Application Report

Characterization of dispersibility

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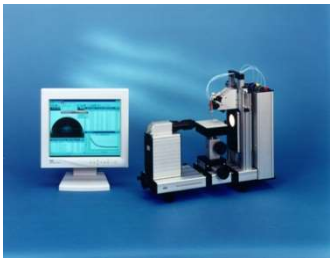

Drop Shape Analysis System DSA10

Force Tensiometer – K12

Methods: SFE

Keywords: Carbon black, polymer melt, conductive plastic composite, dispersibility, polyaniline, Fowkes

Dispersibility predictions – Some practical examples

Wettability tests for carbon black samples in different polymers

Abstract

From the measurement of the surface free energy of carbon black particles and the surface tension of polymer melts, it is possible to make predictions as to the wettability of carbon black in a variety of polymer melts. For this purpose the quantity *free energy of immersion* was calculated from experimental data and correlated to observe dispersibility performance from tests carried out in the laboratory. The results based on the present work can be generalized for other disperse systems.

Background

Conductive composites are made by dispersing conductive particles or powders into polymer matrices. The most widely used conductive additive is carbon black. The conductivity of the product composite strongly depends on how well the carbon black is dispersed within the molten polymer.

However, untreated carbon black is extremely hydrophobic. So, it does not wet or disperse well in many molten polymers. The cost of surface treating carbon black increases exponentially with the extent of surface modification. Therefore, it is important to find an optimal level of surface modification for carbon black for each polymer one wishes to make conductive, in order to best balance the performance-to-cost ratio. The objective of this work was to find a means of predicting the level of surface/modification necessary for carbon black to disperse in any given polymer, prior to running expensive trial extrusions.

Polymer	Trade Name	Manufacturer	Sample Designation
polystyrene	468M	BASF	PS
acrylonitrile butadiene styrene	Terluran®	BASF	ABS
polyethylene terephtalate	Rynite®	Dupont	PET
nylon 6,6	Zytele® 101	Dupont	Nylon 6,6
melamine formaldehyde resin	Melresin®	Althintel	MF

Tab. 1: Polymers used for the production of polymer melts

Contact Angle Data for Carbon Blacks		
Level of Treatment	Contact Angle with Water (degrees)	Contact Angle with Diiodomethane (degrees)
untreated	112.5	79.1
low	102.5	74.2
moderate	97.0	68.3
high	67.4	59.0

Tab. 2: Carbon blacks investigated

Our approach was to use a two-component (polar and dispersive) surface free energy model to determine surface free energy values for the carbon blacks and surface tension values for polymer melts, independently. By obtaining these results with simple wetting thermodynamics, we then sought to establish a predictive theory for the dispersion of carbon black into the polymer matrices. The relevance of this research is that it is extendable to any dispersion problem, to include especially, pigments in coatings and enamels.

Experimental Methods

Four carbon black samples and five polymers were used for the study. The carbon blacks were rendered hydrophilic by varying degrees of surface treatment with polyaniline or polyaniline salts (obtained from Eeonyx Corporation [1]). This resulted in four types of carbon black surface: untreated, low, moderate and highly modified (see table 2). Table 1 shows the polymers used.

Measurements

Determination of the surface free energy of carbon black

Each carbon black was characterized for overall surface energy, with polar and dispersive components and surface polarity in percent using the Fowkes surface free energy theory [2]. The probe liquids for this characterization were water and diiodomethane.

Contact angle values for these two liquids on each carbon black were determined by one of the two following methods:

θ>90°: The sessile drop method was used to obtain contact angle data using the KRÜSS drop shape analysis system [3]. The reported value represents the average contact angle for five droplets placed on a smoothed surface of the carbon black powder (table 2).

θ<90°: Contact angle values were determined by the Washburn method [4] using the KRÜSS processor tensiometer K12 [5]. The Washburn technique involves studying the wicking of the liquid into a packed plug of powder, in this case 2 g.

Surface Energy Data for Carbon Blacks				
Level of Treatment	Surface Energy (mJ/m^2)	Polar Component (mJ/m^2)	Dispersive Component (mJ/m^2)	Surface Polarity (%)
untreated	17.97	0.01	17.96	0.06
low	21.15	0.59	20.56	2.78
moderate	24.85	1.02	23.83	4.11
high	40.20	11.05	29.15	27.49

Tab. 3: Total surface free energy as well as polar and dispersive components for different carbon black powders

All of the carbon blacks were characterized for surface free energy (with polar and dispersive components) using the contact angle data obtained from water and diiodomethane [2] (table 3).

Surface tension determination of polymer melts

The overall surface tension of the polymer melts was determined by the pendant drop technique [3] (table 4). The overall surface tension values obtained were then separated into polar and dispersive components using the Fowkes theory [2] in combination with contact angle data obtained by placing drops of polymer melt onto the surface of PTFE (table 4). It is assumed that PTFE has a surface free energy of 18 mJ/m^2 with no surface polarity. For details on the use of the Fowkes theory for this type of characterization work, please refer to reference [6]. A KRÜSS Drop Shape Analyzer DSA 10 with high temperature chamber G12 was employed for this work.

Polymer Surface Tensions and Contact Angles on PTFE			
Polymer	Temperature (°C)	Surface Tension (mN/m)	Contact Angle on PTFE (degrees)
PS	250	30.25	64.2
ABS	250	37.59	79.7
PET	270	39.64	85.2
Nylon 6,6	270	45.90	90.8
MF	140	58.43	106.6

Tab. 4: Characterization of polymer melts

The prediction – calculation of the free wetting energy

First: the theory behind making a possible prediction. If a particle is dispersed in a liquid then the solid/air surface becomes a solid/liquid interface. From a thermodynamics point of view the free wetting enthalpy can be defined as follows:

$$\Delta G_{\mathrm{i}} = \gamma_{sl} - \gamma_s \qquad \text{(Eq. 1)}$$

where γ_s is the surface free energy of the solid and γ_{sl} the interfacial tension between the solid and the liquid. If this simple model for wetting is combined with the model from Good [7] for the interfacial tension between a solid and a liquid, we obtain the following definition for the free wetting enthalpy:

$$\Delta G_{\mathrm{i}} = \gamma_l - 2\left(\sqrt{(\gamma_s^D \cdot \gamma_l^D)} + \sqrt{(\gamma_s^P \cdot \gamma_l^P)}\right) \qquad \text{(Eq. 2)}$$

where γ_l is the surface tension of the liquid, γ_l^D the disperse fraction and γ_l^P the polar fraction of the surface tension, γ_s^D the disperse fraction and γ_s^P the polar fraction of the surface free energy of the solid.

If the measured data (Tab. 3 and 5) are inserted in the above equation then a wide range of values for the free wetting enthalpy is obtained from the possible graphite/polymer combinations (Fig. 1).

Surface Tension Components for the Molten Polymers			
Polymer Studied	Dispersive Comp. (mN/m)	Polar Component (mN/m)	Surface Polarity (%)
PS	26,18	4,07	13,46
ABS	27,27	10,32	27,45
PET	25,63	14,01	35,35
Nylon	28,45	17,45	38,02
MF	24,20	34,23	58,59

Tab. 5: Characterization of polymer melts

The values range from 15.54 mJ/m² for the combination of untreated graphite-melamine-formaldehyde resin (dispersibility unlikely) down to -40.16 mJ/m² for strongly modified graphite-acryl-butadiene-styrene copolymer (good dispersibility).

How is it now possible to predict whether a powder can be dispersed well or poorly? The smaller ΔG_{i} (Eq. 2) is, the better the dispersibility of the powder in the liquid. This means that for good dispersibility the powder and the liquid should have the same type of polarity ("Surface Polaritiy" in Tab. 2 and 3), so that the second, negative term in equation 2 should have as large a value as possible. In the example for good dispersibility mentioned above the strongly modified graphite powder has a surface polarity of 27.49% and the ABS polymer with 27.45% has a very similar surface polarity to the graphite. In Fig. 1 the calculated wetting enthalpies for all possible graphite/polymer combinations are shown as a block diagram.

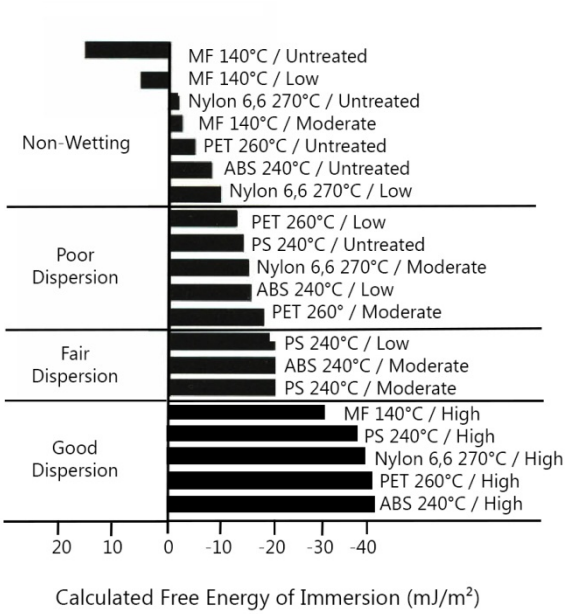

Fig. 1: Wetting enthalpy for various graphite powder / polymer melt combinations

The practical test

The predictions based on the calculation of the free wetting enthalpy are now to be checked by using a simple dispersibility test. In the wetting tests 5 g polymer was molten at the temperature given in Tab. 4 and 0.5 g graphite was added to the molten polymer. A laboratory stirrer was immersed in the polymer to a depth of 1 cm and stirring to disperse the graphite powder was carried out at 1200 min^{-1} for 1 minute. The dispersibility was assessed visually according to the classes defined in Fig. 2. The results of the tests are shown in Fig. 1 on the left-hand side. In comparison to the predicted dispersibilities it is clearly seen to see that the predictions coincide well with the results of our tests. For seven graphite/polymer combinations a wetting enthalpy of more than -10 mJ/m² was calculated and each of these combinations demonstrated the non-wettability of the graphite.

The next *poorly wettable* group contains all combinations with wetting enthalpies between -10 mJ/m² and -19 mJ/m². All combinations with wetting enthalpies between -19 mJ/m² and -25 mJ/m² were classified as *moderately dispersible* and all combinations with wetting enthalpies smaller than -30 mJ/m² as *good dispersibility*.

The results obtained show the validity of the calculations presented here and the predictions derived from them. This means that the method described provides a valuable aid for estimating the dispersibility of powders.

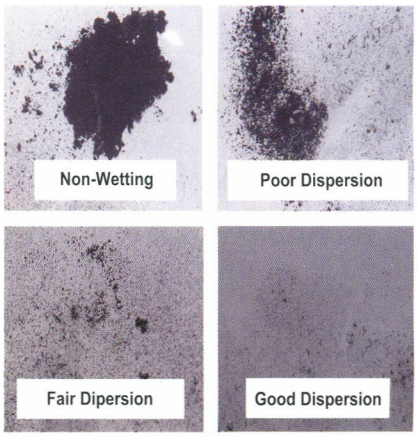

Fig. 2: Classes for the visual assessment of dispersibility

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