Morphological properties of fillers for polymeric materials; the influence on rheological properties of compositions with unsaturated polyester resin

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Introduction

Organic synthetic polymers are the base of many modern materials which are replacing traditional ones. Modifications of traditional polymers have increasing market share. One of the most frequently used methods of polymer modification is filling. Fillers are introduced to the material. It improves mechanical and heat properties and reduce the price of the product. It should not be expected that filling will improve all of the desired properties. Usually improving one of the features leads to worsening other properties. One of the most frequently observed drawbacks of using fillers is worsening of rheological properties.

Effect of fillers on mechanical, dielectric and thermal properties of polymer-filler composite is significant. Usefulness of fillers is not only a result of their composition. Mechanical properties such as specific density, size, shape, specific surface area and porosity of the grain also have the impact [1 – 3]. Morphological structure of fillers mainly influences rheological and mechanical properties of obtained material [4, 5]. Flame retardants have great importance among the fillers.

Some of the fillers have a negative effect on polymers even if they are used in small amounts. Other ones do not have any impact. It is observed that even the fillers of a similar composition but different grain morphology have various impact. It can be assumed that grain size, its shape and specific surface area are the determining factors influencing the polymer properties. The authors of the publications [6, 7] described the influence of grain diameter on viscosity of the composite. The authors of [8] observed the dilatation effect – an increase of viscosity with an increase of shear strength, by introducing fillers of different diameters.

An influence of shape factor on polymer composite viscosity is described in publications [6, 9–10]. The authors claim that viscosity of a filled polymer is inversely proportional to shape factor of a filler grain. This dependence is confirmed by the studies [11–13].

Among morphological properties of fillers, grain specific surface area has a significant impact on composite viscosity. Viscosity of a filled material increases with specific surface area of a filler grain [14, 15].

Unsaturated polyester resins (UP) are widely applied to produce many construction materials. UPs are used to produce glass-polyester tubes (GRP) manufactured in centrifugal casting process [16].

The problem of rheological properties of composites based on UPs is the subject of publications [17, 18]. The authors examined the influence of many UP modifiers on rheological properties of composites. These modifiers were among others bentonites and nanoclays.

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In processing of UP- filler composites, thixotropic properties are used. Thixotropy is a feature of certain types of fluids where the dependence of viscosity on time of shear stress action occurs. As a result of the system's internal structure destruction in isothermal conditions, the internal friction decreases with shear stress duration. A measurable, slow return to the initial consistence during resting is also observed [19]. A decrease of viscosity is desired for example in case of fluid mixing. However, rebuilding the structure and a corresponding increase of viscosity may prevent the particle settling in suspensions. Properties of thixotropic fluids are so complex that it is not possible to determine them quantitatively in precise and repetitive way. There is no single, accepted method of thixotropy measurement. Rheological properties of thixotropic fluids are usually described by two methods: method of hysteresis loop test and method of shear rate step [20].

Many authors stress the role of morphological structure [2–5, 21], that is the size and the shape as the significant parameters of filler structure which have an influence not only on mechanical properties of a material but also on the other desired features, eg. flammability. Some of the authors say that small grain size, low shape factor and minimal specific surface area are the optimal requirements for plastics and paints fillers. However, fillers used in practice have with very different grain characteristics. A size and a shape of a filler not only affects physical and chemical properties of a material but also rheological properties of a composite polymer with filler. In practice it translates into a better or worse behaviour during processing. In case of paints it can affect the consistency and fluidity.

In this work, the authors tried to describe the dependence between the tested morphological properties of the fillers and rheological properties of polymer-filler composite. The influence of fillers on processing properties of polymer composite was tested using unsaturated polyester resin (UP)-filler (N) composite as a model. Rheological properties were determined by measuring viscosity, hysteresis loop area and thixotropy factor.

Experimental

Materials and substrates

During the research Distitron 412 V2 (Polynt SPA) orthophtalic-maleic-propylene resin was used, fillers that were applied are listed below (Tab. 1). The listed fillers, excluding chalk, are used in polymer materials alone or in a mixture to decrease flammability of a material. The chalk is the most widely known filler and it has many functions, therefore it may be used as a reference material for comparison of the tested morphological properties of the less known fillers.

Table 1

Tested fillers

No.	Symbol	Filler	Description
1.	N1	Ecoret MP	melamine phosphate (Zakłady Chemiczne Alwernia S.A.)
2.	N2	Ecoret MPYP	melamine pyrophosphate (Zakłady Chemiczne Alwernia S.A.)
3.	N3	Ecoret MPP	melamine polyphosphate (Zakłady Chemiczne Alwernia S.A.)
4.	N4	MP	melamine phosphate experimental product INS (IChN) in Gliwice
5.	N5	MPP	melamine polyphosphate experimental product INS (IChN) in Gliwice
6.	N6	Exolit AP 442	ammonium polyphosphate (Clariant GmbH)
7.	N7	Martinal ON – 904	aluminum hydroxide $Al(OH)_3$ (Albemarle)
8.	N8	EG	expanded graphite (Sinograf S.A.)
9.	N9	chalkStandard	calcium carbonate („Piotrowice" Sp. z o.o.)
10.	N10	Cloisite	layer aluminosilicate (Souther Clay Products Inc. USA)

Morphological tests of fillers

Based on grain analysis performed using Coulter LS Particle Size Analyser, the size and shape of the grains were determined. A grain size is known as a ratio of a difference between the 90th percentile (L_{90}) and the 10th percentile (L_{10}) to a median:

$$k = \frac{L_{90} - L_{10}}{L_{50}} \quad (1)$$

That ratio was used in many studies like [1].

The heterogeneity factor was analytically determined for heterogeneity distributions. This factor defines a size homogeneity. Low value of this factor means that grains are more homogenous. This parameter is often used interchangeably with a grain shape factor. Heterogeneity factor is defined as:

$$CV = \frac{(L_{84} - L_{16})}{2L_{50}} \quad (2)$$

The specific surface area of the retardant grains was also analysed, using Gemini VII analyser manufactured by Micromeritics and used for determining a single and multiple point specific surface area according to the BET method in the range between 0.001 m^2/g and 4000 m^2/g. The samples were degassed at 130°C for 2 hours, afterwards the relevant specific surface area (A) and pore volume (V) were measured, and the pore diameter was calculated according to the formula:

$$d_p = \frac{4V}{A} \quad (3)$$

UP – N composites preparation

UP composites with fillers of 20% by weight filling level were prepared. The compositions were stirred for 30 minutes and then were degassed in vacuum.

Rheological properties of UP – N composites

Viscosity of UP-N composites was analysed using the rotational viscometer Rheothest with S3 measurement cylinders with a rotation range of 5 – 240 min^{-1}. Measurements were taken at 20°C. Viscosity of a composite was measured by applying a gradually increasing (and subsequently decreasing) rotational speed. The number of measurement points for different shear rates was always 24. Based on the apparatus constant values and determined shear stress, dynamic viscosity was calculated using the formula:

$$\eta = \frac{\tau}{D} \quad (4)$$

Thixotropic properties were defined by calculation of the hysteresis loop surface area (5) and thixotropy index (6) using formula [31]:

$$S = S' - S'' = D_{max} n^{-1} \sum_{i}^{n} \Delta\tau_i \quad (5)$$

where: S – hysteresis loop area, S' and S'' – surface area of the upper and lower branch of the flow curve at a maximum shear speed from $\gamma=0$ to γ_{max} over the sum of the difference of strains of the upper and lower branch of flow curve τ.

And thixotropy index K_t calculated according to the formula:

$$K_t = \frac{S}{\gamma_{max}} \quad (6)$$

Results

In the table below, morphological properties of used fillers are presented (Tab. 2).

Table 2

Morphological parameters of used fillers

No.	Symbol	A, m^2/g	V, cm^3/g	d_p, cm	d_m, μm	d_d, μm	CV	k
1	N1	1.41	3.54E-03	1.01E-06	4.00	3.76	0.72	1.80
2	N2	4.92	1.81E-02	1.47E-06	3.20	2.76	0.80	2.00
3	N3	5.89	1.96E-02	1.33E-06	3.38	2.91	0.79	1.97
4	N4	0.78	1.27E-03	6.55E-07	29.84	15.67	1.23	4.25
5	N5	0.96	1.51E-03	6.28E-07	26.64	16.89	1.39	4.29
6	N6	0.57	1.93E-03	1.35E-06	27.84	17.23	1.28	4.17
7	N7	2.30	8.48E-03	1.47E-06	7.25	4.62	1.50	3.71
8	N8	2.52	6.70E-03	1.06E-06	256.30	228.90	0.72	1.88
9	N9	0.71	2.73E-03	1.53E-06	44.09	26.65	1.69	4.33
10	N10	5.68	2.57E-02	1.81E-06	11.94	10.74	0.72	1.97

where: A – specific surfacearea, V – pore volume d_p – pore diameter, d_m – mean grain size, d_d – dominating grain size, CV – heterogeneity index, k- shape factor

The fillers that were used in the research are different regarding to all of the morphological properties. The specific surface area varies between 0.57 and 5.89 m^2/g, the mean grain size is between 3.2 and 256.3 μm. The majority of the tested fillers' grains are heterogeneous what is confirmed in quite high shape factor and heterogeneity factors values.

Compositions of UP with fillers were subjected to rheological tests. In the Figure 1 and 2, hysteresis loop (Fig. 1) and viscosity curve (Fig. 2) are presented for non-filled and filled UP. The phenomenon of shear thinning was observed during rheological tests. This is an effect of increasing shear rate which causes a decrease of viscosity of composites. This relationship is especially visible at low shear rate. It nearly disappears at high shear rate. Introduction of the fillers to the composites do not cause thickening but the rheological features are changing which is presented in the Figure 1 and 2. Viscosity and flow curves of filled UPs is similar in shape to the curve of non-modified one. These curves are only moved towards higher values. The area of hysteresis loop and thixotropy index of UP composites are presented in Table 3.

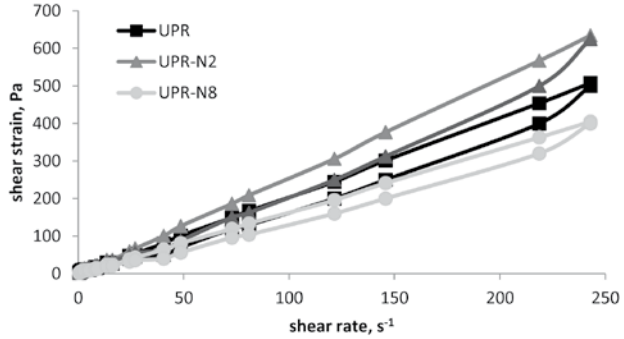

Fig. 1. Flow curves of UP composites

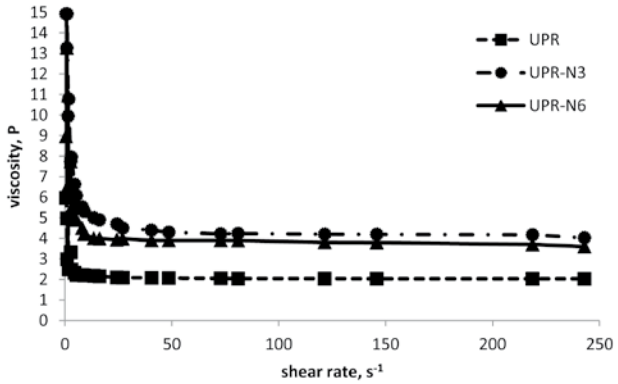

Fig. 2. Viscosity curve of non-modified and filled UP

Table 3

Rheological characteristics of UP-N composite

No.	Symbol	η_{av}, cP	S, Pa/s	K_t, Pa
1	0	210.3	20.82	0.0856
2	N1	533.1	46.26	0.178
3	N2	543.3	57.68	0.237
4	N3	602.4	52.87	0.217
5	N4	401.4	40.86	0.168
6	N5	450.2	41.85	0.171
7	N6	378.2	41.09	0.169
8	N7	539.1	44.28	0.182
9	N8	540.9	29.56	0.122
10	N9	399.8	31.24	0.129
11	N10	594.3	43.56	0.179

where: η_{av} – mean viscosity, S – hysteresis loop area,
Kt – thixotropy index

Introduction of filler N3 to the resin resulted in a threefold increase of mean viscosity of UP-N3 composition in comparison to the non-modified resin. The grains of N3 filler has the biggest specific surface area 5,89 m^2/g and high shape factor. The lowest increase was observed for UP-N6 system. The grain of N6 filler has shown the lowest specific surface area of 0.57 m^2/g and quite high shape and heterogeneity factors.

Thixotropic properties of UP-N system was determined by calculating hysteresis loop area and thixotropy index. The least increase of these parameters was observed in UP-N8 and UP-N9 systems. N8 and N9 have the highest grain size among the tested fillers. The values are respectively 256.30 μm and 44.09 μm. These fillers have small specific surface area. The highest hysteresis loop area and thixotropy index have UP-N2 and UP-N3 compositions. These fillers have similar grains what in evidenced by low shape and heterogeneity factor values. They have the lowest mean size among all of the tested fillers.

The significant impact of fillers' morphological properties on rheological properties of filled resin was observed. The considerable increase of viscosity of the composites was observed with the increase of specific surface area of the grains (Fig. 3), whereas the mean grain size influence the hysteresis loop area (Fig. 4).

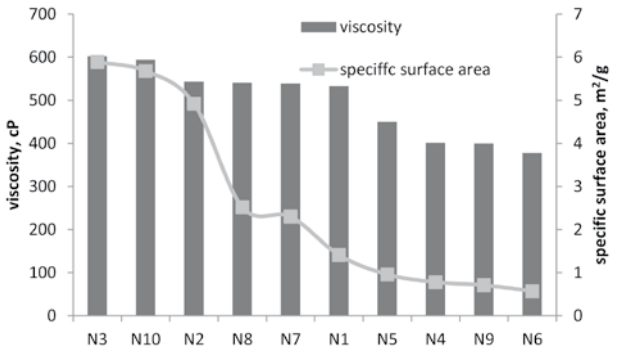

Fig. 3. The relation between the filler grains' specific surface area and UP + 20%N composite viscosity

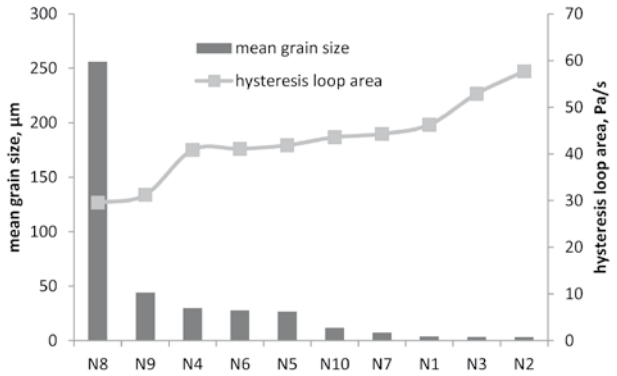

Fig. 4. Mean grain size and hysteresis loop area

Among the morphological properties, the strongest influence on rheology expressed by viscosity, hysteresis loop area, and thixotropy index have grain size and its specific surface area which substantially affects these parameters. The lower area, the lower is the viscosity of composites (Fig. 3). Whereas the hysteresis loop area and thixotropy index are mostly affected by the grain size. The bigger is the filler's grain size the lower are the hysteresis loop area and the thixotropy index (Fig. 4).

Conclusion

Dimensions and shape of a modifier decide on its specific surface area and therefore on its force of interaction with polymer matrix. The factor that influences the properties of a composite UP-N is the interaction between its components.

The strongest effect on rheological properties has the grain's size and specific surface area. Specific surface area, which is a measure of surface development is also a factor determining viscosity of a modified material. The bigger is the surface the greater is the viscosity of a composite. Introduction of fillers with big grain size results in an increase of viscous resistance of flow. Smaller grains improve fluidity which corresponds with bigger hysteresis loop area of a composite's flow curve and higher thixotropy index.

Rheological properties of polymer-filler composite depend on a contact area of dispersed phase (filler) with continuous phase and a character of interaction between continuous and dispersed phase. When shape factor of a filler increases an its transverse dimension decreases, specific surface area of a filler increases and a sum of interactions between a matrix and particles also increases.

Rheological measurements connected with filler's grains morphology facilitate the understanding how filler's morphological characteristics can influence processing properties of a polymer composite. The presented results, obtained from the measurements, characterise only the tested fillers and only the described composites.

All the tested fillers added in amount of 20% respectively to the UP did not cause any significant thickening of the polymer matrix what could have negatively affected the fluidity and consequently affected the processing properties. The tested UP-N composites exhibit generally good processing properties, although the impact of fillers' grain size, their shape and grain distribution curve also have a small impact on the properties which are significant for further processing.

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