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THE EFFECT OF MATRIX-FILLER INTERACTIONS ON THERMAL CAPACITY OF LDPE/GRAPHITE COMPOSITES

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ABSTRACT

Thermal capacity of a particulate composite LDPE filled with graphite was measured by a non-steady state method at 25°C. A non-additive dependence of thermal capacity on the concentration of the filler was observed. A three-phase model was proposed, where the capacity of the interphase was included besides the parameters for matrix and the filler. The model reasonably describes the experimentally observed behavior.

INTRODUCTION

Among the aspects in the investigation of composites and blends with polymer matrix one of the most important is the estimation of polymer-filler interaction and its effect on the properties and processing of the material. From this point of view, the measurement of thermal capacities of two-phase systems with polymeric matrix has been used mainly for determination of glass transition temperatures and consequently, the evaluation of the miscibility [1, 2] or compatibility [3] of the components. Lipatov [4] proposed a method of determination of a volume fraction of the interphase in particulate composites according to a change in the heat capacity in the glass transition region. For two phase systems, all calculations are based on the data of heat capacity at the glass transition region, although attempts have also been made to discuss the relation between a degree of chemical modifi-

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cation of the polymer, e.g. the irradiation of ethylene-propylene copolymers and the changes of the heat capacity in the broad temperature range [5].

In the case of a particulate composite, it is assumed that a special layer is formed around each filler particle [6]. This layer, called interphase or mezophase, is chemically identical with the matrix but its properties, e.g. density, modulus etc. differ from those of a virgin matrix-forming polymer. It is reasonable to expect that the values of thermal capacities of the mixture components could be influenced on the interface by mutual interaction.

In this paper, we measured the thermal capacity outside of glass transition in dependence on the composition of a particulate composite LDPE/graphite . An equation describing the dependence was derived and the physical meaning of the parameters was suggested.

EXPERIMENTAL

Low density polyethylene, LDPE (Bralen RA 2-19, Slovnaft, Bratislava, Slovakia, MFI = 2.1 g/10 min) was used as a matrix, filled with graphite EG-40 (synthetic graphite, SGL Carbon, UK). The blends were prepared in a 50 ml mixing chamber of Plasticorder Brabender PLE 331 at 170°C for 10 minutes. For thermal capacity measurements, the specimens with 50 mm diameter and 10 mm thick have been compression molded at 170°C for 5 minutes with subsequent cooling under the pressure down to 70°C

The thermal capacities were measured using a newly developed multipurpose apparatus (ISOMET, Applied Precision, Bratislava, Slovakia) for non-steady state measurement of thermal properties from the analysis of a time dependence of the thermal flow in the material. Measurements have been made at 25 ± 2°C with a flat probe. Some values were measured also using a Perkin Elmer DSC 2 instrument.

RESULTS AND DISCUSSION

The experimental dependence of thermal capacity on the concentration of graphite in the composite is shown in Figure 1. Significant deviation from additive behavior is obvious. The difference between experimental $Cp^{exp.}$ and those calcu-

$$Cp^{ad.} = Cp_m w_m + Cp_f w_f \tag{1}$$

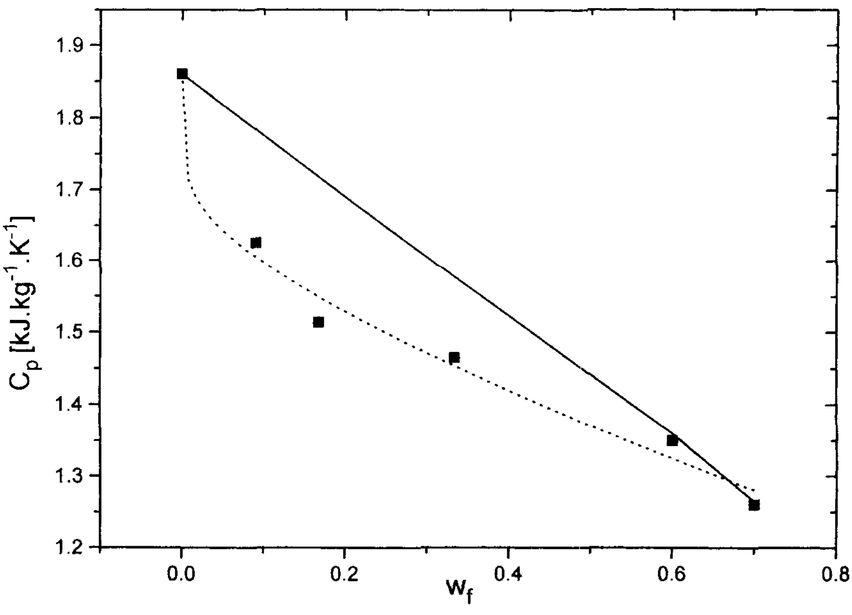

Figure 1. The dependence of thermal capacity Cp on the content of the filler w_f in the composite LDPE/graphite (points). Full line = additive behavior according to Equation 1, dashed line = fit according to Equation 7.

lated according to the additive rule is marked $Cp^{excess.} = Cp^{exp.} - Cp^{ad.}$. The dependence of the deviation $Cp^{excess.}$ from the additive rule on the graphite concentration is shown in Figure 2.

To explain the deviation, a new model has been proposed. The model is based on a three phase concept structure of polymeric composites as suggested by Theocaris [6]. The composite consists of three phases, where beside the matrix and the filler, interphase is considered, possessing properties different from those of the two components of the mixture.

Cp is measured above T_g of the polymer. The thermal capacity of the matrix not influenced by the filler can be considered as Cp^l (l = "liquid"). A decrease in the polymer segment mobility will occur in the vicinity of the filler. This will result in a decrease of a rotational degree of freedom leading to a drop in thermal capacity. If the lowest possible thermal capacity of the matrix is considered as Cp^s (s = "solid"), in the neighborhood of each particle, due to certain levels of polymer-filler interaction, thermal capacity can reach the value between Cp^l and Cp^s.

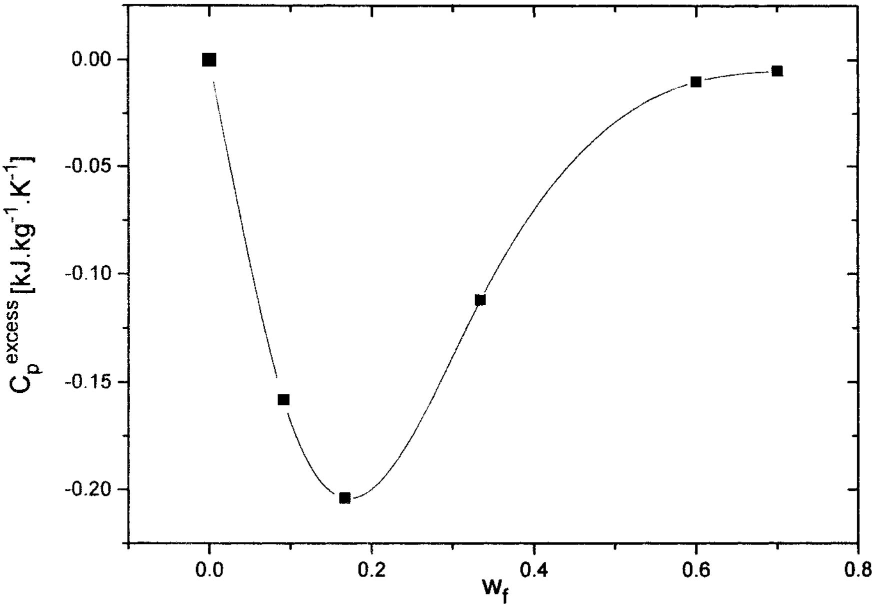

Figure 2. The difference between thermal capacity Cp^{ad} calculated according to the additive rule and experimentally measured $Cp^{exp.}$ in dependence on the filler portion (w_f) for the composite LDPE/graphite.

For each concentration of the filler, certain average value of thermal capacity can be considered, defined as an effective thermal capacity Cp^{eff} postulated by an equation

$$Cp_m^{eff.} = Cp_m^{l} - c\ w_f^{n} \tag{2}$$

Obviously, if $w_f = 0$, $Cp_m^{eff.} = Cp_m^{l}$. At high filler concentrations (close to unity) the polymer matrix will be completely in the "solid" state, i.e.

$$Cp_m^{eff.} = Cp_m^{l} - c = Cp_m^{s} \tag{3}$$

and

$$c = Cp_m^{l} - Cp_m^{s} \tag{4}$$

Thus, Equation 2 can be modified to

$$Cp_m^{eff.} = Cp_m^{l} - (Cp_m^{l} - Cp_m^{s})\ w_f^{n} \tag{5}$$

TABLE 1. A Comparison of Experimentally Obtained Data (Thermal Capacity of LDPE Matrix, Cp_m^{sc}, Graphite Cp_f, and "Solid" State Cp_m^s) with the Values Calculated According to (7)

	calculated	experimental
Cp_m^{sc}	1.86	1.86
Cp_f	1.157	1.01*
Cp_m^s	1.552	1.55 - 1.76**
n	0.158	-

* measured by DSC

** range of published data from various authors [7]

where n is a fitting parameter. Thus, the additive rule is to be modified substituting the thermal capacity of the matrix by the effective capacity $Cp_m^{eff.}$. After substituting Equation 5 into 1, one gets:

$$Cp = [Cp_m^l - (Cp_m^l - Cp_m^s)\ w_f^n]\,(1 - w_f) + Cp_f\, w_f \tag{6}$$

In this equation, $Cp_m l$ is the thermal capacity of the amorphous matrix. In the case of LDPE, this term should be substituted by thermal capacity of the semicrystalline matrix Cp_m^{sc}, resulting in the relation identical with (6)

$$Cp = [Cp_m^{sc} - (Cp_m^{sc} - Cp_m^s)w_f^n]\,(1 - w_f) + Cp_f w_f \tag{7}$$

Equations 6 and 7 should be valid for the temperature above T_g.

The values of the individual parameters calculated according to Equation 7 are compared in Table 1 with the experimental data. A reasonable correspondence between the two sets of data is demonstrated. It is worth mentioning that the calculated value for the thermal capacity of "solid" PE falls within the range of the published data obtained by the extrapolation to room temperature of experimental dependence measured under T_g.

CONCLUSION

The dependence of thermal capacity on the concentration of the filler was found to be non-additive for the LDPE/graphite system. A three-phase model was proposed including the capacity of the interphase besides the parameters for matrix and the filler. The model describes, reasonably well, the experimentally observed behavior.

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