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THERMAL DEGRADATION OF PLASTICS COMPOUNDED WITH PETROLEUM-DERIVED BITUMENS

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Abstract

Thermal analysis-based preparation of blends of selected polymer wastes with pyrolysis oil was studied and results are presented. Selected thermomechanical methods were evaluated as regards the determination of property data of the resulting products. When pyrolysis oil was used in amounts ≥5mass%, homogeneous blends could be prepared with PE and PET wastes; the blends were found to be processible by compression molding or injection molding.

Blends prepared from waste PVC and pyrolysis oil were brittle and hard.

The following properties could be determinated for the thermal products: ring-and-ball softening point, Vicat softening point, melt flow index, and impact strength.

Keywords: polymer wastes, pyrolysis oil, thermomechanical methods

Introduction

Plastic wastes pose a considerable household and economic problem both in highly industrialized and in the developing countries [1]. So far numerous processes have been developed for material, raw material and energy reuse of plastic wastes as a secondary raw material. The greatest hopes are placed in thermal methods for the raw material type recycling of plastic wastes, involving desctructive conversion of the polymers contained therein into benign low-molecular-weight substances that can be used to make fluid fuels, coke or chemical feedstocks. Since thermal recycling is virtually applicable to any kind of plastics, regardless of the type of polymer applied and fillers and additives incorporated, and also of the character and form of the waste material itself, there is no need to presegregate the wastes nor to wash them or to remove from them other organic components [2].

The Polish version of the thermal technique of raw materials recycling of plastics wastes has been targeted on coal coking processes, where the wastes are interspersed with coal blends in the form of premixes prepared by initial thermal degradation carried out in coal bitumens as medium. The studies on compatibility of various

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waste plastics with coal-tar pitches and the behavior of the resulting products under the coking conditions of various coal blends, carried out in the framework of the Ordered Research Project 'Raw Material Recycling of Waste Plastics by Coking' (State Committee for Scientific Research, Project No. 035-07) has allowed to develop a technological process that is mature for commercialization [3–8]. In the course of realization of this project, plastics wastes were investigated also in combination with petroleum-derived bitumens that remain from the secondary processes applied to petroleum fractions, including furfurol extracts, heavy oils from catalytic cracking and heavy residues from olefinic pyrolysis of gasolines [9].

The objective of this work is to explore the possibilities of applying the thermal process to prepare mixtures of selected plastics wastes with a pyrolysis oil and to evaluate selected thermomechanical methods for examining the properties of the resulting products. The assumptions made at the start of the present work were as follows:

a) the amount of plastics wastes to be treated together with pyrolysis oil should be as large as possible ($\geq$80 mass%);

b) the resulting compositions should be homogeneous and stable;

c) the thermomechanical property data should be measured by the methods used for polymers, including

- impact strength by the Dynstat apparatus
- hardness by the Brinell-Vickers indenter
- melt flow index by the IIRT plastometer (MFi)
- melting point by the capillary method
- linear shrinkage of samples 120×15×10 mm in size on cooling.

Experimental

The following plastics wastes were used for investigations:

- poly(vinyl chloride) (PVC) left from spent cellular inserts used in the packing of indigeneous cooling towers operated at the PETROCHEMIA PŁOCK S.A.;
- polyethylene (PE) from worn-out cellular inserts used in the packing of indigeneous cooling towers, produced by the Polimerkholotekhnika (Russia); and
- poly(ethylene terephthalate) (PET) from spent bottles used for beverages.

The wastes were precomminuted and dried. To enable thermolysis to be applied to process these wastes, a pyrolysis oil, *viz.,* BF Pyrolyzate, was used as a plasticizer. The BF Pyrolyzate is produced at the PETROCHEMIA PŁOCK S.A. and currently used in the mining industry as a flotation oil for coal and as an additive to fuel oil or to furnace black oil. The property data of the BF Pyrolyzate were:

– density	1031 kg/m^3
– viscosity	4.1°E (50°C)
– water content	0.3 mass%

Thermal analysis was carried out in a glass reactor equipped with an electronic thermometer, bladed mechanical agitator, cooler, receiver, a wash bottle containing calcium carbonate and serving as a hydraulic seal in the system, and a setup to deliver a nitrogen gas. Compositions were prepared, 300 g of each, containing 80, 85, 90 and 95 mass% of PE, PET, and PVC wastes added to the pyrolysis oil. The compositions were prepared in a nitrogen atmosphere; no liquid products were collected. The individual parameters to mix the components, established for specific groups, are listed in Table 1. The total homogenization time starting with charging of the raw materials to the reactor until the completion of thermal processing, was 2–3 h. If the blends were well fluid when hot, they were cast into molds to yield shaped pieces to be later tested.

Table 1 Parameters for preparation of plastic-BF Pyrolyzate mixtures

Plastic	Temperature	Time*/h
PET	350	2
PE	345–355	1
PVC	250–280	1

*Time of heating at a desired thermal modification temperature

Results

Results of the measurements of thermomechanical and rheological property data of the thermal treatments involving PET and PE wastes and pyrolysis oil (BF Pyrolyzate) are listed in Tables 2–5.

These data indicate that, in case of PET waste, neither the process of thermal modification nor addition of pyrolysis oil have affected the number of polymer's

Table 2 Results of the measurements of thermomechanical and rheological property data of the thermal products involving PET/BF

Composition/wt.%	$^{*}T_{MV}$/°C	$^{**}T_{R\&B}$/°C	$\Delta T = T_{R\&B} - T_{MV}$	$^{***}T_{M}$/°C	MFi g/ 10 min	Linear shrink/mm, (%)
100 PET	266.5±2.5	–	–	245±1	0.18±0.06	–
95 PET 5 BF	83.7±2.05	254.5±0.5	170.8	244.5±1.5	0.49±0.06	1.62± 0.46 (13.88±2.8)
90 PET 10 BF	79	248.5±0.5	169.5	244.5±1.5	1.51±0.28	1.29±0.41 (12.14±3.42)
85 PET 15 BF	64.3±0.47	248	183.7	232.5±2.5	0.75±0.26	1.09±0.26 (11.2±3.15)
80 PET 20 BF	61.3±1.25	246	184.7	237±2	0.43±0.17	1.02±0.174 (10.53±2.36)

*Vicat softening point
**Ring&Ball softening point
***Melting point

Table 3 Hardness and impact strength data for PET/BF thermolyzates

Composition/mass%	Brinell hardness, HB P=153.2 N, D=5 mm	Dynstat impact strength/ kg cm cm^{-2} (J/m^2)
100 PET	12.23±3.15	2.88±1.14 (2822.4±1119.9)
95 PET 5 BF	31.49±5.45	0.611±0.05 (599.19±50.15)
90 PET 10 BF	Sample too fragile to be tested	0.844±0.22 (827.68±218.7)
85 PET 15 BF	Sample too fragile to be tested	1.05±0.42 (1036.6±417.86)
80 PET 20 BF	42.76±5.82	0.716±0.138 (702.16±135.48)

crystalline phases which continue to predominate over the amorphous phase. Confirmation for this conclusion is found in the slight difference of the melting points of the thermal products with respect to the melting point of unmodified PET. The slight increase in the softening point determined by the ring and ball method, with respect to the melting point, indicates that, during the heating step, a small amount of the crystal phase of the polymer has become disintegrated.

In case of PE modified with the BF Pyrolyzate, thermal analysis was found to favor the disintegration of a considerable proportion of the crystal phase in the polymer and, in combination with the oil, to result in the formation of a predominant amount of the amorphous phase. In spite of the heating processes, addition of pyrolysis oil has also resulted in a regular drop of the softening point and the melting point of PE.

The products to be treated composed of waste PET (≥80 mass%) and pyrolysis oil and PE used in amounts of up to 85 mass% could be processed only by the compression technique. It is, however, with the oil used in larger proportions, that the products composed of PE and pyrolysis oil should be processible by injection molding as may be judged from the MFi data.

As the proportion of the pyrolysis oil added to PET and PE is increased, the processes occurring at high and destructive temperatures tend toward reducing the resistance of the products to the dead-weight load. This tendency is evident from the decreasing Vicat softening temperatures and impact strength data and also from the hardness data on PE/BF cast samples.

Regardless of the proportion of the plasticizer added, the PET/BF and PE/BF products exhibit a considerable shrinkage (>10%) on cooling to room temperature, whereby they are more difficult to prepare samples cast into molds.

In the pyrolysis oil as medium, the thermal degradation of PET and PE wastes was smooth under the conditions adopted, whereby uniform liquid (or dense liquid) mixtures could be obtained. In case of PET and PE, mass losses of the composition did not exceed 3.1% and 7.6%, respectively.

Table 4 Thermomechanical and rheological data on PE/BF compositions

Composition/ wt%	$^{*}T_{\mathrm{MV}}$/°C		$^{**}T_{\mathrm{R\&B}}$/°C	$\Delta T=T_{\mathrm{R\&B}}-T_{\mathrm{MV}}$		$^{***}T_{\mathrm{M}}$/ °C	MFi g/ 10 min	Linear shrink/mm (%)
	A	B		A	B			
100 PE	–	137.3±1.69	–	–	–	135	4.23±1.65	–
95 PE 5 BF	113.3±0.94	122±0.81	146	32.7	24	125	58.36±4.21	1.62±0.46 (13.88±2.8)
90 PE 10 BF	112±2.16	112±1.41	133	21	21	120	45.9±5.06	1.29±0.41 (12.14±3.42)
85 PE 15 BF	112±1.41	117.4±0.94	144	32	26.6	120	5.2±1.96	1.09±0.26 (11.2±3.15)
80 PE 20 BF	111	116±1.41	142	31	26	110	8.55+3.16	1.02+0.174 (10.53+2.36)

[*] Vicat softening point; [**] Ring&Ball softening p.; [***] Melting point

A – samples prepared by casting the molten mass into a mold; B – samples prepared by hot compression

Table 5 Hardness and impact strength data for PE/BF therma productsl

Composition/ wt%	Brinell hardness, HB P=613 N, D=5 mm		Dynstat impact strength/ kg cm cm^{-2} (J/m^2)	
	A	B	A	B
100 PE	–	7.61±0.71	–	Sample too elastic to be tested
95 PE 5 BF	19.02±3.94	22.51±4.97	2.92±1.62 (2867.3±1595.4)	2.31±0.28 (2271.9±266.2)
90 PE 10 BF	12.65±1.06	25.43±3.74	5.02±1.53 (4927.8±1499)	1.08±0.27 (1066.2±270.3)
85 PE 15 BF	16.75±1.66	33.06±3.76	2.66±0.99 (2603.7±980.6)	1.77±0.57 (1739.5±558.8)
80 PE 20 BF	13.12±1.73	37.52±5.06	2.89±0.95 (2928.6±928.5)	4.33±0.26 (4250.5±1336.5)

In case of PVC/BF mixtures, where intensive destruction of the polymer and evolution of hydrogen chloride resulted in the formation of coked, hard and brittle products, mass losses being quite considerable (37 to 65%), the product could not be cast into conventional molds. The PVC/BF mixture was ground and used successfully as a filler (30 wt%) for PE or PET. In the present investigations, molten PET wastes and PVC/BF product added in the amount of 30 wt% gave together a homogeneous system; yet at room temperature the material was brittle and it was difficult to hot-press stable shapes to be examined. Blending the PVC/BF mixture with waste PE allowed to prepare a composition which, after having been hot compressed, was characterized by high plasticity and had the following property data:

– Vicat softening point	117.6°C
– melting temperature	138.8°C
– MFi	9.58 g/10 min
– Dynstat impact strength	0.821 kg cm/cm^2 (805.6 J/m^2)

Summary and conclusions

1. Heating at high temperatures of compositions of waste polyethylene and waste poly(ethylene terephthalate) with pyrolysis oil added in amounts of ≥5 wt %, has allowed to prepare homogeneous and castable mixtures.

2. Thermal degradation of waste poly(vinyl chloride) in the presence of pyrolysis oil at temperatures not exceeding 300°C and with no liquid products collected, has yielded infusible (up to 300°C) brittle products; the process involves considerable mass losses with respect to the mass of the original composition (evolution of HCl).

3. In relation to the proportion of the pyrolysis oil added to waste PE and waste PET, the resulting products can be processed either by compression or injection molding.

4. The products composed of poly(vinyl chloride) in amounts of up to 30 wt% and pyrolysis oil can be used as fillers for PE. With 30 wt% of PVC/BF mixture added as a filler, PET becomes increasingly brittle.

5. The shape of the sample tested, and particularly its internal coherence ensuring hardness of the test piece to be examined, was determining the usefulness of a given test method and it decided about the choice of measurement parameters (temperature, load, time). For the mixtures composed of waste PE or PET and pyrolysis oil used in proportions of 5 to 20 mass%, the following property data could be determined:

a) the ring and ball softening point and the melting point; the values obtained were found to correlate well with the real temperatures of MFi measurements;

b) the Vicat softening point which enables the resistance of the system to the dead-weight load to be determined in relation to temperature;

c) the melt flow index which required the test temperature and the dead-weight load to be determined individually for each product;

d) the Dynstat impact strength.

For the products composed of PE and pyrolysis oil, the Brinell hardness test was also applicable, preferably for hot-compressed specimens.

6. The melting point and/or the ring and ball softening point could help us establish the temperature at which to determine MFi for PET–pyrolysis oil products; for PE/BF mixtures no such correlation was found to occur.

7. The present results show that more extensive experimental studies are worthwhile, including new types of petroleum bitumens, e.g., cracking residue or furfurol extracts, and using thermally treated PVC-pyrolysis oil mixtures as fillers.

References

1 A. B. Błędzki, Ed., Recycling of polymeric materials (in Polish), WNT, Warsaw, 1997.
2 J. Polaczek, IIIrd International Symposium ‘Chemical Forum’, Warsaw, 1997, p. 20.
3 M. Ściążko, A. Sobolewski, J. Śliwa and J. Polaczek, IIIrd International Conference on ‘Combustion of Wastes – Processes and Problems’, Szczyrk, (Poland) 30 September–2 October, 1997.
4 J. Polaczek, Z. Machowska, Z. Wielgosz and J. Bednarek, Conference on ‘Polymers–Environment–Recycling’, Szczecin-Międzyzdroje, (Poland), 1995, p. 255.
5 J. Polaczek, A. Winiarska, E. Rudnik and Z. Machowska, ICRI Annual Report ‘95, 96 (1995) 43.
6 J. Zieliński, B. Osowiecka, B. Liszyńska and E. Gurdzińska, Research Works ‘Modification of Polymers’ of Wrocław University of Technology, 45 (1995) 394.
7 M. Ściążko, A. Sobolewski, J. Śliwa and J. Polaczek, 2nd Congress on Chemical Technology, TECHEM 2, Wrocław, (Poland) 15–18 September, 1997, p. 619.
8 G. Collin, B. Bujnowska and J. Polaczek, Fuel Proc. Technol., 50 (1997) 179.
9 J. Polaczek, Z. Machowska and J. Zieliński, Polish Pat. Appln. P-321 124 (1997).