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THERMAL PROPERTIES OF BIOCOMPOSITES

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Thermal properties of new biocomposites prepared from modified starch matrix reinforced with natural vegetable fibres were studied. DSC and TG methods were applied to study thermal behaviour of biocomposites. Biocomposites were obtained in the laboratory twin-screw extruder. Two kinds of natural fibres were used, i.e. flax and cellulose in the amount of 0–40 mass%. DSC curves of biocomposites reveal glass transition temperature, attributed to the amorphous nature of the plasticized starch matrix. In general, incorporating natural fibres into modified starch matrix leads to an increase in glass transition temperature.

Thermal degradation of modified starch matrix and cellulose reinforced biocomposites proceeds in three steps, whereas the degradation process of flax reinforced biocomposites occurs in two steps. For unreinforced matrix as well as for all biocomposites, regardless of type and amount of reinforcement, the major mass loss is observed at the temperature above 300°C. The increase in thermal stability with introduction of natural fibre is observed for both flax and cellulose reinforced biocomposites.

Keywords: *biocomposites, DSC, glass transition, thermal degradation, thermal stability, TG*

Introduction

Biocomposites are composite materials composed of biodegradable matrix and biodegradable natural fibres as reinforcement [1–4]. The development of biocomposites has attracted great interest due to their environmental benefit (i.e. biodegradability) and improved performance. Usually the improvement in mechanical properties with inclusion of natural fibres is reported.

Biodegradable matrix include polymers obtained from renewable resources like agro-polymers (e.g. polysaccharides) and aliphatic polyesters (e.g. polyhydroxyalkanoates, polylactic acid) as well as biodegradable polymers synthesised by the petrochemical process (e.g. polycaprolactone). Plant-based fibres like flax, jute, sisal and kenaf have been frequently used [1].

Most of studies concern biodegradable matrix based on aliphatic polyesters (PHB and its copolymers) reinforced with various vegetable fillers [1, 2, 4, 5]. However, poor mechanical properties has been reported [1]. Another matrix commonly used is so-called thermoplastic starch matrix, i.e. physically modified starch, developed in 1987 by Stepto and Tomka [3, 6–11]. Under the action of temperature and shear, starch can be processed into thermoplastic starch [11]. The problem in the use of thermoplastic starch lies in its susceptibilty to water and poor mechanical properties.

Studies of biocomposites have been usually focused on their mechanical properties, less attention is given on the thermal stability. Biocomposites, made using lignocellulosic materials as the reinforcing filler, were examined, in order to measure thermal stability and thermal expansion as a function of the filler loading [12]. Studies on mechanical and thermal properties of wood flour and biodegradable matrix based on polycaprolactone and polybutylene succinate-butylene carbonate composites have been reported by Lee and Ohkita [13]. Thermal properties of agro-flour (i.e. rice husk and wood flour) filled biodegradable polybutylene succinate biocomposites were studied by DSC, TG and DMTA methods [14, 15].

The aim of the work was to study thermal behaviour of new biocomposites prepared from chemically modified starch (hydroxypropyl starch) reinforced with natural vegetable fibres. Natural fibres were used in the amount of 0–40 mass%. The effect of kind and amount of natural reinforcement on thermal properties of biocomposites was studied.

Experimental

Materials

Biocomposites were built from etherified starch derivative, i.e. hydroxypropyl starch and plant-based natural fibres. Hydroxypropyl starch (National Starch and Chemical) was used as biodegradable thermoplastic matrix. Two kinds of natural fibres: flax and cellulose were applied as reinforcement fillers. Flax fibres were from Experimental Farm (Stęszew, Po-

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land). Fibres were cut in the SM 100 cutting mill (Retsch) using sieves with diameter 0.25 mm. Cellulose obtained from native, highly bleached beech tree in the form of powder of about 20 μm diameter was kindly supplied by Mikro-Technik GmbH. The biocomposites were prepared in a ThermoHaake PTW 16/245D twin extruder. The extrusion conditions were: temperature profile: 65/80/90/100/105°C; screw speed: 70 rpm. During extrusion process 20% glycerol solution was added as a plasticizer agent.

Thermoanalytical measurements

DSC measurements were carried out using a PerkinElmer DSC 7 analyser. Samples of ca. 20 mg were heated from 30 to 200°C at a rate of 10 K min^{-1}.

Thermogravimetric analysis (TG) was performed on a Netzsch TG 209 thermal analyser, operating in a dynamic mode at a heating rate of 10 K min^{-1}. The conditions were: sample mass, ca. 5 mg; atmosphere, argon; open α-Al_2O_3 pan.

Results and discussion

Figure 1 shows the examples of DSC curves of unreinforced matrix (curve 1), as well as biocomposite reinforced with 20 mass% vegetable filler, i.e. flax (curve 2) and beech cellulose (curve 3). Results of DSC measurements are summarized in Table 1. The modified starch exhibits glass transition T_g at about 69.1°C, indicating the amorphous nature of plasticized starch matrix. By incorporating natural fiber fillers into modified starch matrix, the T_g transition for starch rich phase shifts to higher temperature from 69 to 118°C. In general, the similar behaviour is observed for both types of fibers. This evolution might be attributed to strong fibre-matrix interactions between the two carbohydrates [3, 16]. Such interactions decrease starch mobility and consequently increase the matrix glass transition. However, for biocomposites with 40 mass% fiber content (samples 6 and 11) the decrease in T_g value is observed which may be explained by the poor adhesion between matrix and fiber for the biocomposites with high filler content. The increase in T_g with the increase of filler content is more pronounced for flax reinforced biocomposites. The T_g value increases from 69 to 112 and to 76°C for flax reinforced and cellulose reinforced composites, respectively, when fiber content ranges from 0 to 10 mass%. It may be explained by the higher flax fiber length (approx. 0.25 mm) in comparison with cellulose fiber one (approx. 20 μm) used in this work. It was reported by Avérous *et al.* [3] for the plasticized starch – leafwood cellulose fibres composites that the plasticized starch glass relaxation temperature increases with fiber length.

Table 1 Summary of DSC results

Sample	Type of fibres	Filler content/ mass%	Glass transition temperature T_g/°C
1	0	0	69.1
2	Flax	5	94.1
3	Flax	10	112.2
4	Flax	20	108.7
5	Flax	30	118.3
6	Flax	40	105.1
7	Cellulose	5	66.5
8	Cellulose	10	75.9
9	Cellulose	20	82.2
10	Cellulose	30	92.5
11	Cellulose	40	66.8

DTG curves of modifed starch and 20 mass% flax and cellulose reinforced biocomposites are given in Figs 2, 3 and 4, respectively. Thermal degradation of modified starch matrix proceeds in three steps. The first step occurs at about 250°C; the second peak is at 317°C and the third one is above 500°C. The similar behaviour is observed for cellulose reinforced

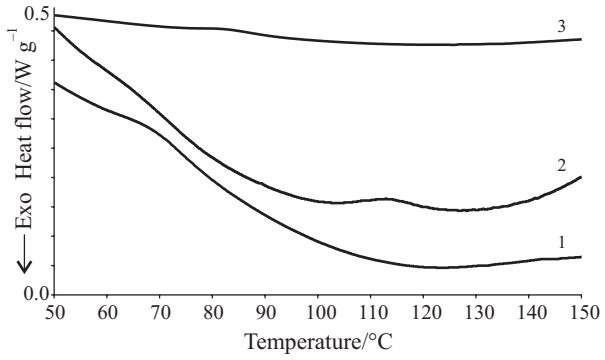

Fig. 1 Examples of DSC curves of biocomposites; 1 – unreinforced matrix (modified starch), 2 – flax reinforced biocomposite (20 mass% of fibre content), 3 – cellulose reinforced (20 mass% of fibre content)

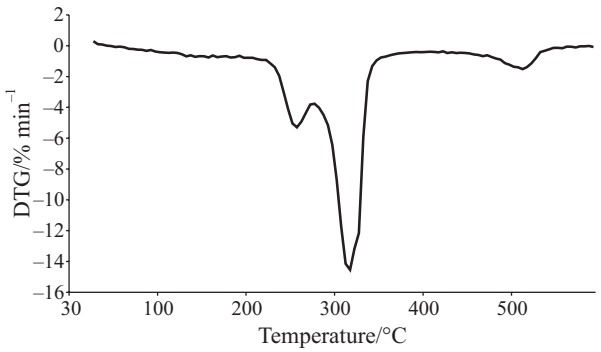

Fig. 2 DTG curve of biodegradable matrix (modified starch)

Table 2 Results of thermogravimetric analysis of biocomposites

Sample	Type of fibres	Filler content/ mass%	$T_{5\%}$/ °C	$T_{10\%}$/ °C	DTG-T_p/°C 1 peak	2 peak	3 peak
1	0	0	168.0	227.6	257.4	317.2	510.9
2	Flax	5	188.1	252.7	–	307.8	506.1
3	Flax	10	219.9	265.9	–	307.0	483.9
4	Flax	20	210.9	260.5	–	300.4	469.0
5	Flax	30	195.9	255.5	–	305.3	503.7
6	Flax	40	203.0	252.6	–	302.4	461.3
7	Cellulose	5	175.9	235.4	255.3	315.2	543.4
8	Cellulose	10	191.3	250.8	260.7	320.5	538.9
9	Cellulose	20	196.6	246.2	256.1	325.8	544.1
10	Cellulose	30	202.9	242.7	242.7	322.2	500.9
11	Cellulose	40	174.7	224.4	234.3	323.8	512.3

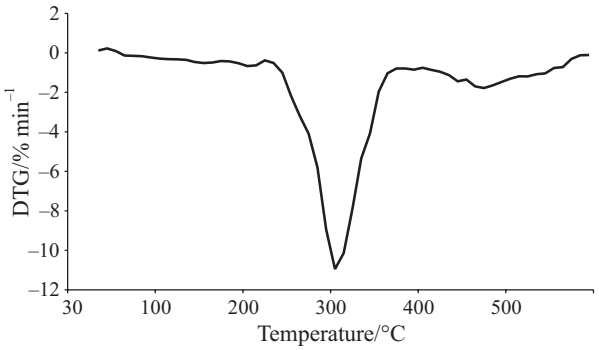

Fig. 3 DTG curve of flax reinforced biocomposite (20 mass% of fibre content)

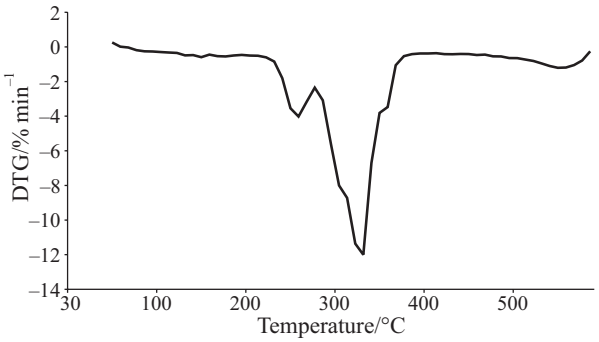

Fig. 4 DTG curve of cellulose reinforced biocomposite (20 mass% of fibre content)

biocomposites. DTG curves of flax reinforced biocomposites do not reveal the first peak (cf. Fig. 3]. However, the major mass loss, starts at the temperature above 300°C for unreinforced matrix as well as for all studied biocomposites, regardless of type of filler. In general, dehydration and depolymerization have been reported as the two main processes associated with the degradation mechanism of polysaccharides [17–19].

The results of thermogravimetric analysis in a nitrogen atmosphere are collected in Table 2. Thermal stability of biocomposites was determined by the temperature at which 5% mass loss occurred. It can be seen that the decomposition of modified starch matrix begins at 168°C ($T_{5\%}$), whereas the biocomposites start to decompose at a higher temperature. The increase in thermal stability with introduction of natural fibre is observed for both flax and cellulose reinforced biocomposites.

DSC and TG results indicate that the addition of natural fibers improves thermal behaviour of biocomposites.

Conclusions

DSC curves of biocomposites reveal glass transition temperature, attributed to the amorphous nature of the plasticized starch matrix. In general, incorporating natural fibres into modified starch matrix leads to an increase in glass transition temperature.

Thermal degradation of modified starch matrix and cellulose reinforced biocomposites proceeds in three steps, whereas the degradation process of flax reinforced biocomposites occurs in two steps. For unreinforced matrix as well as for all biocomposites, regardless of type and amount of reinforcement, the major mass loss is observed at the temperature above 300°C. The increase in thermal stability with introduction of natural fibre is observed for both flax and cellulose reinforced biocomposites.

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References

1 M. Wollerdorfer and H. Bader, Ind. Crops Prod., 8 (1998) 105.
2 U. Riedel and J. Nickel, Angew. Makromol. Chem., 272 (1999) 34.
3 L. Avérous, C. Fringant and L. Moro, Polymer, 42 (2001) 6565.
4 K. Van de Velde and P. Kiekens, Polymer Testing, 21 (2002) 433.
5 A. K. Mohanty, M. A. Khan and G. Hinrichsen, Comp. Sci. Technol., 60 (2000) 1115.
6 R. F. T. Stepto and I. Tomka, Chimia, 41 (1987) 76.
7 A. Dufresne and M. R. Vignon, Macromolecules, 31 (1998) 2693.
8 A. A. S. Curvelo, A. J. F. Carvalho and J. A. M. Agnelli, Carbohydr. Polym., 45 (2001) 183.
9 A. J. F. Carvalho, M. D. Zambon, A. A. S. Curvelo and A. Giandini, Polym. Degrad. Stab., 79 (2003) 133.
10 L. Avérous and N. Boquillon, Carbohydr. Polym., 56 (2004) 111.
11 X. Ma, Y. Yu and J. F. Kennedy, Carbohydr. Polym., 62 (2005) 19.
12 H.-S. Yang, M. P. Wolcott, H.-S. Kim and H.-J. Kim, J. Therm. Anal. Cal., 82 (2005) 157.
13 L. Yu, K. Dean and L. Li, Prog. Polym. Sci., 31 (2006) 576.
14 S. Lee and T. Ohkita, J. Appl. Polym. Sci., 90 (2003) 1900.
15 H.-S. Kim, H.-S. Yang, H.-J. Kim, B.-J. Lee and T.-S. Hwang, J. Therm. Anal. Cal., 81 (2005) 299.
16 Y. Lu, L. Weng and X. Cao, Carbohydr. Polym., 63 (2006) 198.
17 P. Aggarval, D. Dollimore and K. Heon, J. Thermal Anal., 50 (1997) 7.
18 R. M. D. Soares, A. M. F. Lima, R. V. B. Oliveira, A. T. N. Pires and V. Soldi, Polym. Degrad. Stab., 90 (2005) 449.
19 E. Rudnik, G. Matuschek, N. Milanov and A. Kettrup, J. Therm. Anal. Cal., 85 (2006) 267.

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