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Use of additive compatibilization for recycling of municipal plastics waste

Summary — It is shown that various grades of polyethylene, polypropylene and polystyrene are the main components of municipal plastics waste after separation of poly(ethylene terephthalate) bottles. We found that a mixture of commercial copolymers is very efficient compatibilizer for polyethylene/polypropylene/polystyrene blends. This compatibilizer is very efficient also for application on real municipal plastics waste. Proper mixing conditions must be chosen. In this case, materials with satisfactory toughness are achieved. Using this procedure should broaden the area of application of recycled materials and strongly improve economy of recycling.

Key words: municipal plastics waste, recycling, compatibilization.

Plastics are very important materials with ever-increasing production. Due to their advantageous properties, they are widely used in various branches of industry. High consumption of plastics inevitably leads to the production of large amounts of plastic wastes especially because substantial part of produced plastics is used for packaging. Therefore, suppression of the environment pollution by the plastics wastes is the task of great and increasing importance.

There are two main possibilities of solving the problem. The first is substitution of the plastics by other materials, the other is efficient collection and recycling of plastics wastes. Some properties of plastics are unique and, therefore, plastics can hardly be substituted by other types of materials in many applications. Moreover, recycling of the substitutes should be also considered. Substitution of common plastics by the environmentally degradable ones seems to be promising possibility. The degradable plastics are prepared mostly from renewable resources and, after utilization, they can be composted. Their great advantage is the fact that the life-time of uncollected environmentally degradable plastics (EDP) in the landscape is several orders of magnitude shorter than that of the common ones. On the other hand, there are many technical and economical problems which limit competitiveness of EDP with the common ones. For instance, well established efficient technologies are available for production of common plastics, while production of EDP is much less elaborated and investments are required for their production. The requirement of long term use of some plastics products or parts is in strong contradiction with environmental degradability. Therefore, total substitution of common plastics by EDP is a matter of far future and recycling of common plastics is still a topical problem.

There is three main methods of plastics waste recycling [1]: thermal (incineration), chemical and material one. Thermal recycling utilizes only a small part of energy stored in the waste. Its advantage is the fact that plastics do not need to be separated from other flammable wastes (paper, food residues, *etc.*). Plastics wastes must be incinerated at sufficiently high temperatures where dangerous substances are not formed. Incineration of halogenated polymers is a serious problem. In our opinion, thermal recycling should not be *a priori* rejected if plastics waste substitutes oil, gas or coal in energy production.

Chemical recycling is based on depolymerization of the waste to monomers and the use of the monomers for preparation of new virgin polymers. This method utilizes a larger part of the stored energy than the thermal recycling. Because different polymers need different methods of depolymerization, it is difficult to apply this method to the mixed plastics waste. The efficiency of chemical recycling of plastic waste is dependent on chemical nature of a plastic and, therefore, on the method of its depolymerization. Serious problems with separation and rectification of monomers must be solved if single homopolymers are not used. In practice, chemically recycled are separated poly(ethylene terephthalate)

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(PET) bottles [1]. PET produced by this method is suitable for contact with food products. This is very important because a considerable part of PET production is used as bottles for beverages.

Material recycling of the plastic wastes utilizes the largest part of the stored energy. It is widely and successfully used for single-sort industrial waste, where frequently only reprocessing and possibly additional stabilization is required. In other cases, plastics waste is added to virgin polymers without loss of their properties. Much more difficult is material recycling of municipal plastics waste. The municipal plastics waste is a mixture of various sorts of plastics with different degrees of damage. An approach to the material recycling is separation of individual plastics followed by their reprocessing. However, separation of individual plastics is difficult and expensive. Another possibility is recycling of unseparated mixed waste. It is well known that most polymer pairs are incompatible. This means that only coarse phase structure, poor adhesion at the interface and hence poor mechanical properties can be achieved for their blends. Therefore, materials prepared from municipal plastics waste by down-cycling have poor mechanical properties (low impact strength, tensile strength, elongation at break, *etc.*). These recycled materials can be used only for very limited applications and, therefore, only very low prices are achieved on the market.

It is well known that properties of incompatible polymers blend can be improved by compatibilization, *i.e.*, addition of block or graft copolymers with blocks identical or compatible with the blend components [2]. The copolymers are premade (additive compatibilization) or are formed during mixing by chemical reaction (reactive compatibilization). In some cases, also statistical copolymers behave as compatibilizers [3]. Compatibilization of most polymer pairs is well described in the literature and was successfully commercialized [4]. On the other hand, efficient simultaneous compatibilization is an open problem, which complexity increases with ever-increasing number of polymers. In recycling of municipal plastics waste, also a damage of individual plastics should be considered and problems of destabilization of recycled materials should be solved. In spite of the complexity of this problem, we would like to show the efficient material recycling of municipal plastics waste is possible by its compatibilization.

COMPOSITION OF MUNICIPAL PLASTIC WASTE

If poly(vinyl chloride) (PVC) is not used for packaging and PET bottles are separated, municipal plastics waste should contain mostly various polyolefins (high-density, low-density and linear low-density polyethylenes and isotactic polypropylene) and polystyrene (neat, high-impact and foamed). This consideration is supported by the analysis of samples of the real plastics waste recycled in Transform Bohdaneč (see Table 1). One of the possibilities is to separate polyolefins from other polymers by flotation in water. Polyolefin fraction can be efficiently compatibilized and a material with good mechanical properties can be obtained [5]. If the separation of municipal plastics waste can be avoided, an efficient compatibilizer for polyethylene/polypropylene/polystyrene blends must be found. We showed [6] that the blends can be quite efficiently compatibilized by using a reactive compatibilization system based on liquid polybutadiene or styrene/butadiene block copolymers. Recently we found that a synergistic compatibilizer based on a mixture of commercial copolymers is superior to those mentioned above blends [7]. In this contribution, it is shown that the synergistic compatibilizer is also efficient in real plastics waste. As follows from Table 1, real plastics wastes can contain some PET in spite of mechanical separation of PET bottles. The fact should be considered when choosing an efficient compatibilization procedure.

EXPERIMENTAL

Materials

Model blend PE-LD/PE-HD/PP/PS-HI (54/18/18/10), where: PE-LD — commercial low-density polyethylene Bralen RA 2-19 (Slovnaft a.s., Bratislava, Slovakia, M_w = 120 000); PE-HD — commercial high-density polyethylene Liten BB 29 (Chemopetrol a. s., Litvínov, Czech Republic, M_w = 420 000); PP — commercial isotactic polypropylene Mosten 52 522 (Chemopetrol a. s., Litvínov, Czech Republic, M_w = 140 000); PS-HI — commercial high-impact polystyrene Krasten 562E (Kaučuk a. s., Kralupy n/V, Czech Republic, M_w = 190 000, 7 wt. % polybutadiene).

Samples of real plastics waste Transform D and V (Transform a. s., Bohdaneč, Czech Republic), see Table 1.

Table 1. Composition of samples of real plastics waste from Transform Bohdaneč

Sample	PE-LD, %	PE-HD, %	PP, %	PS, %	PET, %
Method	DSC	DSC	DSC	Extraction	DSC
Transform D	20.5	25.8	28.2	25.5	—
Transform V	22.8	26.5	30.4	18.0	2.3

Compatibilizers: EPDM — commercial ethylene/propylene/diene statistical terpolymer Buna AP 437 (Hulls, Germany); SBS — commercial styrene/butadiene block copolymer Europrene SOL T 168 (EniChem, Italy) with styrene content 43 wt. %, M_w = 81 000 and M_w of styrene block 13 000; synergistic compatibilizer [7] — a mixture of EPDM and SBS used through the study.

Blend preparation

The blends were prepared by mixing in the chamber W 50 EH of a Brabender Plasticorder at 190°C and 60 rpm for 10 min (model blends and waste without PET) or at 250°C and 90 rpm for 8 min (PET-containing waste). The samples used for the determination of impact strength were shaped from compression-molded plates prepared in a Fontijne table press.

Determination of tensile-impact strength

Tensile-impact strength (a_ε) was measured at 23°C using a Zwick tester, which was equipped with a special fixture for the test specimen according to DIN 53 448. The specimens type S according to ASTM 1822 standard were cut into dog-bone shape with the short narrow section from the plates 1.6 mm thick. The specimen length of overall was 64 mm, the width of overall 9.5 mm and the width of narrow section 3 mm. The maximum pendulum energy was 2 J. The values obtained are presented as arithmetical means of the measurements on 10 specimens.

RESULTS AND DISCUSSION

The results of the study of the effects of various compatibilizers on the tensile-impact strength of the model blend and on a sample of municipal plastics waste (mixed at 190°C) are summarized in Fig. 1. It follows that the compatibilization efficiency increases in the order EPDM < SBS < synergic compatibilizer for both the model blend and real plastics waste. For all the compatibilizers under study, the model blend has higher tensile-impact strength than the real plastics waste. The main reason for this effect is apparently the higher content of polyethylene (the toughest component) in the model blend than in the real waste. The tensile-impact strength of systems compatibilized with the synergic compatibilizer is almost three times higher for the model system and more than three times higher for the real waste than that of the related system without a compatibilizer. It should be mentioned that the tensile-impact strength of the real waste compatibilized by the synergic compatibilizer is near that of virgin polypropylene (a_ε = 52.4 kJ/m^2 was found for PP used in the model blends).

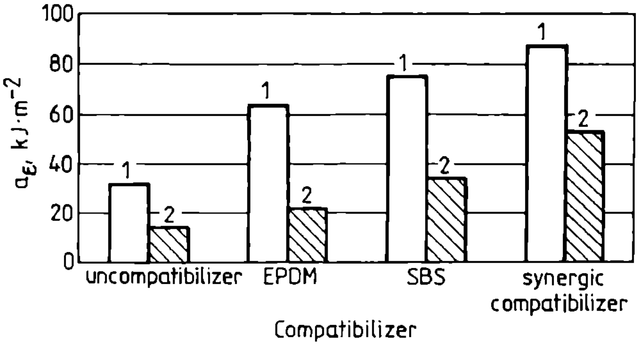

Fig. 1. Effect of various compatibilizers (5%) on the tensile-impact strength (a_ε); 1 — PE-LD/PE-HD/PP/PS-HI (6/2/2/1), 2 — municipal plastics waste (sample mixed at 190°C)

A substantial part of samples of real plastics waste after separation of PET bottles still contain non-negligible amounts of PET. PET pieces with characteristic dimensions in the millimeter range persist in samples mixed at 190—200°C. This has a detrimental effect on the tensile-impact strength of the product. During the mixing process at 250°C, PET is molten and a uniform material is achieved. We found that the synergistic compatibilizer (with a small amount of low-molecular-weight additive) is very efficient also for the waste containing PET, mixed at 250°C (see Table 2). In this case, the tensile-impact strength achieved in compatibilized real plastics waste (sample V) is comparable with that of virgin polyethylene (a_ε = 204 kJ/m^2 was found for PE-LD and a_ε = 133 kJ/m^2 for PE-HD used in the model blends). Somewhat surprising is the strong difference between the tensile-impact strength of compatibilized samples V and D with similar compositions. The samples have different origin and, therefore, they can differ in the polystyrene/high-impact polystyrene ratio, in degree of the components damage and in contents of nonpolymeric contaminants. All these factors can affect a_ε of the resulting materials. It seems that the efficiency of the compatibilization procedure is very sensitive on mixing conditions. It is probably the main reason of a higher a_ε for the compatibilized Transform V sample than for the related model blend (Fig. 1). We believe that described procedure can be also applied to plastics waste containing other plastics with higher melting points (polyamides, polycarbonate, *etc.*).

Table 2. Tensile-impact strength (a_ε) of the samples of municipal plastics waste mixed at 250°C

Sample	Compatibilizer	a_ε, kJ/m^2
Transform D	—	17.8
Transform D	synergistic	58.3
Transform V	—	23.9
Transform V	synergistic	150.0

CONCLUSIONS

Recycling of municipal plastics waste using proper compatibilizers and stabilizers is a promising approach to its utilization.

The mentioned above synergistic compatibilizer (a mixture of commercial copolymers) proves to be an efficient, cost effective compatibilizer for municipal plastics waste. Moreover, its application does not need substantial changes in recycling technology.

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KALENDARZ IMPREZ

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Organizatorzy: Chang Gung University + The Polymer Processing Society, Taipei.

Tematyka ogólna: formowanie wtryskowe, wytłaczanie, reologia mieszaniny i stopy polimerowe, prace związane z rozwojem zagadnień morfologii i struktury polimerów, kształtowanie termiczne, formowanie z rozdmuchiwaniem, formowanie obrotowe, modelowanie matematyczne, przetwarzanie reaktywne, kompozyty polimerowe, włókna i folie, sporządzanie mieszanek gumowych i mieszanin polimerowych, właściwości mechaniczne, optyczne i elektryczne.

Tematyka specjalistyczna: przetwarzanie żywności, uwidocznianie przepływu, czujniki w procesie przetwarzania, formowanie wtryskowe wspomagane gazem, biopolimery, zastosowania w optyce i elektronice/elektrotechnice, nowe procesy przetwórcze.

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Organizator: International Plastic Fair (IPF).

Informacje: IPF, Show Management Office, Kasumigaseki Bldg. 12F, 3-2-5 Kasumigaseki, Chiyoda-Ku, Tokio 100-6012, Japan. Tel.: +81-3-3503-7320, fax: +81-3-3503-7620, internet: http://www.a-tex.co.jp/plasttics.

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Informacje: IUPAC-PC 2002 Secretariat, The Society of Polymer Science, Shintomicho-Tokyu Building, 3-10-9 Irifune, Chuo-ku, Tokyo.

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