

PHASE STRUCTURE AND MORPHOLOGY OF POLYPROPYLENE COMPOSITES WITH VARIOUS SILICA GRADES

A. Pustak¹, I. Šmit¹, I. Pucić¹, M. Denac², I. Švab³, J. Pohleven², V. Musil²

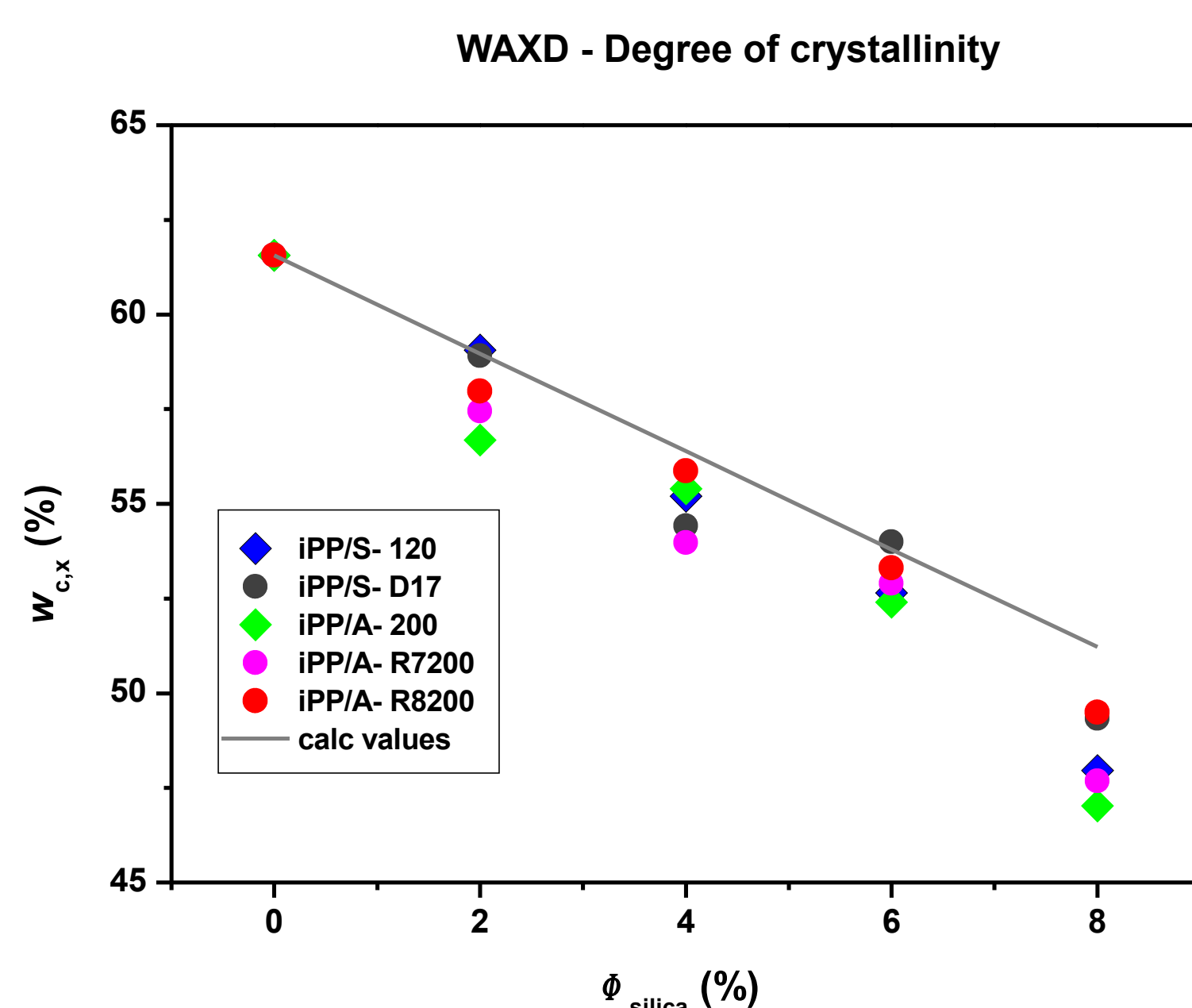
¹ Ruđer Bošković Institute, Zagreb, Croatia

² University of Maribor, FEB Maribor, Institute of Technology, Maribor, Slovenia

³ ISOKON, Ltd, Slovenske Konjice, Slovenia

Micro- and nanocomposites are prepared to improve various properties like tensile and impact strength, elastic modulus, heat resistance, barrier performance, etc. of commercial polymers like isotactic polypropylene (iPP). The fillers influence ultimate mechanical properties in two ways: they act directly as hardener particles and they affect crystallization of polymer matrix and ultimate morphology of composite. Microfillers are easily homogeneously dispersed but high loadings (10–40 wt%) are needed. Similar improvements can be obtained by low nanofiller contents (below 10 wt%) but nanoparticles strongly tend to agglomerate so it is very difficult to finely disperse them into the molten polymer matrix. The agglomeration and aggregation problem increases with filler content in samples and various surface treatments of fillers were proposed in order to overcome that problem. Surface treatment of fumed silica nanoparticles by grafting of selected polymers or foaming agents reduced the agglomeration but not to a satisfying degree. Organosilane nanosilicas showed increased nucleation activity on the polymer matrix. Recently some researchers achieved reduced agglomeration and better homogeneity between polypropylene matrix and silica nanofillers by adding reactive compatibilizers like unfunctionalized polymers (e.g. PP-g-MA), epoxy resins and silsesquioxanes. Deterioration of impact properties by incorporation of filler into polymer matrix could be avoided by addition of an appropriate elastomer to the binary composites. Understanding of structure-property relationships in such composites is necessary for successful optimization of their properties.

The aim of our investigation was to determine the effect of selected silica micro- and nanofillers on final structure and morphology of the iPP/silica composites. The silicas were untreated or variously surface-treated.

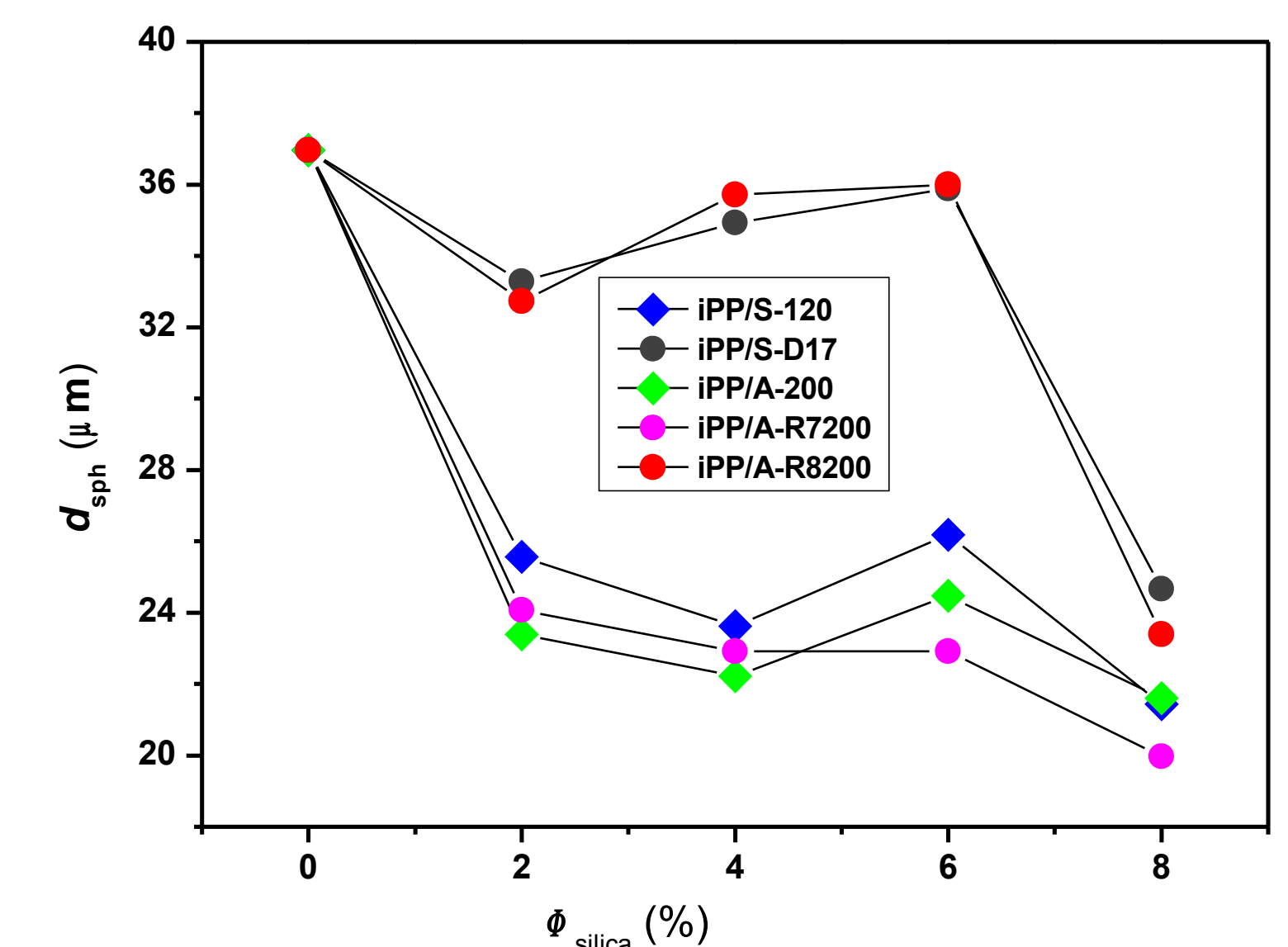


The experimental crystallinity values are lower than calculated because all silica fillers restructured the iPP matrix and reduced the degree of crystallinity. This effect is the least pronounced in samples containing relatively non-polar micro-silica modified with carbon and nanosilica modified with hexamethyl-disilazane up to concentrations of 6%. Additional mechanical restraints seem to have occurred on addition of 8% of any filler resulting in further decrease in crystallinity.

Filler characteristics

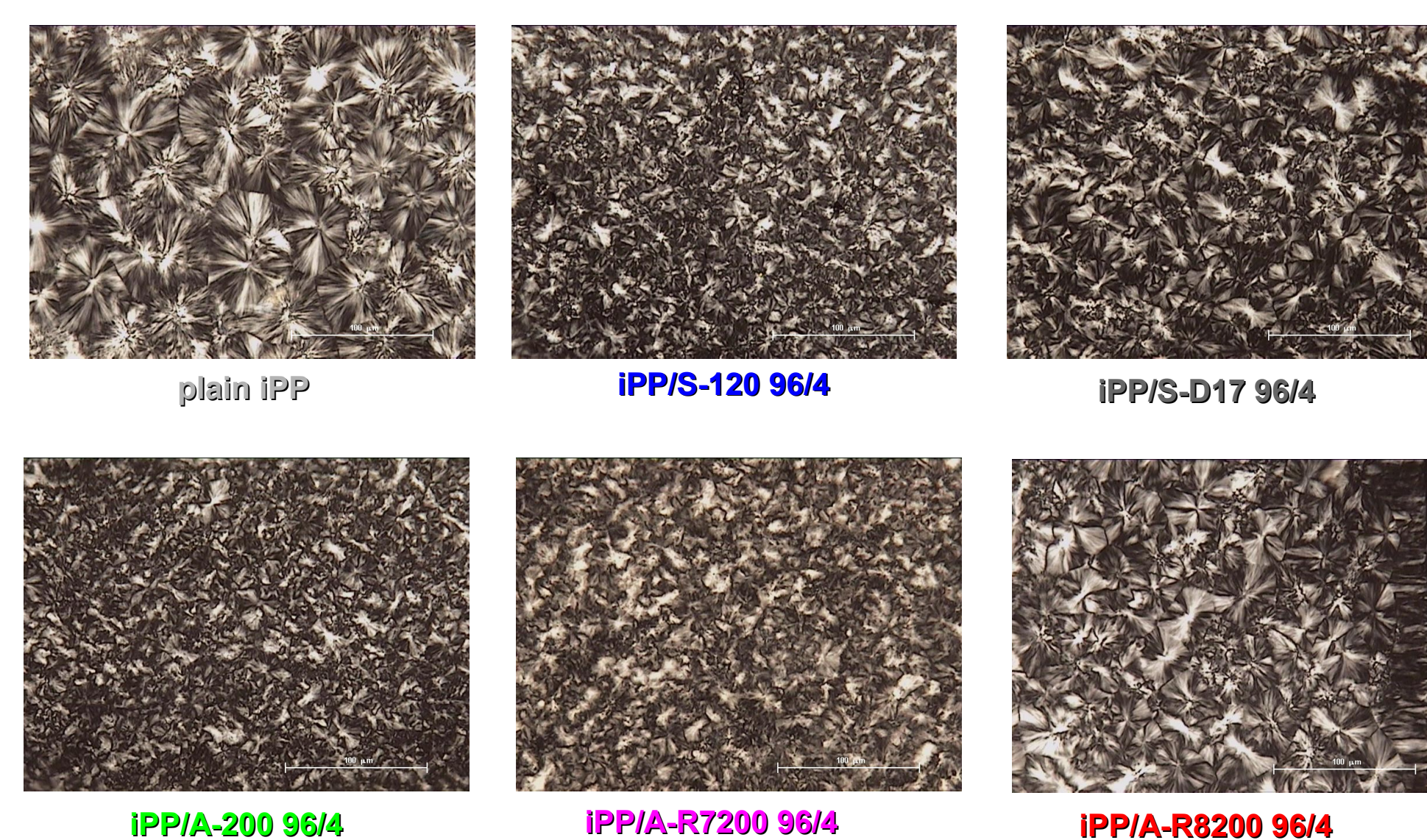
Sample	Trade name	Tapped density (g/l)	Modification of surface	Specific surface area (BET) (m ² /g)	Particle size, d ₅₀
A-200	Aerosil 200 nanosilica	~ 50	- / -	200	12 nm
A-R7200	Aerosil R7200 nanosilica	~ 230	methacryl-silane	150	12 nm
A-R8200	Aerosil R8200 nanosilica	140	hexamethyl-disilazane	160	12 nm
S-120	Sipernat 120 microsilica	185	- / -	125	14.5 μm
S-D17	Sipernat D17 microsilica	150	2 % chem. bound carbon	100	10 μm

Average spherulite diameter



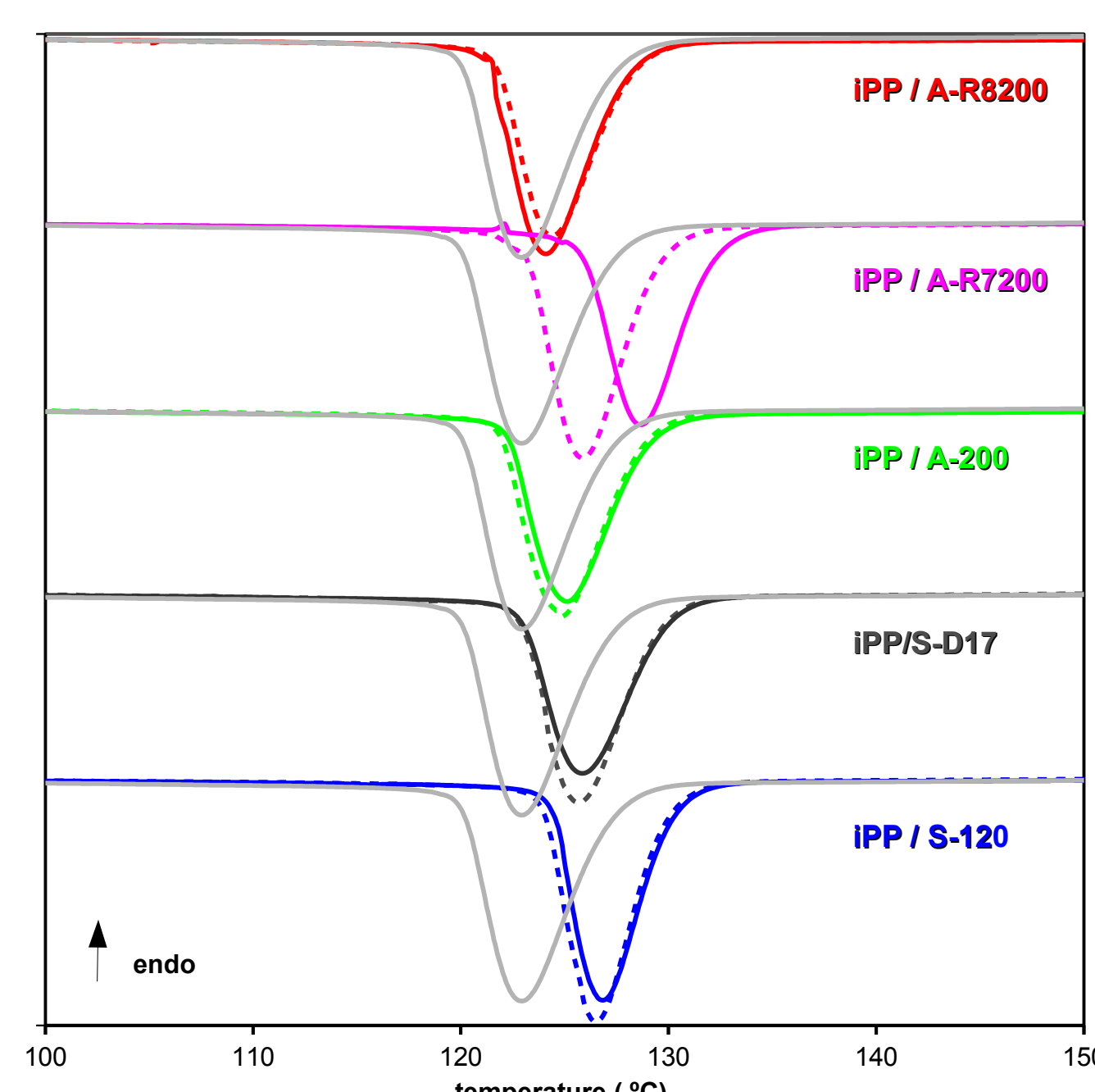
The reduction of spherulite size caused by nucleation effect achieved its maximum at 2 vol% of any silicas. The nucleation effect is very pronounced for less compatible silicas. The reduction of spherulite size is much lower in composites containing relatively non-polar microsilica modified with carbon and nanosilica modified with hexamethyl-disilazane, similar to the changes in crystallinity observed by WAXD. Another significant decrease in spherulite size occurred at 8 vol% of added silica fillers. Since the spherulite sizes become very similar at that concentration irrespectively of surface modification, it seems that spherulite growth becomes restrained just by the filler amount.

Polarization micrographs



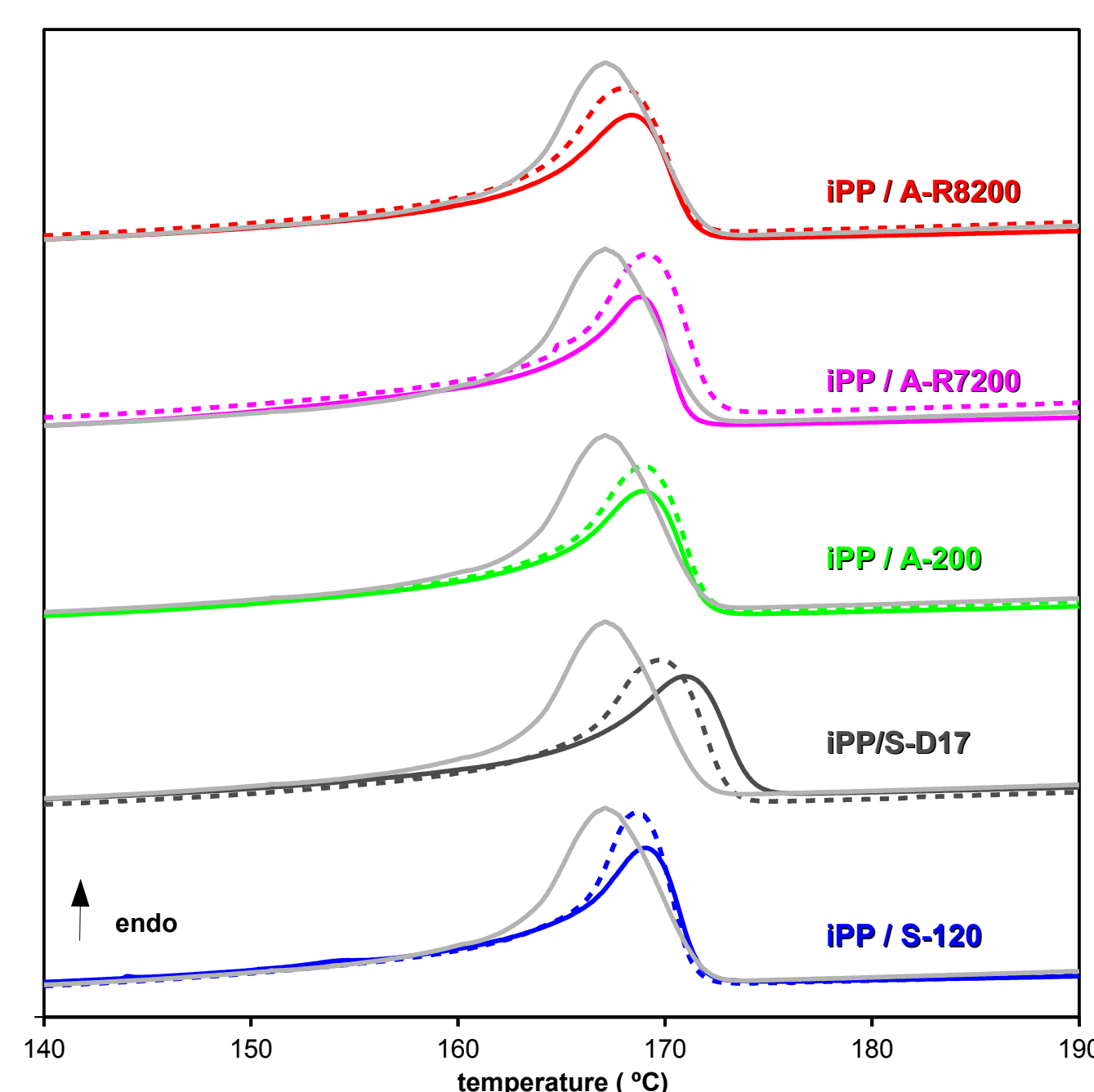
Hydrophobic silicas modified with carbon and hexamethyl-disilazane (S-D17 and A-R8200) contribute to formation of bigger spherulites at all content ratios. Composites containing unmodified hydrophilic silicas, (S-120 and A-200) and methacrylsilane modified (A-R7200) reveal the morphology with small, irregular spherulites due to stronger nucleation effect of particles with relatively polar surfaces.

DSC thermograms



DSC thermograms of first coolings (above) of iPP/silica composites with volume content ratios 96/4 (dotted lines), 92/8 (full lines) and of neat iPP (gray lines).

The increase in the crystallization peak temperature of the iPP matrix with 4% and 8 vol% of silicas was approximately the same except for the composite containing methacryl-silane modified nanosilica probably because of strong nucleation effect.



The crystallization and melting data for selected iPP/silica composites

composite	1 st crystallization				2 nd melting				$\Delta T = T_m - T_c$	
	Peak / °C		$\Delta H / Jg^{-1}$		Peak / °C		$\Delta H / Jg^{-1}$			
	94/6	92/8	94/6	92/8	94/6	92/8	94/6	92/8	94/6	92/8
iPP		122.95		-100.78		167.12		94.70		44.17
IPP/A-200	124.86	125.11	-91.31	-82.08	168.94	168.97	85.53	77.30	44.08	43.86
IPP/A-R7200	125.88	128.65	-96.39	-83.78	169.14	168.8	89.82	80.86	43.26	40.15
IPP/A-R8200	124.09	124.36	-91.11	-80.53	167.96	168.38	85.04	77.05	43.87	44.02
IPP/S-120	126.51	126.85	-89.83	-80.78	168.61	169.02	87.03	81.49	42.10	42.17
IPP/S-D17	125.66	125.88	-89.7	-81.83	169.76	170.99	83.98	77.51	44.10	45.11

DSC thermograms of second heatings (left) of iPP/silica composites with volume content ratios 96/4 (dotted lines), 92/8 (full lines) and of neat iPP (gray lines).

The shifts in peak temperatures of melting are almost independent on the filler type except for composite containing carbon modified microsilica. End temperatures were affected in cases of composite with containing carbon modified microsilica and, in a lesser degree, in that with methacryl-silane modified nanosilica.

Supercooling was observed only in case of carbon-modified microsilica at the highest concentration. It is another indication of its compatibility with iPP.

CONCLUSIONS

- The particles of all silica grades disturbed and transformed well-developed spherulitic morphology of iPP matrix by nucleation and steric hindrance effects.
- In the case of more isotropic particles like silicas the surface character of filler particles and strength of cohesion between them and polymer matrix seems to be more influential than the difference in particles size.
- The differences in the spherulite size between composites with hydrophobic and hydrophilic silica fillers are greater than between composites with microsilica and nanosilica fillers.
- Nanosilica particles and their agglomerates are more cohesive connected with the iPP matrix than microparticles.
- DSC and WAXD showed difference in sensitivity towards the effects surface modification.

MATERIALS AND METHODS

The Moplen HP501L, Basell iPP (melt flow rate [MFR] = 6 g/10 min, $\rho = 0.90 \text{ g/cm}^3$, $M_n = 120,000 \text{ g/mol}$) was used. The silica fillers were produced by Degussa, Germany, filler characteristics are listed in Table 1. Binary iPP/silica composites of volume content ratios 100/0, 98/2, 96/4, 94/6 and 92/8 were prepared in an oil-heated Brabender kneading chamber at 200 °C with a rotor speed of 50 min⁻¹ and were kneaded for 7 min. On homogenization the melt was rapidly transferred to a preheated laboratory press and compression molded into 1-mm thick plates at 220 °C and 100 bar for 14 min and then cooled in the air to room temperature. The wide-angle X-ray diffractograms (WAXD) of 1-mm thick plates were taken on a Philips PW 1820 diffractometer using monochromatic CuK α radiation in the diffraction range of $2\theta = 5-40^\circ$. A degree of crystallinity, $w_{c,x}$ was evaluated by the Ruland method.

Thermal analysis of the samples cut from compression molded plates (about 10 mg), in aluminum pans and sealed was performed on a Perkin Elmer Diamond DSC. The dynamic thermograms of the samples were recorded at heating rate of 5 °C/min in extra pure nitrogen environment. Two heating-cooling cycles were performed by heating the sample from 50 °C to 200 °C, keeping it at that temperature for 5 min and the cooling it back to 50 °C. A Leica light microscope (Model DMLS) with digital camera was used for observation of thin crossed microtomed sections of plates. A maximal anisotropic diameter of spherulites ($d_{i,max}$) was measured on several polarization micrographs of each sample and an average spherulite diameter (d_{sph}) was calculated: $d_{sph} = \sum N_i d_{i,max} / \sum N_i$ where N_i is the number of measured spherulites with the average diameter d_i .