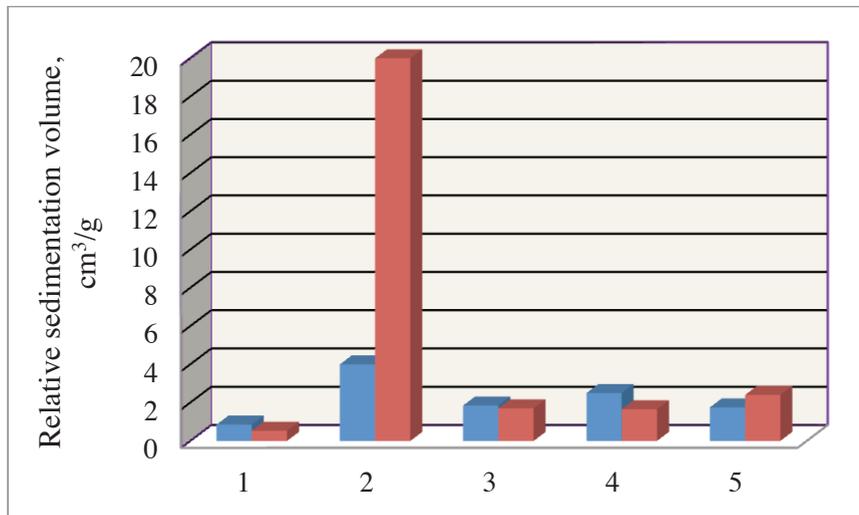


Fig. 1. Diagram of relative sedimentation volumes of components in liquids of different polarity:

1 – DBDPO; 2 – calcium stearate; 3 – Sb₂O₃; 4 – talc; 5 – Irganox
■ in octane; ■ in water

The amount of moisture absorbed on the surface of polar particles of the filler depends not only on the physical properties of particles (particle size, contact angle, adsorption properties, etc.), but on the ambient humidity. The more humidity the greater amount of moisture is adsorbed on the polar surface. Thereby, a large amount of water is introduced into the polymer matrix.

During the study the hygroscopic of powdery fillers placed in a desiccator with water at the defined intervals was determined. Analyzing the obtained results (Table 1) the following conclusions can be made. The most hygroscopic powders are chalk and titanium dioxide. Their maximum hygroscopicity at 100% humidity was 5.08% and 5.00%, respectively. The lowest limiting hygroscopicity of talc is 1.20%.

Table 1. Hygroscopicity of powdery fillers

Filler name	Natural moisture, %	Hygroscopicity of powders in time, %				
		1 hour	2 hours	15 hours	23 hours	1 week
BN	0.40	0.77	0.79	1.96	2.14	3.70
Sb ₂ O ₃	0.20	0.47	0.55	1.16	1.46	3.00
DBDPO	0.14	0.27	0.63	0.76	1.01	1.58
TiO ₂	0.62	0.82	0.83	2.04	2.34	5.00
Chalk	0.26	0.38	0.48	1.79	2.21	5.08
Talc	0.18	0.05	0.10	0.37	0.42	1.20

The next stage of the research was to determine relative sedimentation volumes of the powders pre-dried at a

temperature of 105°C to a completely dry condition, natural moisture, 50% and 100% moisture absorption of the limiting hygroscopicity (Tables 2, 3).

Table 2. Relative sedimentation volume of fillers in polar medium

Filler name	Relative sedimentation volume at different moisture absorption of fillers, cm ³ /g			
	Completely dry	Natural moisture	50 %	100 %
Sb ₂ O ₃	1.5	1.4	1.2	1.2
TiO ₂	1.4	1.5	1.3	1.2
Chalk	2.9	2.65	2.7	2.7
Microcalcite	0.7	1.0	–	1.9
Talc	2.0	1.65	–	1.7

Table 3. Relative sedimentation volume of fillers in apolar medium

Filler name	Relative sedimentation volume at different moisture absorption of fillers, cm ³ /g			
	Completely dry	Natural moisture	50 %	100 %
Sb ₂ O ₃	1.5	1.85	1.7	1.9
TiO ₂	1.1	1.2	1.2	1.3
Chalk	3.0	3.8	3.8	3.7
Microcalcite	0.65	1.0	–	2.0
Talc	2.0	2.5	–	2.55

By the above formula the ratio of powders wetting was determined, and obtained results are summarized in Table 4.

Table 4. Wetting coefficient of fillers

Filler name	Ratio of wetting K of fillers at different moisture absorption			
	Completely dry	Natural moisture	50 %	100 %
Sb ₂ O ₃	1.0	0.76	0.71	0.63
TiO ₂	1.27	1.25	1.30	0.92
Chalk	0.97	0.70	0.71	0.73
Microcalcite	1.08	1.0	–	0.95
Talc	1.0	0.66	–	0.67

Analyzing the results the following conclusions can be made. The pre-dried samples of the material are substantially equal in volume in liquids of different polarity. This is evidenced by a wettability coefficient close to a unit. This indicates that hydrophobic interactions are not shown in an absolutely dry material. However, the powders with natural moisture or specially humidified to a maximum hygroscopicity have different volumes both in polar and apolar liquids, i.e. water molecules, adsorbed on the surface of a powdered material, provide the hydrophobic interactions.

Moreover, different materials behave differently. Thus, with an increase in hygroscopicity Sb₂O₃ occupies a smaller volume in the aqueous medium; but in the apolar medium sedimentation volume increases. That is the more water molecules are adsorbed on the surface of the powder the more precipitate is in octane. The same can be said about the other testing materials. However, by the value of a wettability coefficient it can be assumed that TiO₂ powder has more apolar surface but while chalk and Sb₂O₃ powders have a polar surface.

The results indicate that the determination of the relative sedimentation volume and the wettability coefficient calculation can be used for preliminary evaluation of the compatibility of the components in granules.

3. Conclusion

These studies allow making the following practical conclusions:

1. Relative sedimentation volumes of all powder components included in polymer composition in liquids of different polarity have been determined. It has been found that calcium stearate and Irganox have a hydrophobic surface, other components have a hydrophilic surface.
2. The dependence of powder filler hygroscopicity on relative sedimentation volume of powders and a wettability coefficient has been investigated.
3. It has been found that hydrophobic interactions are not observed on the surface of absolutely dry materials placed in liquids of different polarity.
4. In order to prevent aggregation of fine-dispersion filler with a polar surface in a polymer matrix it is necessary to develop deep drying process of the filler with its further loading in molten polymer eliminating contact with production area air.
5. The role of surface modifying of polar filler is to prevent moisture sorption from air on a particle surface, to reduce their hygroscopicity. In this regard, it is recommended to access the hydrophobization state of filler powder particles by changing their maximum hygroscopicity before production start-up at the stage of incoming control.
6. Improvement of production technology of composite materials with polyolefin is associated with their concentrate formation containing polymers, stabilizers, dyes and fillers. It is possible to obtain concentrates of polymer composite materials with particles of size from 3 to 6 mm from fine-dispersed material by granulating in a liquid medium that together with the major purpose allows utilizing dust fraction of polyolefin.

Acknowledgement

This work was performed on the unique scientific IRT-T equipment and financially supported by Government represented by the Ministry of Education and Science of the Russian Federation (RFMEFI59114X0001).

References

1. Zimon AD, Andrianov EI. *Autoadhesion of loose materials*. M: Metallurgy; 1978. 288 p.
2. Yaminskiy VV, Pchelin VA, Amelina EA. *Coagulation contacts in disperse systems*. M: Chemistry; 1982. 185 p.
3. Lipatov YS. *Physicochemical basis of polymer filling*. M: Chemistry; 1991. 260 p.
4. Yakhnin ED, Pavlova VG. Principles of structure formation in systems of polymer-solvent-filler. *Colloid Journal*. 1976. Volume 8. №4. p. 767–773.
5. Pchelin VA. Modeling of hydrophobic interactions. *Proceedings of Academy of Sciences of USSR*. 1970. Volume 194. №3. p. 621–624.
6. Pchelin VA. Hydrophobic interactions in colloid chemistry. *MSU Vestnik*. 1972. № 2. p. 131–142.
7. Yaminskiy VV, Pchelin VA. Hydrophobic interactions and effect of electrolytes on water structure. *Proceedings of Academy of Sciences of USSR*. 1973. Volume 210. №1. p. 157–160.
8. Pchelin VA. Hydrophobic interactions, their physical nature and value in colloid chemistry. *Associated water in disperse systems*. M: MSU; 1974. Issue 3. p. 111–117.
9. Pchelin VA. *Hydrophobic interactions in disperse systems*. M: Knowledge, 1976. 64 p.
10. Berger GS. Classification of water mineral suspensions taking into consideration their temperature resistance. *News of Higher Education Institutions: Nonferrous Metallurgy*. 1979. №3. p. 61–64.
11. Berger GS, Evdokimov SE. Hydrophobic-hydrophilic interactions in mineral suspensions. *News of Higher Education Institutions: Nonferrous Metallurgy*. 1980. №4. p. 12–14.
12. Berger GS, Evdokimov SE, Baymakhanov MT. Coupling of mineral grains in water suspensions. *Theoretical basis and flotation process monitoring*. M: Science; 1980. p. 28–33.
13. Babenko SA, Semakina OK. *Surface phenomena and processes in heterogenetic systems with solids*. Tomsk: TPU Publishing House; 2002. 110 p.
14. Tagiltseva SA, Babenko SA, Semakina OK. Processes of wet-out in technology of polymeric composite materials. *Proceedings of III All-Russian Scientific Conference "Chemistry and Chemical Engineering at the term of Millenium"*. Tomsk. 2004. p. 304–305.
15. Babenko SA, Semakina OK. *Surface phenomena in heterogenetic systems with solids*. Tomsk: TPU Publishing House; 2012. 210 p.