Effect of Thermal Contacts between Components on Thermal Conductivity of Multicomponent Systems

E. PIORKOWSKA and A. GALESKI, *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90 362 Lodz, Boczna 5, Poland*

Synopsis

In the paper the influence of thermal contacts of the interface between the inclusions and matrix on thermal conductivity of a multicomponent system is studied. It is shown that the modification of the interface which improves the adhesion between components causes also the increase of the thermal conductivity of a composition.

INTRODUCTION

The physical properties of blends and filled polymers are mainly determined by the properties and contents of the components. Another important factor is the interaction between the components. One can modify the behavior of a composition by changing the properties of the interface. The properties and the structure of the interfacial layer affect the mechanical properties and also transport phenomena, e.g., heat conduction. The paper reports the results of the thermal conductivity measurements of polypropylene/ethylene–propylene copolymer blends and polypropylene filled with chalk. It is shown that the modification of the adhesion between components usually made in order to change the mechanical properties of a composition also causes changes in the thermal contacts between components and that this is reflected in the thermal conductivity of multicomponent systems.

EXPERIMENTAL

Samples. Two systems were chosen for studying the change in the thermal contacts between the components: the blend of isotactic polypropylene (iPP) with ethylene–propylene copolymer (EPR) in which the interface can be modified by partial compatibilization and isotactic polypropylene filled with chalk in which the interface can be modified by addition of a liquid. In both systems the purpose of the modification was to improve their tensile and impact properties as is described elsewhere.[1][4] The following systems were studied:

—Isotactic polypropylene (iPP): Moplen S30G, Montedison (melt flow index

1.75 g/10 min at 230°C, 2.16 kg) and J-400, Polish product (melt flow index 3.0 g/10 min).

—Ethylene–propylene random copolymer (EPR): Dutral CO54, Montedison (ρ = 0.865 g/cm^3, M_w = 1.8 × 10^5, melt flow index 0.55 g/10 min, 45% propylene content).

—Blend of iPP (Moplen S30G, Montedison) with 20 wt % of EPR.

—Compatibilized blend (Moplen/EP/SP/G/32/NAT, Montedison) containing approximately 80 wt % of isotactic polypropylene fraction and 20 wt % of ethylene–propylene rubber fraction.

—iPP (J-400, Polish product) filled with 40 wt % of chalk.

—iPP (J-400, Polish product) filled with 40 wt % of chalk modified by 5 wt % of ethylene oxide oligomer (OEO) of M_w = 300.

The blend of iPP with EPR was prepared by several extrusion passes in a single screw extruder in order to obtain good dispersion of EPR in iPP. Filled iPP samples were obtained in a two-step procedure consisting of premixing of chalk and iPP granulate in a mixer followed by an extrusion. In the case of modified chalk the modification was conducted during the premixing step by adding an appropriate amount of OEO. The 1 mm thick samples for thermal conductivity measurements were prepared by compression molding at 200°C and cooled in iced water. After several minutes the samples were taken out from water, dried at room temperature, and stored at ambient conditions for several days. Pure iPP samples were prepared from an unprocessed granulate and from granulates extruded so many times as blend and filled system.

In order to characterize the samples, the DSC studies were performed using a DSC Perkin-Elmer 2 apparatus in the temperature range of −50–+200°C. The iPP/EPR blends were also studied by means of scanning electron microscopy (SEM). The samples were cooled down to liquid nitrogen temperature and then quickly broken. The surfaces of fracture were evaporated with gold and examined under SEM.

Thermal conductivity measurements were conducted on samples cut out from 1 mm thick films in a form of disks of 15 mm in diameter by means of transient method described recently in details in Refs. 5–7 and briefly presented below.

Thermal Conductivity Measurements. The scheme of the temperature cell of the apparatus for thermal conductivity measurements by transient method is shown in Figure 1. Two samples of the examined material (3) in a form of flat disks having 15 mm in diameter are separated by a heating element (2) placed between them and clamped between two copper blocks (1) with the force of about 10 N. Thermal contacts between the samples and a heating element and copper blocks are ensured by means of a grease prepared from aluminum powder and silicon oil. The heating element contains a heater surrounded by a guard ring, a pile of thermocouples controlling the power supply of the guard ring, and resistance thermometers—all made using thin film photoresist techniques. Another thin film resistance thermometer is attached to the surface of the copper block. The pair of resistance thermometers measures the temperature difference between the surfaces of a sample. The sandwich
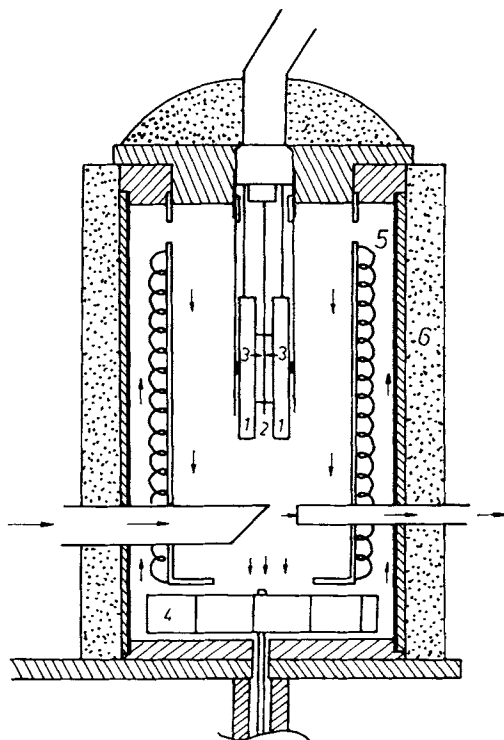
Fig. 1. Scheme of the temperature cell for transient measurements of the thermal conductivity of polymer samples: (1) copper blocks; (2) heating element; (3) samples; (4) fan; (5) electrical heater; (6) thermal insulation. Arrows indicate vapor circulation.

consisting of samples, heating element, and copper blocks is placed in a temperature cell equipped with an electric heater (5) connected to a temperature controller and a supply of liquid nitrogen vapors. A fan (4) at the bottom of the cell ensures quick circulation of the vapors in the cell, improves the exchange of heat between copper blocks and vapors, and reduces the temperature gradients within the copper blocks. During the measurements the heater in a heating element (2) generates the heat flow across the samples while the temperature of the copper blocks (1) is being changed continuously at the programmed constant rate v in a wide temperature range.

As was previously shown by us,[6] the temperature difference between the sample surfaces, ΔT, for the cooling or heating rate v can be written as follows:

$$\Delta T(t) = \frac{Pl}{2sk(t)} - \frac{vl^2}{2a(t)} + \frac{16l^2 k_0 v}{\pi^3 a_0 k(t)} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3}$$

$$\times \exp\left[\frac{-(2n+1)^2\pi^2}{4l^2 v} \int_0^{vt} a(z)\, dz\right] + \frac{16vl^2}{\pi^3 k(t)} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3}$$

$$\times \int_0^{vt} \exp\left[\frac{-(2n+1)^2\pi^2}{4l^2 v} \int_s^{vt} a(z)\, dz\right] \frac{d}{ds}\left[\frac{k(s)}{a(s)}\right] ds \quad (1)$$

where P and s denote the power and the surface of the heater placed between the samples, $k(t)$ and $a(t)$ the thermal conductivity and thermal diffusivity of samples at time t, respectively, $a_0 = a(0)$, $k_0 = k(0)$, and l the thickness of the sample. If the cooling or heating rate ranges several degrees per minute and the sample thickness is about 1 mm, the last term in eq. (1) is always less than 0.002 K for polymeric samples while the third term approaches zero within several seconds after the change of the ambient temperature is started. The thermal conductivity can be determined from two runs of the instrument with the different power densities, P/s, from the following formula:

$$\Delta T' = \Delta T_1(t) - \Delta T_2(t) = \frac{(P_1 - P_2)l}{2sk(t)} \qquad (2)$$

where ΔT_1, ΔT_2, P_1, and P_2 denote the temperature differences and the powers supplied to the heater, respectively, during two independent transient measurements. The terms depending on the cooling (or heating) rate v are identical for both runs and disappear upon substraction of ΔT_2 from ΔT_1. The deviation may occur if ΔT_1 and ΔT_2 differ more than a few degrees.

In the present study the measurements were conducted during cooling from $+100$ to $-100°C$ at the rate -4.5 K/min. The power supplied to the heater and the difference between temperature of sample surfaces were measured continuously during each measurement. The thermal conductivity coefficient for temperatures from the range -100–$+100°C$ was determined on the basis of results of two transient measurements according to eq. (2). The temperature differences measured ranged as follows: ΔT_1 from 0.0 to 0.4 K and ΔT_2 from 2.0 to 2.4 K. Before each measurement samples were annealed at $+100°C$ for 10 min. In order to ensure the same thermal history of samples during both measurements, the samples were subjected to annealing and cooling from $+100$ to $-100°C$ at the rate -4.5 K/min prior to measurements. Also several steady-state measurements ($v = 0$) at various temperatures were performed for each sample for the sake of occasional checkup of the transient measurements. The systematic error of all measurements was estimated to be about 1%; the accidental, about 1.5%.

RESULTS

The results of the thermal conductivity measurements are shown in Figures 2 and 3. The curves represent the continuous temperature dependence of the thermal conductivity coefficient measured by means of the transient method. Points represent results of steady-state measurements. The results of DSC measurements are shown in Figures 4 and 5. No change in the thermal conductivity and the DSC data of iPP J-400 and Moplen S30G introduced by the extrusion step was observed.

The results of thermal conductivity measurements of pure and chalk filled iPP are compared in Figure 2. The addition of 40 wt % of chalk causes significant increase of thermal conductivity. The system containing chalk modified with OEO is characterized by higher thermal conductivity than that for samples
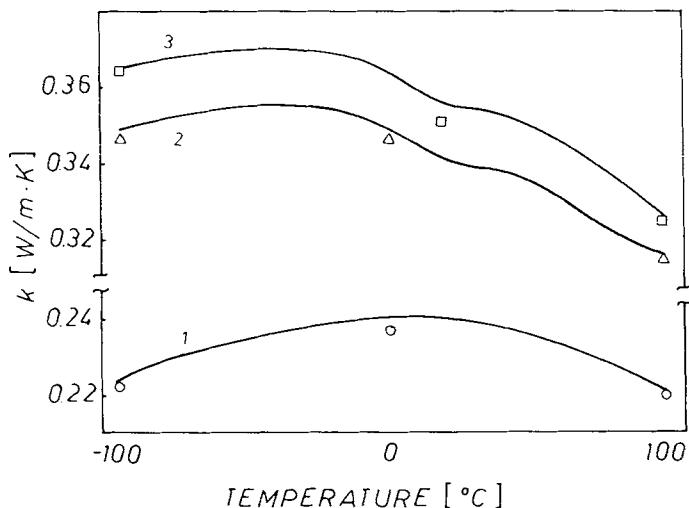
Fig. 2. Temperature dependence of the thermal conductivity of: (1) iPP J-400; (2) iPP J-400 filled with 40 wt % of chalk; (3) iPP J-400 filled with 40 wt % of modified chalk. Lines denote the results of transient measurements. Points denote the results of steady-state measurements.

containing unmodified chalk. DSC measurements reveal that there is no significant change in the crystallinity degree of the iPP matrix due to the presence of chalk and the modification by OEO. All filled samples as well as pure iPP J-400 have similar degree of crystallinity of about 40 wt % as determined from DSC data from enthalpy of fusion.

The results of measurements of thermal conductivity of iPP/EPR blends and the component materials are depicted in Figure 3. The iPP/EPR blends
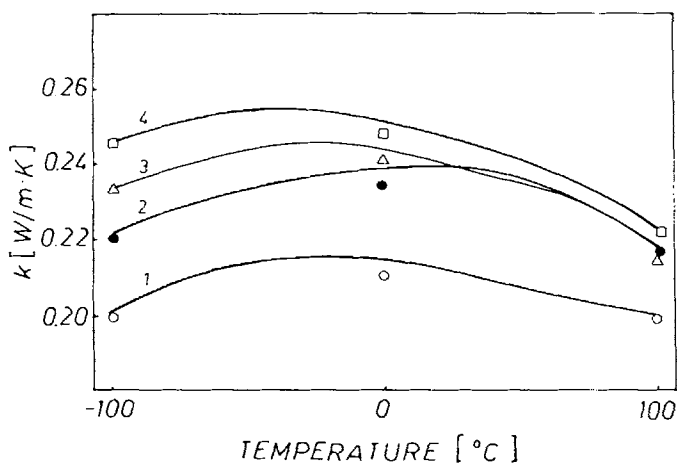

Fig. 3. Temperature dependence of the thermal conductivity of: (1) EPR Dutral CO54; (2) iPP Moplen S30G; (3) Moplen S30G/EPR blend; (4) Moplen/EP/SP/G/32/NAT. Lines denote the results of transient measurements. Points denote the results of steady-state measurements.
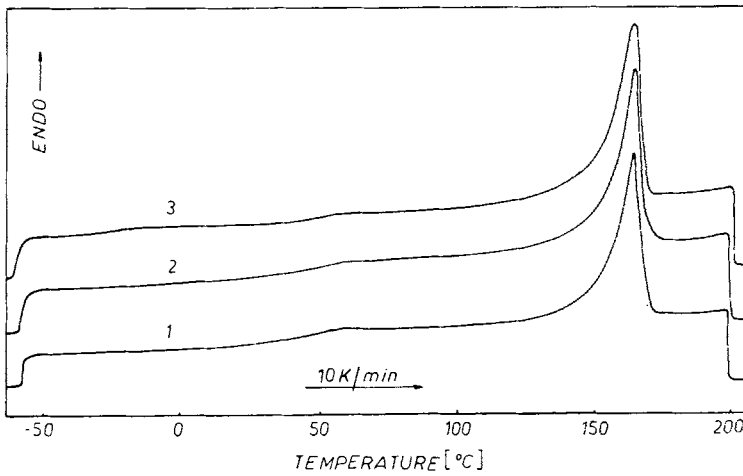
Fig. 4   DSC runs for: (1) iPP J-400; (2) iPP J-400 filled with 40 wt % of chalk; (3) iPP J-400 filled with 40 wt % of modified chalk.

have equal or higher thermal conductivity than pure iPP, although EPR has lower thermal conductivity than polypropylene itself. The thermal conductivity of compatibilized blend (Moplen/EP/SP/G/32/NAT) is higher than that of Moplen S30G/EPR blend. With the decrease in temperature the difference between thermal conductivities of the blend and compatibilized blend slightly increases. The results of DSC measurements of blends and their components are shown in Figure 5. Besides the significant peak resulting from melting of iPP crystalline phase in the DSC curves in Figure 5 is seen the effect of melting of a small amount of crystalline phase identified as polyethylene small crystals present probably in rubber inclusions. The determination of the degree of crys-
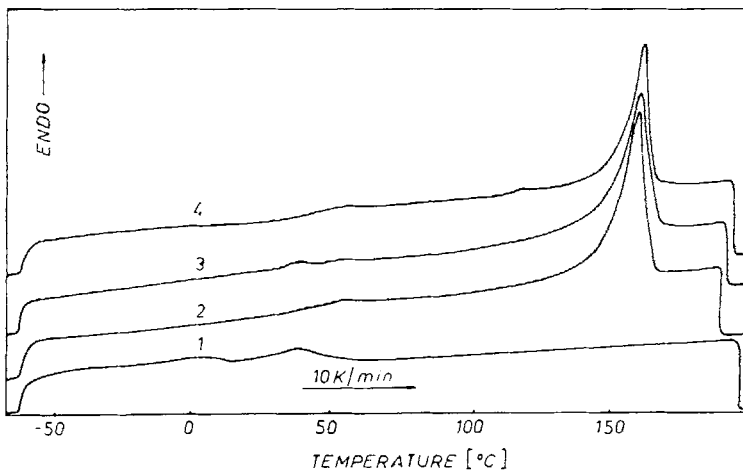

Fig. 5.   DSC runs for: (1) EPR Dutral CO54; (2) iPP Moplen S30G; (3) Moplen S30G/EPR blend; (4) Moplen/EP/SP/G/32/NAT.

tallinity of the iPP matrix of the blends gives approximately the same value 41.4 wt % for both Moplen S30G/EPR and Moplen/EP/SP/G/32/NAT systems. This value is higher than the degree of crystallinity obtained for the pure iPP Moplen S30G sample which amounts to 36.2 wt %. Figures 6(a) and 6(b)
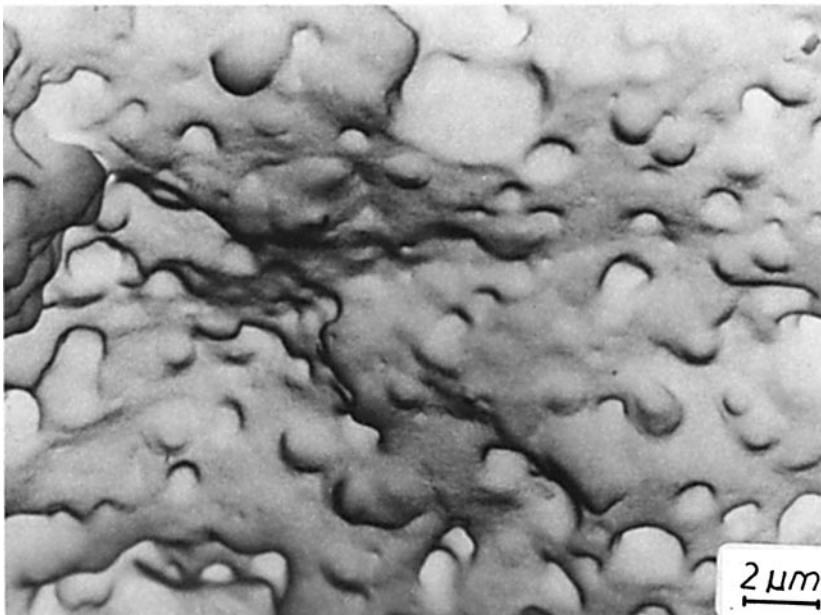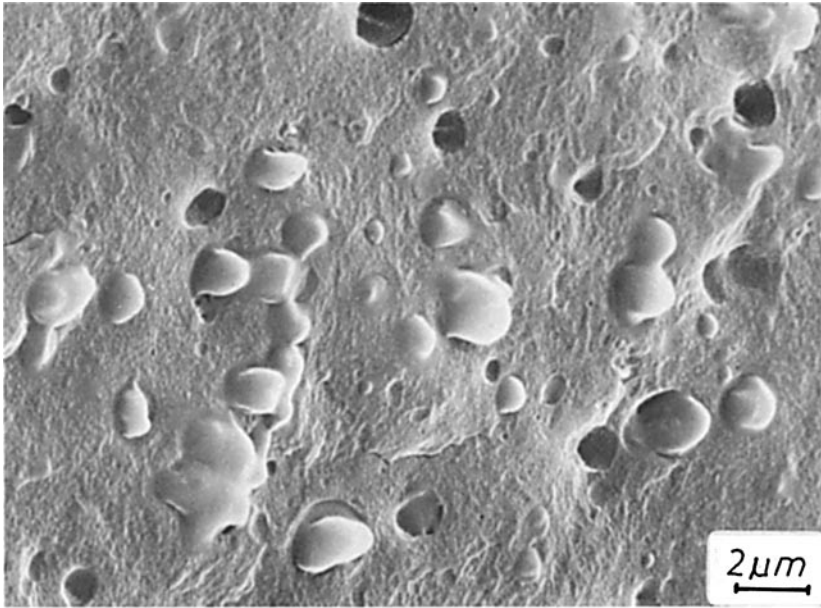

Fig. 6.   SEM micrographs of fracture surfaces of blends: (a) Moplen S30G/EPR; (b) Moplen/ EP/SP/G/32/NAT.

show the scanning electron micrographs of fracture surfaces of Moplen S30G/EPR and Moplen/EP/SP/G/32/NAT blends. On the fracture surface of Moplen S30G/EPR blend one can see clearly the borders of EPR inclusions. On the electron micrograph of fracture surface of Moplen/EP/SP/G/32/NAT the boundaries of inclusions are not marked significantly.

MAXWELL MODEL

For the purpose of calculating the thermal conductivity of compositions consisting of inclusions incorporated within the matrix the Maxwell model transferred from electrostatics may be adapted.[8-10] The thermal conductivity k of such a system is expressed by the equation

$$k = \frac{2k_m + k_i + 2s(k_i - k_m)}{2k_m + k_i + s(k_i - k_m)} k_m \qquad (3)$$

where k, k_m, and k_i denote the thermal conductivities of the composition, the matrix, and the inclusions, respectively, and s denotes the volume fraction of the inclusions.

The experimental results concerning the iPP/EPR blends indicate some polypropylene matrix changes due to the presence of EPR and so we apply the formula (3) only to filled system. Due to a significant difference between thermal expansion coefficients of chalk (10^{-5} K^{-1})[11] and iPP $(6.8 \times 10^{-5} \text{ K}^{-1})$[12], one can expect the separation of inclusions from the matrix at some temperature during thermal conductivity measurement. We will try to estimate the influence of that effect on thermal conductivity of the system. Let us assume that the inclusion is separated from the matrix by a gap filled with air and that the gap width in respect to the inclusion radius is equal to A. Therefore, the inclusion volume fraction in such cavity is $(1 + A)^{-3}$. The thermal conductivity of such cavities calculated from formula (3) for A up to 1% is depicted in Figure 7(a) considering the fact that the thermal conductivity of chalk particles (single crystals of calcite) is around 3 W/m K[11] and the thermal conductivity of air is 0.0243 W/m K.[13] Using the obtained values as k_i and taking into account that at room temperature the thermal conductivity of iPP matrix is around 0.24 W/m K and chalk density is 2.6 g/cm^3, one can calculate also from the formula (3) the thermal conductivity of the whole system. The results obtained are depicted in Figure 7(b). For good adhesion and no separation of components the thermal conductivity of the system is 0.365 W/m K. The lack of contact and presence of air gaps between components decrease the thermal conductivity to 0.333 W/m K.

DISCUSSION

The addition of chalk causes an increase of the thermal conductivity of the system due to its high thermal conductivity compared to polymers. The system with modified chalk has a higher thermal conductivity. It is known that there
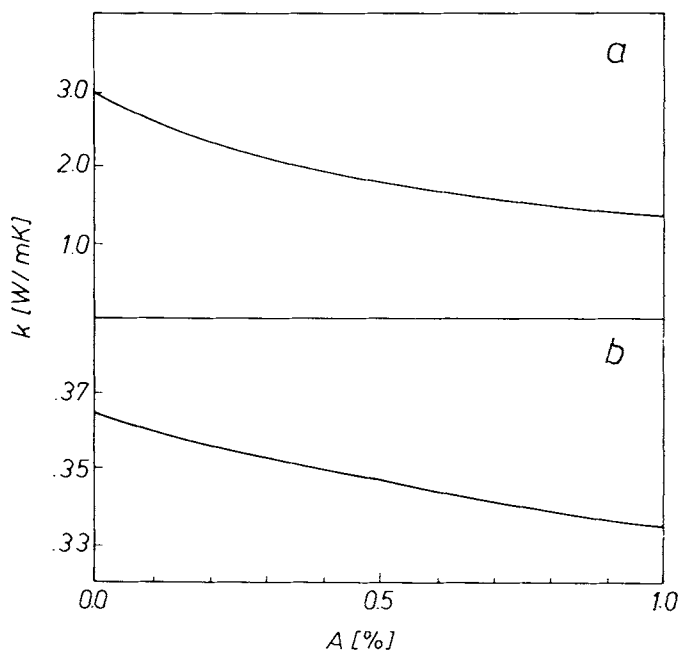
Fig. 7.   Thermal conductivity of (a) chalk particle surrounded by an air layer and (b) iPP filled with 40 wt % of chalk vs. the width of air layer with respect to particle radius.

is no significant difference in iPP matrix morphology between the systems containing modified or unmodified chalk.[1,2] The DSC measurements show that there is no significant change of crystallinity of iPP matrix. The system with modified chalk contains a smaller amount of chalk 38 and 2 wt % of modifier having the thermal conductivity close to polymeric materials and much lower than chalk. It is known from other studies of that system[1,2] that OEO wets well the chalk particles and forms thin layers on their surfaces and adheres well to iPP. Due to the difference between thermal expansion coefficients of chalk and iPP, one can expect the separation of chalk from matrix at a temperature higher than the temperature of sample crystallization and the loss of thermal contact between components. The presence of OEO on the interface prevents to some extent the loss of contact between the particles and the matrix. The increase of the thermal conductivity of the system due to the modification of the interface is in agreement with the estimation performed on the basis of Maxwell model. The Maxwell model, however, assumes the spherical shape of the inclusions and their random distribution within the matrix. Such effect as shape anisotropy or aggregation of inclusions may also influence the thermal conductivity.[14-16] Both effects are similar in samples with modified and un-modified chalk[1,2]; hence they influence the obtained result in a similar way. Chalk has a lower coefficient of thermal expansion; hence it is expected that the decrease of the temperature will promote the improvement of contacts between particles and the matrix. Since the thermal conductivities of both filled systems increase while their difference does not increase with the tem-perature decrease, one can conclude that the effect of higher thermal shrinkage

of the matrix promote the improvement of thermal contacts to the same extent in both systems.

The increase of thermal conductivity of iPP due to the addition of EPR as compared to pure iPP can be explained as an effect of changes of polypropylene matrix morphology. The influence of EPR on iPP morphology was a subject of several papers.[3,4,17,18] The DSC measurements confirmed the increase of the overall crystallinity of polypropylene in the presence of EPR. However, the two investigated iPP/EPR and compatibilized blend Moplen/EP/SP/G/32/NAT have similar EPR contents and crystallinity degrees. In both systems the ethylene–propylene copolymer forms inclusions in iPP matrix. Due to a higher thermal coefficient of rubber $(2 \times 10^{-4} \text{ K}^{-1})$[19] than that of iPP, one can expect that the separation of rubber inclusions from the matrix occurs during cooling. The SEM examination of fracture surfaces reveals different behavior of those samples which manifests itself also in different impact properties.[3] The separation of inclusions from the matrix occurs in Moplen S30G/EPR blend while in the compatibilized system Moplen/EP/SP/G/32/NAT the separation is not observed. The compatibilization of such systems is achieved by the addition of copolymer containing polypropylene blocks which form interfacial layers, improving the adhesion of components. The stronger adhesion between the components in Moplen/EP/SP/G/32/NAT system prevents the loss of contacts between components. Hence, the highest thermal conductivity of that system may be attributed to the improvement of thermal contacts between inclusions and the matrix. Since the thermal expansion coefficient of EPR is higher than that of iPP, the thermal contacts between inclusions and the matrix should decrease with decreasing temperature. From the analysis of the thermal conductivity behavior, one can conclude that at high temperature the contacts between the components in both blends investigated are similar. With the decreasing temperature a difference arises due to the separation of EPR inclusions from the matrix in Moplen S30G/EPR blend.

One can conclude from the above that there is a direct relation between the thermal conductivity of heterogeneous systems and thermal contacts between their components. Since the improvement of adhesion always improves thermal contacts, it is possible to study adhesion by means of thermal conductivity measurements.

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