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THERMAL PROPERTIES AND CRYSTALLIZATION KINETICS OF $PP/CaCO_3$ AND $PP/EPDM/CaCO_3$ COMPOSITES

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ABSTRACT

The thermal properties and crystallization kinetics of $PP/CaCO_3$ and $PP/EPDM/CaCO_3$ composites in dependence on the quantity, particle size and the surface treatment of the filler as well as the addition of EPDM were examined by differential scanning calorimetry. It was found out that the addition of the filler as well as the filler and EPDM slightly influences the melting temperature of PP, so that the enthalpies of fusion of PP with the addition of filler as well as filler and EPDM are decreased.

The results of the study of the crystallization kinetics show significant impact of the filler and EPDM on morphology composites based on PP.

INTRODUCTION

It is well-known that composite materials are widely used because of their good mechanical properties/cost ratio (1), (2). However, practical consequences of adding filler to polymers in a physical context are not well-known in spite of the fact of having a great importance to predict their mechanical properties. It is obvious that a filler will interfere with polymer chain mobility and orientation either by adsorption or occlusion. The consequence of this a priori fact is that changes in glass transition temperature (T_g), crystallinity, specific heat and other intrinsic properties should occur (3).

The addition of EPDM or PIB causes drastic modifications in the morphology, nucleation density, spherulite growth rate and thermal behaviour of iPP (4).

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This paper is only a part of a more general study on the properties of filled polypropylene. In the current work diferential scanning calorimetry was used as a method in order to determine the thermal properties and crystallization kinetics of PP/$CaCO_3$ and PP/EPDM/$CaCO_3$ composites in dependence on the quantity, particle size as well as the surface treatment of the filler.

EXPERIMENTAL

The polypropylene - PP (Hipolen FY 6 : ϱ = 0,90 g/cm^3, MFI = 1,6-2,8 g/10 min), ethylen-propylen-dien terpolimer-EPDM-1 (Vistalon 2504 : ϱ= 0,86 g/cm^3), ethylen-propylen- dien terpolymer - EPDM-2 (Dutral CO 054 : ϱ= 0,85 g/cm^3), calcium carbonate - $CaCO_3$-1 (Kredafil RM-5 : d<10 μm, untreated), calcium carbonate - $CaCO_3$-2 (Kredafil RM-5-S : d < 10 μm, treated with stearic acid), calcium carbonate - $CaCO_3$-3 (Kredafil 150 Extra : d < 30 μm, untreated) and calcium carbonate - $CaCO_3$-4 (Kredafil 150 Extra - S : d < 30 μm, treated with stearic acid) were applied in this study.

The samples were prepared in a kneading chamber of a Brabender Plasticorder at 200°C in a period of 15 min and 60 rpm. The milled crepe was then hot pressed at 200°C into compression moulded plaques of about 0.8 mm thickness. The material was quenched from this temperature by plunging the sample and moulding plates into cold water.

Thermal characteristics were measured by a Perkin Elmer differential scanning calorimeter DSC-7. Melting temperature (T_m) were determined from DSC curves obtained by heating the samples at a rate of 10°C min^{-1} and correcting the maximum melting temperatures for the melting slope of indium. The enthalpy of fusion (ΔH_m) was calculated from the area between the DSC curve and the baseline using the melting enthalpy of indium as standard. The crystallinity (X_c) of the samples was determined by taking as fully crystalline PP enthalpy value 138,6 J/g.

The crystallization temperatures (T_c), enthalpies of crystallization (ΔH_c) and non-isothermal crystallization were determined as follows: the blend sample (about 5-6 mg) was heated to 180°C and kept at this temperature for 5 min. Then the samples were cooling with the rate 10°C min^{-1} while same of those but also with the cooling rate 5 - and 2°C min^{-1}.

To study non-isothermal crystallization of composites PP/$CaCO_3$ as well as PP/EPDM/$CaCO_3$ the Avrami equation was used. The exponent n was determined and the overall rate constant of crystallization - Z_1, which include the nucleation and the growth rate of crystals was calculated.

RESULTS AND DISCUSSION

In the table 1 the results of the thermal properties and the crystallization kinetics of PP and related composites are given.

The values of the melting point of PP with the addition of the filler in generally slightly increased while the values of the melting point by addition of EPDM are slightly decreased.Similar findings proceed from the authors' research work Acoste and coworkers (5) and Karger-Kocsis et al. (6).

The values of the enthalpy of fusion with the addition of $CaCO_3$ respectively of EPDM are decreased. The change is almost linear as regards the increasing amount, the particle size and surface treatment of the filler or the addition of EPDM. Such results are expected, as by addition of the mineral fillers to PP or the amorphous elastomer component to PP the content of the crystalline phase is diminished.

The results also show that the theoretically calculated values for the enthalpy of fusion based on the additivity are somewhat higher in view of the experimentally obtained.

As we calculated the crystallinity from the values for the enthalpies of fusion for crystallinity the similar findings as well as for the changes of the enthalpy of fusion are valid. Regardless of the fact that in the literature various values for the enthalpy of fusion for full crystalline PP (117,6 - 138,6 J/g) are illustrated, and although the surface tension of the crystalls has the impact on the heat of fusion the results show a decrease of crystallinity of the studied composites.

The crystallization temperatures of PP with the addition of the filler as well as the filler and EPDM is increased, while the particle size and the surface treatment of the filler doesn't influence the crystallization temperature.

TABLE 1: The results of the thermal properties and the crystallization kinetics of PP and related composites

Sample	Composition (wt %)	T_m (^oC)	ΔH_m (J/g)	X_c (%)	T_c (^oC)	n	Z_1 (s^{-n})
PP	100/0	163,5	86,0	62,0	111,0	6,4	$9,6.10^{-14}$
PP/$CaCO_3$-1	90/10	163,5	76,7	55,3	113,0	6,3	$2,7.10^{-13}$
	80/20	164,0	68,0	49,0	115,5	6,2	$1,4.10^{-12}$
	70/30	164,0	61,8	44,5	116,0	5,3	$8,2.10^{-11}$
PP/$CaCO_3$-1/EPDM-1	70/20/10	163,0	66,2	47,7	114,0	5,4	$2,0.10^{-11}$
PP/$CaCO_3$-1/EPDM-2	70/20/10	163,0	62,4	45,0	113,0	7,6	$7,9.10^{-16}$
PP/$CaCO_3$-2	90/10	165,0	76,2	54,9	112,0	6,0	$5,8.10^{-13}$
	80/20	163,5	70,9	51,1	113,5	6,1	$4,5.10^{-13}$
	70/30	163,5	59,6	43,0	114,0	5,3	$1,7.10^{-11}$
PP/$CaCO_3$-2/EPDM-1	70/20/10	163,0	62,9	45,4	113,0	6,8	$1,2.10^{-14}$
PP/$CaCO_3$-2/EPDM-2	70/20/10	164,0	60,2	43,4	113,5	5,6	$4,6.10^{-12}$
PP/$CaCO_3$-3	90/10	165,5	78,3	56,5	112,5	7,8	$9,9.10^{-17}$
	80/20	164,5	69,5	50,2	115,0	5,0	$7,0.10^{-7}$
	70/30	164,0	57,1	41,2	116,5	3,7	$3,9.10^{-8}$
PP/$CaCO_3$-3/EPDM-1	70/20/10	162,0	62,2	44,8	114,5	5,1	$6,1.10^{-11}$
PP/$CaCO_3$-3/EPDM-2	70/20/10	163,5	62,0	44,7	113,0	8,7	$2,4.10^{-18}$
PP/$CaCO_3$-4	90/10	164,0	75,1	54,1	112,5	7,8	$9,2.10^{-17}$
	80/20	163,0	67,5	48,7	113,0	5,1	$3,3.10^{-11}$
	70/30	164,0	62,0	44,7	115,0	6,7	$4,5.10^{-14}$
PP/$CaCO_3$-4/EPDM-1	70/20/10	163,5	59,3	42,8	112,5	9,1	$2,4.10^{-19}$
PP/$CaCO_3$-4/EPDM-2	70/20/10	164,0	63,0	45,5	113,0	8,4	$1,0.10^{-17}$

It can be seen, that the type of EPDM doesn't influence the crystalization temperature.

We have also found out that the filler and EPDM have similar influence on the changes of the thermal properties. A small amount of foreign particles play role as a nucleating agent. Polymer structure may be affected by the presence of fillers due to interaction between two phases and formation of a boundary layer on the surface of the filler particles.

During the study of the non-isothermal crystallization it was found out that the values n with the addition of the filler d < 10 μm are slightly changed, while the differences of values n are more visible by addition of the filler with the particle size d<10μm. The causes of changes are result of different mechanism and the crystallization kinetics.

While the constant Z_1 is exponential dependence on n, the values Z_1 shows relatively great differences.

We have found out that Z_1 with the addition of filler to PP is increased while the change of Z_1 is dependent on the choice of EPDM in PP/EPDM/$CaCO_3$ composites.

Regardless of the fact that the part of individual phase of crystallization is not possible to determ, the constant Z_1 have immediate impact on the morphology and in this way on the mechanical properties of composites.

Table 2 illustrates the results of certain parameters independence on the cooling rate of the selected samples of the composites.

It can bi seen that independence on cooling rate the crystallization temperature is decreased while the enthalpies of crystallization and values n are increased. The curve shows the exponential growth as established also by N. Hay (7).

Table 2: Variation of some parameters with cooling rate

Sample	Parameteres	Cooling rate $2^{o}Cmin^{-1}$	$5^{o}Cmin^{-1}$	$10^{o}Cmin^{-1}$
PP	T_c (^{o}C)	121,0	115,0	111,0
	ΔH_c (J/g)	-99,4	-93,6	-89,9
	n	5,0	5,4	6,4
PP/$CaCO_3$-1 70/30	T_c (^{o}C)	125,0	120,0	116,0
	ΔH_c (J/g)	-71,0	-66,0	-65,1
	n	3,1	3,7	5,3

CONCLUSIONS

The melting point of PP with the addition of $CaCO_3$ is generally slightly increased while the melting point by addition of EPDM is slightly decreased.

The enthalpies of fusion of PP with the addition of $CaCO_3$ and EPDM are decreased. The similar findings are valid for crystallinity. The crystallization temperature of PP with the addition of the filler as well as the filler and EPDM is increased, where the type of EPDM does not have impact on the crystallization temperature. The results of the study of non-isothermal crystallization shows that the values n at addition of filler with little particle size slightly decreasing and that the changes in values n are more visuable by addition of the filler with larger partilce sizes. The constant Z_1 with the addition of the filler is thus increased.

The results confirm that the cooling rate of samples essentially influences the changes of the investigated parameters.

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