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Thermogravimetric investigations of carbonaceous materials—Syndiotactic polystyrene systems

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Abstract

A system of a syndiotactic polystyrene (s-PS)-carbonaceous material, obtained as a result of syndiotactic polymerisation of styrene in the presence of carbonaceous materials of organic origin of different degree of coalification before and after their ammoxidation, was studied. The initial materials were plum stone waste, brown coal and hard coal. The interactions between the system components were studied by the method of differential scanning calorimetry (DSC). It has been found that the type of the carbonaceous material used determines the thermal effects of the phase transitions in s-PS (detected on thermograms) and the melting point of s-PS. It has been shown that on melting of the syndiotactic polystyrene in the presence of the carbonaceous materials containing a relatively large number of oxide groups, the polymer oxidation reactions occur. This effect does not occur when carbonaceous materials with preliminary ammoxidation are applied.

Keywords: Polystyrene; Fillers enriched in nitrogen; Texture; Differential scanning calorimetry (DSC)

1. Introduction

Carbonaceous materials such as soot, active carbon, cellulose and straw are used as plastic fillers. They can interact with the polymer or be neutral towards it, so they can be active or passive fillers. In general, the use of fillers permits obtaining more stable systems characterised by better mechanical properties as, e.g. stronger resistance to ageing [1]. The systems are obtained by mechanical mixing of the components in a calandria or in an extrusion process. Often dispergation of particular phases, i.e. polymer and filler, does not reach a state required, which means that the plastic obtained does not show target properties. The optimum degree of dispergation can be achieved when the process of polymerisation is conducted in the presence of the properly refined filler [1] or when polymerisation occurs on the active centres anchored on its surface [2–4]. On the processing of such a system the polymer undergoes partial or total melting, which enables the filler to be wetted by it. In thus obtained final product the interaction polymer-filler should be the strongest [5,6].

We used as fillers the carbonaceous materials obtained from the plum stone waste, brown coal and hard coal. The materials differ in the degree of coalification and thus in the number and type of functional groups on their surfaces. The carbonaceous fillers were preliminary subjected to ammoxidation getting a series of materials of characterised by different physical and chemical properties [7–10]. We assumed that all these fillers should exhibit different interactions with the polymer and they should contribute to interesting materials for the production of plastics of different properties, like, e.g. the syndiotactic polystyrene—a new thermoresistant construction thermoplastic.

The type and strength of the interaction can be determined by many methods, usually by thermal analysis (DCS, TG). The interactions between the filler and the polymer are manifested in the thermal effects of the components and affect the temperature at which the mass loss of the components occurs [11–13].

The paper presents the DSC results characterising the systems of the syndiotactic polystyrene—carbonaceous organic materials obtained as a result of syndiotactic polymerisation of

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styrene in the presence of grains of a carbonaceous material. The catalytic system used was $CpTiCl_2(OC_6H_4Cl\text{-p})/MAO$, where Cp = cyclopentadienyl and MAO = methylaluminoxane.

2. Experimental

2.1. Starting materials

The starting raw samples, e.g. waste plum stones, Polish brown coal (lignite) from Konin mine and Polish young coking coal (sub-bituminous) from Sośnica colliery were crushed and sieved to collect the grain fraction ≤0.01 mm for coals and ≤3 mm for plum stones. Both, brown and sub-bituminous coal, were subjected to demineralisation by hydrochloric and hydrofluoric acids, according to the Radmacher and Mohrhauer method [10].

2.2. Preparation of samples

Ammoxidation (N) of carbonaceous materials was carried out using a mixture of ammonia and air at a volume ratio of 1:3 (250/750 cm^3/min) in a flow reactor at 523 K for plum stones and at 573 and 623 K for coals, for 5 h [11–13].

2.3. Elemental analysis

The chemical composition of the samples investigated was determined on an Elementar Vario EL III microanalyser. The apparatus permits determination of the contents of carbon, hydrogen, nitrogen and total content of sulphur and oxygen.

2.4. Polymerisation of styrene

Polymerisation of styrene was conducted according to the procedure described in [1] using 15 ml of toluene, 10 ml of styrene (0.086 mol), 1 ml of a 30% solution of methylaluminoxane (MAO) (5 mmol Al) in toluene (WITCO) and 0.02 mmol of the precursor of the catalyst $CpTiCl_2(OC_6H_4Cl\text{-p})$ dissolved in toluene (0.01 mol solution) and 0.2 g of preliminary refined organic material. Prior to use the carbonaceous material was heated for 4 h at 473 K at $p = 4$ Pa, and then it was cooled to room temperature in the atmosphere of deoxygenated and dry argon. The substrates were used in the following proportions: styrene:Al:Ti = 4300:300:1. The process of polymerisation was conducted for 2 h, and then stopped by addition of methanol with 2% HCl. The solid product obtained was isolated and dried at 363 K in vacuum ($p = 4$ Pa) to a constant mass.

2.5. Differential scanning calorimetry (DSC) analysis

The thermal properties of the polymer/support system were measured on a Setsys TG-DSC 15 Setaram instrument. Samples of about 20 mg were closed in aluminium crucibles with pierced lids. The following temperature program was used: heating range 298–623 K, heating rate 3 K min^{-1}, isothermic phase 3 min in the helium atmosphere.

2.6. Porous structure

The pore structure of the materials investigated was characterised by Sorption apparatus Micrometrics ASAP 2010. Adsorption isotherms were determined by N_2 adsorption at 77 K. Prior to measurement, the samples were outgassed under vacuum 1.33×10^{-4} Pa at 623 K until constant weight and then subjected to measurement of nitrogen adsorption and desorption. Calculation of the micropore volume (V_{micro}), mesopores volume (V_{meso}) and their volume distribution from the nitrogen adsorption isotherms was performed using the BJH method. The values of the surface area were calculated according to the BET method (S_{BET}).

3. Results and discussion

3.1. Characteristic of investigated organic materials

The carbonaceous materials used as fillers were subjected to elemental analysis and textural study; the results are given in Table 1. The surface area of the materials is not much developed and reaches only a few m^2/g. From among the samples studied those obtained from brown coal are characterised by the greatest volumes of micro- and mesopores and surface area. As expected, with increasing degree of coalification of the initial material that is in the series from the plum stones to hard coal the content of carbon increases and the total content of oxygen and sulphur (the main volatile components) decreases. In raw plum stones (P) the total content of oxygen and sulphur reaches 45% of the sample mass. Ammoxidation of the initial materials leads to changes in the contents of carbon—an increase in the plum stone material and a decrease in coals (e.g. BDN and SDN). The observed decrease in the content of hydrogen and total con-

Table 1
Elemental analysis (wt.%) and specific surface area (S_{BET}) carbonaceous materials used as support of $CpTiCl_2(OC_6H_4Cl\text{-p})$

Sample code	C	H	N	(O + S)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	S_{BET} (m^2/g)
P	48.8	6.1	0.1	45.0	–	–	–
BD	62.3	5.4	0.6	31.7	0.008	0.015	6
SD	77.8	5.8	0.9	16.7	0.004	0.008	2
PN_1	72.3	5.0	5.3	17.4	0.001	0.002	1
BDN_1	57.0	3.1	21.6	18.3	0.013	0.025	8
SDN_1	68.4	3.0	12.4	16.2	0.004	0.008	5
PKN_1	78.2	2.4	7.8	11.6	0.065	0.022	123

P, plum stones; B, brown coal; S, sub-bituminous coal; D, material demineralised; N, ammoxidation in lower temperature; K, material carbonized.

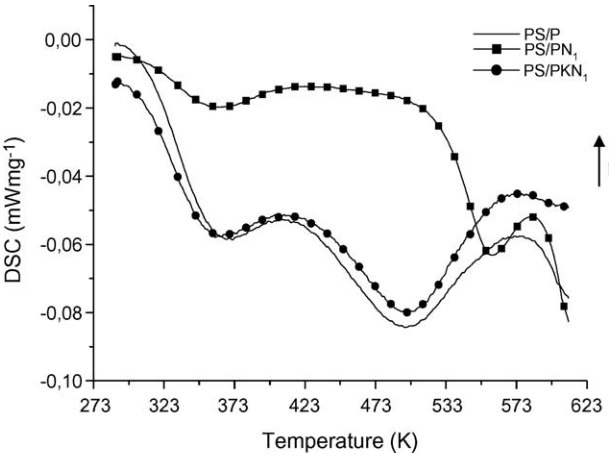

Fig. 1. DSC curves of s-PS/organic material (plum stones) systems.

tent of oxygen and sulphur is a result of the interaction of the modified carbonaceous material surface with the air–nitrogen mixture. The process of ammoxidation leads to an increase in the content of nitrogen in the sample to the highest level in the samples obtained from brown coal (BDN) 21.6 wt.%, and the lowest (e.g. 5.3 wt.%) in the samples obtained from plum stones (PN).

3.2. DSC system s-PS-organic material

The thermograms of the systems made of unmodified organic material and s-PS, presented in Figs. 1–6, show broad peaks of different intensity in three temperature ranges: 323–403, 423–473 and 493–573 K. The first corresponds to the release of the earlier adsorbed water and possibly toluene—used as a solvent and a glass transition of polystyrene.

This peak is observed in the thermograms of all systems and its broadened shape seems to confirm the possibility of overlapping of the above-mentioned effects. The signal in the second temperature range corresponds to the transformation of the zigzag polystyrene into the linear form, while the maximum observed in the third range corresponds to the melting of polystyrene.

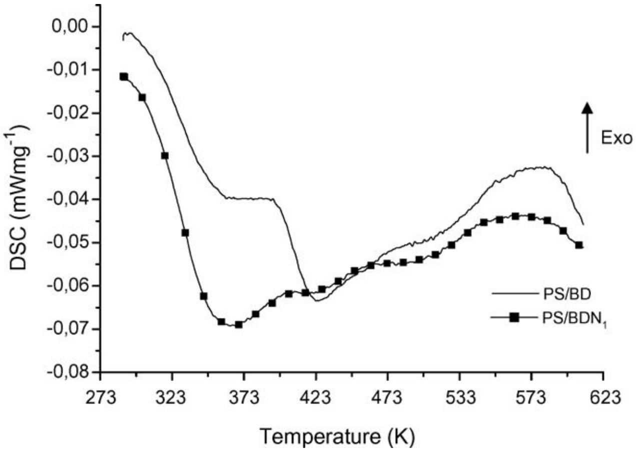

Fig. 2. DSC curves of s-PS/organic material (brown coal) systems.

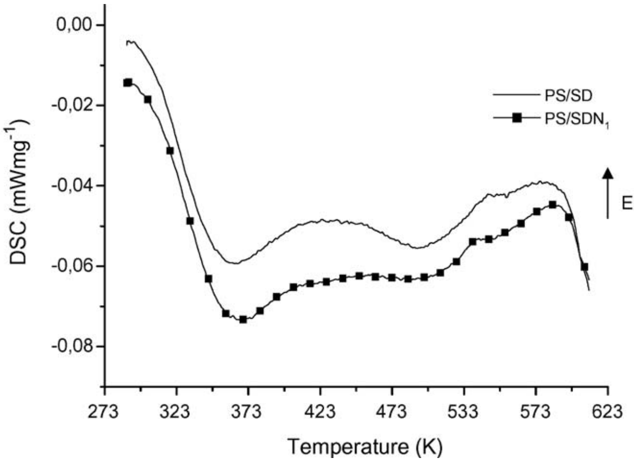

Fig. 3. DSC curves of s-PS/organic material (sub-bituminous coal) systems.

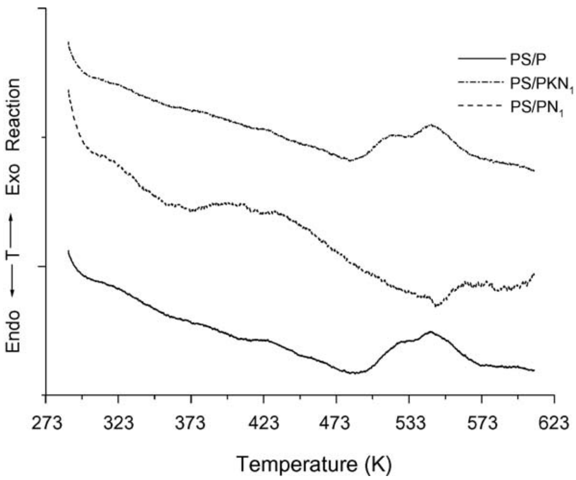

Fig. 4. DTA curves of s-PS/organic material (plum stones) systems.

Ammoxidation of the organic components of the systems studied caused a shift of the peak corresponding to the s-PS melting towards higher temperatures by about 50 K (see Fig. 1).

According to literature data, typical DSC curves of syndiotactic polystyrene s-PS reveal three maxima. The first exothermic

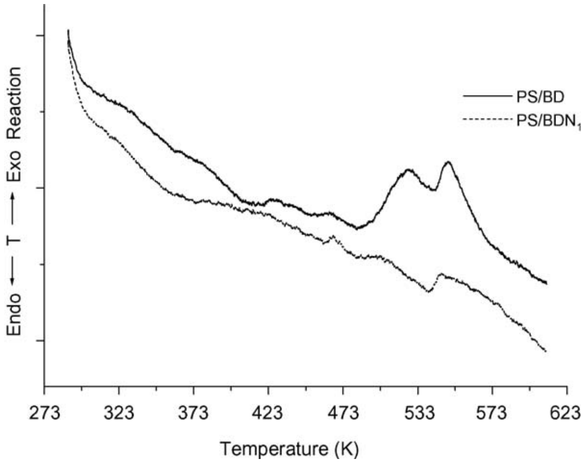

Fig. 5. DTA curves of s-PS/organic material (brown coal) systems.

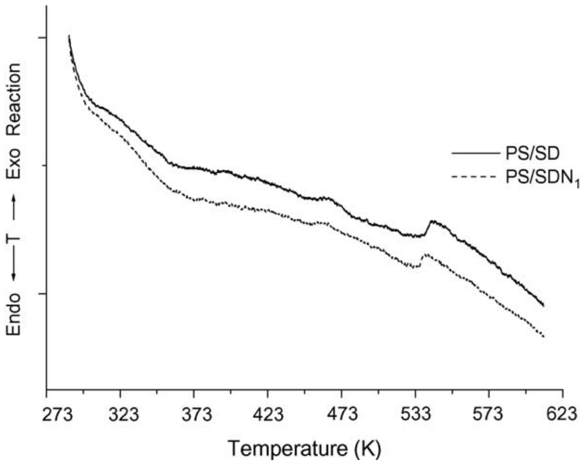

Fig. 6. DTA curves of s-PS/organic material (sub-bituminous coal) systems.

Table 3
The values of the mass loss (wt.%) of investigated systems

Sample code	Mass loss (wt.%)			
	353–373 K	423 K	473–493 K	533 K
PS-P	5.3	–	11.3	–
PS-PN$_1$	3.4	–	–	12.2
PS-PKN$_1$	3.7	–	7.4	–
PS-BD	2.5	7.8	–	–
PS-BDN$_1$	5.0	4.2		
PS-SD	9.3	–	5.5	–
PS-SDN$_1$	5.5	–	3.6	–

P, plum stones; B, brown coal; S, sub-bituminous coal; D, material demineralised; N, ammoxidation in lower temperature, K, material carbonized.

one at about 373 K is assigned to the glass transition (T_g), the second exothermic one in the range 423–453 K is assigned to crystallisation of amorphous forms of s-PS (at about 453 K there is a transition between the crystalline helical s-PS to the crystalline zigzag planar form) and the third endothermic peak with a maximum between 523 and 543 K—assigned to the melting of s-PS. The exact position of the latter peak depends on the degree of defects in its chain [4,5,14,15].

In the DSC curves of the systems we studied the above thermal effects appeared as relatively broad signals, which suggests a diversity of interactions of the s-PS polymer with the surface of the carbonaceous materials analysed. The signals were the most regular and narrow for the systems with the materials of the highest degree of coalification (SD, SDN), which meant that their surface was the most homogeneous.

As follows from the thermogravimetric study (TG), the broad endothermic signals in the range 323–403 K, in the curves of all the systems studied, are accompanied with a mass loss (see Tables 2 and 3). It is a consequence of the overlapping of the thermal effects related to the release of the adsorbed water and toluene used as a solvent and the effect of the glass transition in s-PS.

The DSC curves of the systems with modified and unmodified brown (BD, BDN) and hard coal (SD, SDN) as fillers, in the range characteristic of s-PS crystallisation and the phase transitions between its crystalline forms show only the signals assigned to the phase transitions. In contrast, the DSC curves of the systems with plum stone filler (P, PN, PKN) show only the signals assigned to the crystallisation of the amorphous s-PS. The differences are caused by the different degree of coalification of the fillers.

The thermograms of all systems above 473 K show clearly endothermic signals assigned to the melting of s-PS, while the thermograms of the systems with BD and P as fillers reveal additionally a relatively strong exothermic signal. It can be assigned neither to s-PS as this polymer shows no thermal effects in this range nor to the carbonaceous materials as they also show no signals in this range [7,8]. Taking into regard that the exothermic effects are observed only for the systems containing the filler not modified with nitrogen and characterised by the greatest content of oxygen and sulphur (over 30 wt.%, see Table 1), that is the main volatile components released in temperatures above 473 K, it is reasonable to suppose that this effect is a result of the reactions of the melting polymer with the functional groups on the surface of the carbonaceous materials studied. Such reactions can be effective only when the melting polymer begins wetting the surface of the fillers ensuring a better contact between the polymer and the functional groups on the filler surface. The DSC measurements were performed in the helium atmosphere so the interferences from the air oxygen can be excluded. In

Table 2
Characteristic temperatures (K) evaluated from DSC data

Sample code	T_{max}	T_{onset}	ΔH (μV s/mg)	T_{max}	T_{onset}	ΔH (μVs/mg)	T_{max}	T_{onset}	ΔH (μVs/mg)
PS-P	373.7	329.8	3.1	486.0	436.9	18.8	539.1	529.2	−1.6
PS-PN$_1$	372.4	322.3	7.6	–	–	–	543.9	537.4	0.8
PS-PKN$_1$	408.1	330.6	2.8	482.8	462.2	8.3	539.0	528.4	−3.4
PS-BD	408.1	380.2	12.5	489.6	467.8	3.8	533.9	525.8	1.7
PS-BDN$_1$	359.4	324.7	20.9	–	–	–	532.4	519.7	0.9
PS-SD	365.3	321.7	9.3	–	–	–	526.0	483.5	6.7
PS-SDN$_1$	407.4	322.6	21.7	–	–	–	–	–	–
BD-toluene	348.6	316.3	1.3	467.2	394.4	33.6	–	–	–
PS-toluene	–	–	–	499.9	455.1	15.7	–	–	–
PN$_1$-toluene	381.9	315.1	0.5	478.9	456.8	7.9	519.1	513.5	0.5

P, plum stones; B, brown coal; S, sub-bituminous coal; D, material demineralised; N, ammoxidation in lower temperature; K, material carbonized.

the other systems the oxidation reaction does not take place in the above conditions, which suggests that the groups containing oxygen are within the grains and are not available even to the molten polymer or are not sufficiently active in the oxidation reaction. The interactions between the molten polymer and the oxide groups on the filler surface should be taken into account in production of composites or nanocomposites whose components contain active oxide groups. The interactions can have significant effect on the yield of the product obtained. The results have shown that ammoxidation of the fillers can eliminate the active oxide groups from the surface of the carbonaceous materials studied and used as fillers. The melting points of s-PS appearing in the DSC curves of the systems s-PS/SD, s-PS/SDN and s-PS/P, at 525 and 526 K are typical of the polymers of the chain structure and high density of defects. They are obtained in the presence of the catalysts with no substituted cyclopentadienyl groups as ligands [16,17]. So low melting points can also be a result of the s-PS interactions with the fillers (SD, SDN and P). The melting points of s-PS observed for the systems PS/BD, PS/BDN and PS/PN are 535, 531 and 541 K, respectively. The differences are clearly a result of the type of the carbonaceous material used and its effect on the polymer.

According to literature data, the relatively high melting points of s-PS are a result of the presence of small defects in the structure of the polymer chain [16] and a specially designed program of thermal treatment of s-PS samples can bring the appearance of the melting point signal on DCS curves even above 563 K.

It is assumed that the active centres of the syndiotactic polymerisation of polystyrene are cyclopentadienyl titanium cations of the general formula $[LTiR]^+$, where L = the cyclopentadienyl ring and R = alkyl or growing polymer chain. Syndiotactic polystyrene of a relatively low density of chain defects is obtained over the catalysts containing substituents in the cyclopentadienyl ring, i.e. penthamethylcyclopentadienyl ring or indenyl ring [16,17]. The steric hindrances caused by these substituents in the vicinity of the polymerisation centre inhibit the non-stereo-regular propagation. If the above process was to determine the melting point of the obtained s-PS systems, then the cyclopentadienyl ring of the $[CpTiR]^+$ cation would be adsorbed by the surface centres of the carbonaceous materials studied, which would lead to the appearance of steric hindrances.

All the DSC measurements of the samples studied were carried out using the same procedure. As the appearance of the s-PS melting point signals in high temperatures did not depend on the density of defects in the s-PS chains, it should be assumed that the structure of the carbonaceous material in the systems studied determines the way the energy is provided from external sources to s-PS, leading to similar results as the application of the special thermal treatment program in the DSC measurements.

4. Conclusions

The carbonaceous materials studied do not show much developed surface area, which is of an order of a few m^2/g, or inner pore surface area. The highest volume of the micro- and mesopores and the highest surface area have been found for the samples obtained from brown coal. The most striking result is that the introduction of organic materials with different degree of coalification into polymerisation process leads to differentiation in the value of melting temperature of the samples of syndiotactic polystyrene obtained (s-PS).

Ammoxidation of the organic carbonaceous material used as filler in the polymer systems studied has been found to lead to a shift of the s-PS melting point signal towards higher temperatures. Moreover, this process can eliminate the active oxide groups from the surface of the carbonaceous materials studied, which may significantly affect the yield of obtaining syndiotactic polystyrene.

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