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Research paper

The Influence of Conditions of Secondary Propylene Recycling in the Presence of Vegetable Fillers on Thermal Properties of Polymer Composites

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Abstract

This article discusses the influence of conditions of secondary polypropylene recycling in the presence of vegetable fillers on thermal properties of polymer composites. Secondary polypropylene was recycled by the following methods: extrusion using two-screw extruder, agitation in mixing chamber of laboratory station (plastograph), die casting. Polymer composites on the basis of secondary polypropylene in the presence of vegetable fillers (wood dust, rice hulls, buckwheat hulls, and chaff) were produced by extrusion. Thermal properties of polymer composites were determined by thermogravimetric analysis and differential scanning calorimetry. It is established that recycling of secondary polypropylene by various methods does not change melting and crystallization points of polymer phase but is accompanied with decrease in melting enthalpy (by 9-11%) and crystallinity (by 5.6-6.5 %). The polypropylene samples obtained by recycling are characterized by lower thermal stability in air in comparison with initial polypropylene. Addition of vegetable filler to polymer composite on the basis of secondary polypropylene significantly decreases (by 1.13-1.48 times) melting enthalpy and crystallization of polymer phase. The compounds are characterized by relatively high thermal stability: their initial destruction points are close to parameters of initial polymer.

Keywords: *secondary polypropylene, vegetable fillers, extrusion, die casting, crystallinity, thermogravimetric analysis, differential scanning calorimetry.*

1. Introduction

Global production of polypropylene (PP) is more than 20% of total amount of synthetic polymers which determines appropriate portion of all available synthetic polymer materials in domestic solid wastes [1, 2]. One possible approach to decrease the amount of wastes comprised of used polymer materials on the basis of PP is secondary recycling by means of production of polymer composites, in particular, wood polymer composites [2-5].

It is known that addition of filler to polymer significantly changes physicochemical and mechanical properties of polymer composite materials [6-8]. This is related mainly with the change in mobility of macromolecules in boundary layers, influence of filler surface on interaction with polymer [6, 7]. The presence of filler also exerts significant influence on behavior of polymer composites at higher temperatures. Most processing methods of thermal plastics, including PP, with conversion into products (die casting, extrusion, rolling, pressing) involve heating, melting or transfer into plastic state of polymer.

In addition, at higher temperatures in filled polymers there occur substantial stresses due to significant difference between thermal expansion coefficients of polymer binder and fillers, which exerts its influence on behavior of polymer at high temperatures [9, 10].

Thus, this work is aimed at study of influence of conditions of secondary PP recycling in the presence of vegetable fillers on thermal properties of polymer composites.

2. Methods

Samples of secondary PP were used as polymer binder in the form of milled off-grade material produced by die casting.

Wood dust, rice hulls, buckwheat hulls and chaff were used as natural vegetable fillers. Content of natural vegetable filler was 10 weight portions per 100 weight portions of PP.

The formulated problem was solved by variation of secondary PP recycling: firstly, extrusion using a Haake Polylab OS two-screw extruder, screw diameter: 16 mm, screw length: L/D 40, temperature of working areas: from 180 to 190°C, screw rotation rate: 35 rpm; secondly, mixing in chamber of laboratory station, Plastograph EC (Brabender), at 180°C, rotor rotation rate: 30 rpm, during 15 min at 200 N; thirdly, die casting using a Babyplast 6/10P injection molding machine with the following zonal temperatures: H_1 235°C, H_2 230°C, H_3 220°C, injection pressure: 30 bar, injection rate: 30%, clamping force: 35 bar. Polymer composites on the basis of secondary PP in the presence of vegetable fillers were produced by extrusion.

The polymer composites were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The samples were analyzed under the following conditions: TGA: 25-600°C; dynamic mode: heating rate 5 deg/min; medium: air; TGA-DSC (Mettler Toledo, Switzerland), DSC: 40-200°C; dynamic mode: heating/cooling rate 10 deg/min; medium: air; DSC-1 (Mettler Toledo, Switzerland).

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Polymer crystallinity χ was calculated as follows: $\chi = (\Delta H_i/\Delta H_o) \times 100\%$, where ΔH_i was the specific heat of melting in terms of polymer content (i) in sample; $\Delta H_o = -147$ J/g was the specific melting heat of totally crystalline; the polymer content (i) in the considered samples was the weight portion of product decomposed at heating to 600 °C.

3. Results and Discussion

While interpreting DSC analyses of secondary PP, it has been established that irrespective of recycling method the polymer samples are characterized by close melting points T_{melt} (166.0–170.2°C) and crystallization points T_{cryst} (116.0–116.8) (Table 1). The mentioned temperatures are close to appropriate values for initial secondary PP (T_{melt} = 168.8°C; T_{cryst} = 116.7°C). The sample obtained after recycling in plastograph chamber has lower melting point (166.0°C) in comparison with the other ones. At the same time the melting enthalpy ΔH_{melt} of PP samples after recycling by various methods is sufficiently (by 8-10 J/g) lower in comparison with initial polymer, whereas the crystallization enthalpy ΔH_{cryst} varies to a lower extent.

Table 1: DSC analysis of secondary PP produced by various methods

Secondary PP	T_{melt}, °C	ΔH_{melt}, J/g	T_{cryst}, °C	ΔH_{cryst}, J/g	χ, %
Initial	168.8	-90.2	116.7	106.7	62.5
Die casting	170.2	-82.1	116.0	97.5	56.9
Extrusion	167.8	-80.4	116.8	105.3	56.2
Mixing in plastograph chamber	166.0	-80.4	116.2	102.1	56.0

Melting enthalpy is related with such parameter as polymer crystallinity χ. It follows from Table 1 that recycling of secondary PP by various methods is accompanied by decrease in polymer crystallinity by 5.6-6.5% in comparison with initial PP. At the same time the crystallinity of secondary PP actually does not depend on recycling method.

The obtained results agree with TGA analyses according to which the melting point of PP after recycling by extrusion and die casting does not change and is the same as for the initial polymer: 173°C (Table 2). After recycling in plastograph the melting point T_{melt} slightly decreases to 171°C. The PP melting enthalpy noticeably decreases, herewith, significant decrease in ΔH_{melt} (by ~38%) occurs after recycling by die casting, whereas after extrusion ΔH_{melt} varies not so significantly.

It has been established that after recycling by various methods the samples of secondary PP are characterized by lower thermal stability in air in comparison with initial PP. Destruction of samples starts at lower temperatures (T_{ini} = 211–227°C), whereas for initial PP the initial temperature of decomposition is 235°C (Table 2). Similar dependences are observed for the temperature when the weight decreases by 1% (T_1) and 5% (T_5).

Table 2: TGA analysis of secondary PP produced by various methods

Secondary PP	$T_{ini.}$, °C	T_1, °C	T_5, °C	Remainder, % at 400°C	Remainder, % at 600°C	T_{melt}, °C	ΔH_{melt}, J/g
Initial	235	254	269	4.54	1.79	173	-39
Mixing in plastograph chamber	211	243	262	5.35	2.35	171	-27
Die casting	225	244	260	5.76	1.81	173	-24
Extrusion	227	249	264	6.12	2.65	173	-37

It should be mentioned that the weight of remainder after heating to 400 and 600°C slightly decreases in comparison with initial secondary PP (Table 2). The latter fact can indirectly indicate at existence of thermally stable impurities in recycled products, probably products of oxidation or cross-linking of macromolecules.

As follows from Table 3, addition of vegetable filler into secondary PP does not change significantly melting and crystallization points of polymer phase. These variables for compounds with various fillers are in sufficiently narrow range (T_{melt} = 166.5–169.5°C; T_{cryst} = 116.0–117.2°C) and close to similar variables for nonfilled secondary PP. In addition, filler exerts significant influence on enthalpy of melting and crystallization of polymer phase. Addition of 10 weight portions of filler to polymer leads to noticeable decrease in melting enthalpy (by 11–29 J/g) and crystallization enthalpy (by 12–35 J/g) of polymer (Table 3). The highest variation of ΔH_{melt} and ΔH_{cryst} (by 1.48 times) is observed for composites with rice hulls, the lowest (by 1.13 times) – for compounds with chaff. It should be mentioned that ΔH_{melt} and ΔH_{cryst} for the mentioned composites with regard to initial secondary PP vary by one and the same quantity. The observed variations of enthalpy can be related both with the decrease in portion of polymer phase in the composite and with the decrease in PP crystallinity stipulated by the influence of filler and recycling conditions of polymer (extrusion).

Table 3: DSC analysis of composites on the basis of secondary PP in the presence of natural vegetable fillers produced by extrusion. Filler content is 10 weight portions per 100 weight portions of PP

Sample	T_{melt}, °C	ΔH_{melt}, J/g	T_{cryst}, °C	ΔH_{cryst}, J/g
Secondary PP, initial	168.8	-90.2	116.7	106.7
Secondary PP+rice hulls	167.5	-61.1	117.0	71.9
Secondary PP+chaff	169.5	-79.5	116.0	94.3
Secondary PP+wood dust	166.5	-73.2	117.2	92.7
Secondary PP+buckwheat hulls	169.3	-77.6	117.0	94.4

The considered composites on the basis of secondary PP and vegetable fillers are characterized by sufficiently high initial temperatures of decomposition T_{ini}: 230–238°C (Table 4). It should be mentioned that the mentioned values are close to T_{ini} of initial PP (235°C) but significantly higher than those of vegetable fillers added to the composites. Thus, the added rice hulls are characterized by low T_{ini} (Table 4): decrease in weight of the product starts already at temperatures above 26°C (Table 4). Noticeable (by ~4%) weight decrease upon heating to 100°C indicates at existence of sufficiently high amount of volatiles in the filler. From a practical standpoint, it is important that the initial temperature of decomposition T_{ini} for the considered compounds on the basis of secondary PP is noticeably higher (by 58–66°C) than the polymer melting point, thus enabling its consistent recycling in melt without decomposition.

Moreover, filler addition to polymer results in noticeable (by several time) increase in remainder portion after heating: to 400°C (corresponds to termination of polymer decomposition) – from 4.5 to 8.5–13.7%; to 600°C (characteristic for existence of inorganic impurities in the product) – from 1.8 to 2.9–7.6% (Table 4). The obtained results should be related with existence of more thermally stable compounds in vegetable filler in comparison with polymer (including inorganic impurities). The most significant increase in the remainder weight after heating to 400 and 600°C (by 3.0 and 4.2 times, respectively) was observed for the composite with rice hulls, the minimum increase in the remainder weight was for the compound with wood dust (by 1.9 and 1.6 times, respectively).

Table 4: TGA analysis of composites on the basis of secondary PP in the presence of natural vegetable fillers produced by extrusion. Filler content is 10 weight portions per 100 weight portions of PP

Sample	$T_{ini.}$, °C	T_1, °C	T_5, °C	Remainder, % at 400°C	Remainder, % at 600°C	T_{melt}, °C	ΔH_{melt}, J/g
Secondary PP, initial	235	254	269	4.54	1.79	173	-39
Secondary PP+rice hulls	238	251	265	13.69	7.57	172	-17

Secondary PP+chaff	230	250	266	8.98	5.36	172	-20
Secondary PP+wood dust	236	254	270	8.54	2.85	171	-13
Secondary PP+buckwheat hulls	235	250	265	9.19	3.24	172	-30
Rice hulls	172	193	208	27.9	17.2	-	-

Therefore, addition of natural vegetable fillers to PP matrix in amount of not more than 10 weight portions per 100 weight portions of polymer exerts moderate influence on thermal properties of compounds and significantly increases the initial temperature of their decomposition which is of great practical importance.

4. Conclusions

Thus, recycling of secondary PP by various methods (mixing in chamber of laboratory station (plastograph), extrusion, die casting) does not change melting and crystallization points of polymer phase but is accompanied with the decrease in melting enthalpy (by 9-11%) and crystallinity (by 5.6-6.5 %). The PP samples obtained by recycling are characterized by lower thermal stability in air in comparison with initial PP. Addition of vegetable filler to polymer composite on the basis of secondary PP significantly decreases (by 1.13-1.48 times) melting enthalpy and crystallization of polymer phase. The compounds are characterized by relatively high thermal stability: their initial destruction points are close to parameters of initial polymer. Addition of filler to polymer is accompanied with significant (by several times) increase in the portion of remainder after heating to 400 and 600°C, which should be interrelated with the existence of more stable compounds in comparison with polymer, including inorganic impurities.

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