Recycling of Polymeric Composites

Thomas Mang*, Friedhelm Haulena

Laboratorium für Makromolekulare Chemie und Kunststofftechnologie,
FH Aachen, FB 3, Worringer Weg 1, D-52074 Aachen, Germany

Abstract: For material recycling, composites have to be separated into their components, as only non-mixed raw materials can grant high quality standards. A combined mechanical and subsequent electrostatic separation can be classified as highly economic because it is a dry treatment. This is demonstrated on wire scrap. The separated copper and synthetic materials are obtained in a high degree of purity.

Chemical disaggregation of composites has been worked out with medicinal blister packs and beverage packs. Two methods of separation were used: separating the plastic–aluminium composite by dissolving the plastic material or dissolving the adhesive that bonds together the plastic and aluminium. To demonstrate the technical feasibility of the processes, a pilot plant with a capacity of up to 25 tons of blister pack material per year was built. Chemical separation with non-problematic aqueous media was demonstrated with flocked plastics.

When integrating composites into chemical processes, questions concerning material specification as well as preparation and chemical utilization must be answered. Mechanical preparation of appropriate raw materials has been exemplified by mixed packing waste, carpet-floor waste, and synthetic material from electrical waste. After the raw materials were analyzed and studies of their quantity and compositions were made, their possible re-use as raw material within a chemical process has been elaborated.

INTRODUCTION

Besides the recycling of various kinds of metal, glassware and paper, the recycling of plastics has achieved world-wide importance. The reasons are short-running landfill sites and the intention to take advantage of the valuable substance character of the plastics to spare the natural raw material resources. Therefore in many countries, plastic recycling is prescribed by legislation. For example, the quantities to be recycled and the method of recycling are regulated by a packaging law in Germany (Ref. 1) and in Europe as well in the Packaging Waste Directive (Ref. 2). For other sectors with a high content of plastics, such as from old cars or electronics, scrap directives are issued or planned (Refs. 3,4). These directives have led to a construction of collecting systems and of a variety of waste managing plants and companies.

While recycling of pure plastics from the production scrap has been a fact in many cases since a long time ago, the plastic scrap from consumer goods, like packing, old cars, electronic scrap, requires additional processing because of dirt, metal portions, etc.

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Depending on quantity and quality, the plastic scrap is recycled as material, as raw material or thermally.

The recycling of polymeric composite materials meets special demands: for mechanical recycling, they have to be separated into their various components, as only non-mixed raw materials can grant high-quality standards (Ref. 5). To re-use composites as raw materials within chemical processes, questions concerning the material specification for a chemical process as well as preparation and chemical utilization must be answered (Ref. 6). Additional difficulties arise if not only the composition of the composite materials varies with every manufacturer but also changes over the years. In the following, methods of recycling are demonstrated for some selected groups of composites and elaborated with the aim of an as high-grade recovery as possible.

RESULTS AND DISCUSSION

Influence of scrap raw material

A number of projects that have been conducted at the FH Aachen recently were aimed at elaborating methods of recycling composite materials containing polymers like blister packs, beverage packs, flocked materials, carpet-floor, etc. (Refs. 7-12). Since all these composites are composed of different materials, the processing and re-use have to be checked and elaborated individually. While medicinal blister packs are easily cut into pieces, cutting carpet floor is more difficult because of its high elasticity.

Also, the variety of composites from manufacturer to manufacturer and changes in their composition over the years lead to additional difficulties with respect to the processing and to the use of the resulting material.

Market analyses of carpet-floor scraps, where the main types are fleeced, tufted, woven and knotted carpets, demonstrate that the composition of the carpet-floor types is quite different and variable (Table 1).

Table 1 Carpets offered in Germany (Ref. 13)

Year	Area x 10^6 m^2	Tufted wt.-%	Fleeced wt.-%	Woven wt.-%	Knotted wt.-%
1980	220	76.8	10.8	9.0	2.4
1985	220	71.3	17.5	17.8	1.9
1990	308	63.9	25.2	8.7	2.2

Furthermore, the tufted type itself shows great differences depending on whether it contains unfilled latex or chalk-filled latex (Table 2).

Table 2 Components in tufted-type carpet-floor (Ref. 13)

Component wt.-%	Tufted unfilled wt.-%	Tufted with chalk-filled latex wt.-%
Fibre	47	30
Latex	53	12
Chalk	-	58

Additionally, the carpet-floor contains different kinds of fibers like polyamide, polypropylene, polyester, polyacrylonitrile, and wool as well as different kinds of latex, which vary with manufacturer. Thus, the kind and variety of the components of composites will determine the method of recycling.

Mechanical recycling: mechanical preparation

The easiest way to separate composites into their individual components is by applying mechanical preparation, demonstrated by grinding wire scrap. Wire scrap consists of copper, plastics and rubber. The plastics and rubber are composed of different types of PVC, synthetic rubber, polyethylene and polypropylene, depending on their intended use (like electric cables, telephone cables, energy cables), manufacturer and date of production.

In a mechanical process, the compound materials are separated by grinding but they remain mixed. A corona electrostatic separator subsequently separates copper from its synthetic jacket achieving a high degree of purity (>99 %). The pure copper then is passed on to further preparation in copper mills.

Within the remaining scrap the different plastics, in particular PVC and rubbers, are separated with a plate-type electrostatic separator (Fig. 1).

The remaining scrap from different wires from waste-managing companies was analyzed. One, for example, contained 82 % plasticized PVC and 18 % PE. The whole separation process was optimized regarding the voltage used, separator materials, humidity, particle size and triboelectric charging of the scrap mixture. Different positions of baffles led to different quantities and purity of the PVC, PE and middle fractions. PVC could be separated by a single separation step with a 99.4 % degree of purity. Regarding the input PVC material, the yield of its PVC fraction of 22 % can be enhanced by lowering simultaneously the mass of middle fraction and the PE fraction whereby, of course, the purity of the bigger PVC fraction then worsens (Table 3).

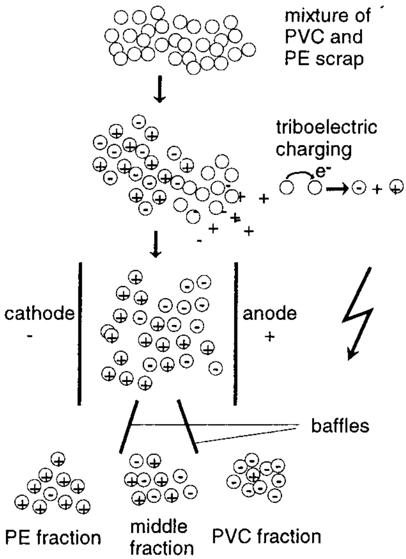

Fig. 1 Separation of a mixture of PVC and PE scrap with a plate-type electrostatic separator

Table 3 Electrostatic separation of a mixture from cable scrap with 82 % PVC and 18 % PE

Run No.	Purity of PVC fraction wt.-%	Yield of PVC fraction wt.-%
1	99.4	22
2	99.1	25
3	92.5	50
4	86.0	70

High economy of such a process of PVC separation from a plastics mixture, i.e., a high degree of purity and a high yield of the separated PVC, is achieved if not sufficiently pure fractions, like the middle fraction, are subjected to subsequent separation steps with the plate-type electrostatic separator.

In general, this method of combined mechanical and electrostatic separation can be classified as highly economic since it is a dry treatment and no expensive waste water purification or drying is necessary.

Mechanical recycling: chemical preparation

Should mechanical separation processes fail, chemicals come into play. Chemical disaggregation and subsequent utilization of composite materials were tested with medicinal blister packs and beverage packs, for instance with those used for milk, juice and like. In both cases, plastic components are tightly bonded together with aluminium by a varnish so that the components of these composites cannot be separated mechanically from each other.

One way to separate these plastic–aluminium composites was dissolving the plastic. This way was used with recycled aluminium–polyethylene composites, which accumulate after processing beverage packs in paper mills. Pure aluminium and polyethylene were recovered by dissolving the polyethylene in a halogen-free organic solvent at 150 °C. The aluminium was sieved out, washed and dried. Then the polyethylene-containing solution was cooled, whereby the polyethylene completely precipitated as powder. The powdery polyethylene was filtered off and dried, the solvent was recycled. This process is scaled up in a pilot plant with a capacity of 350 t per year by the RWE AG at Wesseling in Germany.

Another way used to separate plastic–aluminium composites was to dissolve the adhesive that bonds together the plastic and the aluminium (Fig. 2a).

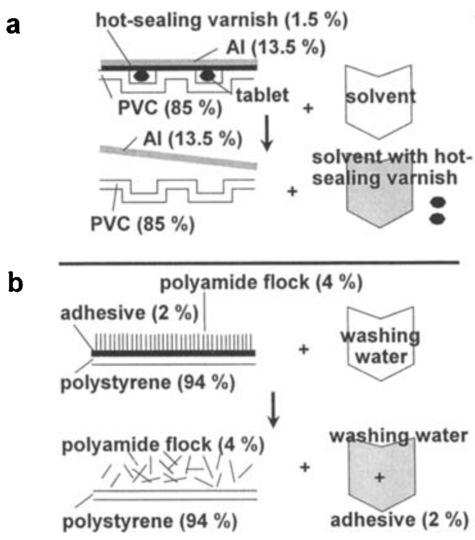

Fig. 2 Process of separating components by dissolving the adhesive: (a) tablet-blister packs, (b) flocked polystyrene foils

These were medicinal blister packs, which are composed of a plastic substrate, usually PVC, and an aluminium covering strip, the two being bonded together by a hot-sealing varnish. Separation into the main constituents, aluminium and PVC, is achieved by the selective dissolution of the hot-sealing varnish (Refs. 8-10). This destroys the bond between the aluminium and PVC, freeing the two materials from each other. The solvent is an acetone-water mixture. Its composition can be varied to control the course of the process and the quality of the products. When the solvent is drained away from the aluminium-plastic mixture, the two components, aluminium and plastic, are dried and afterwards separated by air classification.

To demonstrate the technical feasibility, a pilot plant with a capacity of up to 25 t of blister pack material per year was built at the FH Aachen (Fig.3).

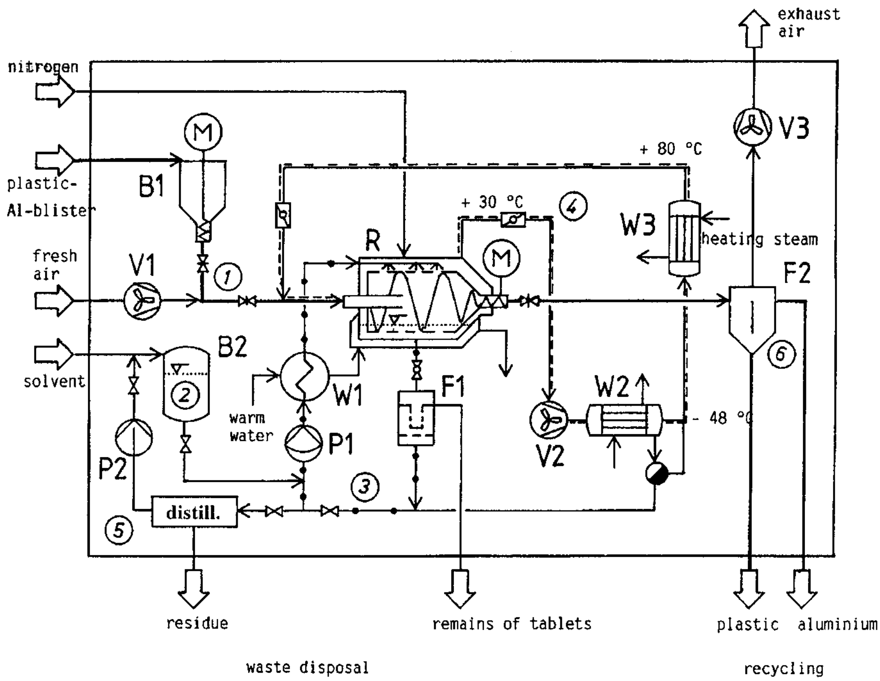

Fig. 3 Pilot plant for recycling of plastics and aluminium (or flock and base material) from composite materials

At the input (1), the blister material held in a container (B1) is blown into the reactor (R) by a fan (V1) driven by a motor (M). The reactor is the central separation unit and consists of a sealed housing in which a sieve drum mounted on bearings rotates.

The separation is achieved by spraying the solvent from a system of perforated pipes above the sieve drum. When the required quantity of solvent has been drawn from its storage reservoir (2), the solvent is passed round the circuit (3) by the pump (P1) so that some of it accumulates at the bottom of the reactor. The sieve drum rotates so that all the blister-pack material contained is regularly immersed in the solvent.

Once the two components have been separated, the solvent is drained into a collection tank (5). The aluminium and plastic in the reactor are then dried by an air flow (4) blown by a fan (V2) through a heat exchanger (W3) and into the reactor, where it becomes saturated with solvent vapour. The solvent is then condensed at -48 °C by the heat exchanger (W2). Finally, the dried material is extracted by an air-blast winnowing system (6), where it is separated into its components, aluminium and PVC.

The PVC obtained is colourless, free of aluminium and suitable for the use as foils in the printing sector or for office supplies, in the combination 50 % recycled material and 50 % virgin material (Ref. 9). Analyses of the aluminium (Ref. 8) did reveal that the recovered metal can be fed straight back into the wrought-alloy cycle. In fact, the recycled aluminium can be reprocessed into aluminium cover-strip for tablets just like the original, thus turning the material cycle into a closed loop.

This reaction and separation principle was also applied to flocked plastic foils for decorative packaging (Ref. 12), which accumulate both as clippings and as used consumer goods (Fig. 2b). The examined probes of flocked foils for decorative purposes consisted mainly of polystyrene (94 %), whereas the portions of flock (4 %) and adhesive (2 %) were relatively small.

Flocked clippings cut into pieces weighing about 0.5 g were treated with an aqueous substance the process being supported mechanically. About 2 h later, the adhesives dissolved in the aqueous substance and the flock was released from the polystyrene. After that, rough pieces of the polystyrene base were separated from the flock and the aqueous substance by passing through a large-mesh screen, and the flock from the aqueous substance by passing through a fine screen. Here, about 94 % of pure polystyrene and about 4 % of pure flock were reclaimed. As performed in a pilot plant (Fig. 3), the chemical separation process is ecologically harmless with non-problematic aqueous media.

Raw material recycling process

For composites that do not permit an economically justifiable processing of materials, raw material recycling comes into question. Here, the plastic materials are no longer used as materials, but as chemical raw materials or source products, and petrochemical processes such as hydration, gasification, thermal decomposition and coking are used. This concerns industrial technical processes in which plastics of different composition are partly transformed into low-molecular-weight decomposition products, which can then find their place in the range of products of the industrial chemistry.

One of these processes, which has taken off to a great extent, is the use of plastics for the reduction of iron ore in blast furnaces. Here, the carbon and hydrogen portion of the injected plastics reduce the iron ore into the metal under the formation of carbon dioxide and water and thus replace the customary heavy oils and coke.

The precondition for use in one of these industrial processes is the conversion of the waste materials into a flowable granulate whilst observing very special specifications. Thus, for example, in the steel works, only specified limits of various metals, halogens and sulfur are permitted (Ref. 6). This is intended to hinder lowering of the steel quality by metal pollution of other kinds, for example by zinc from plastic additives. It is therefore necessary to know before the granulation the input materials as well as to have quality control of the granulates concerning the required specifications.

For the required conversion into granulates, several processes are available, such as agglomeration and regranulation in the extruder. Another process, at favourable costs, is the pellet press with which, at the FH Aachen, fitted carpet scraps were recycled (Ref. 11). Pressing tools squeeze the material down onto a rotating matrix (Fig. 4).

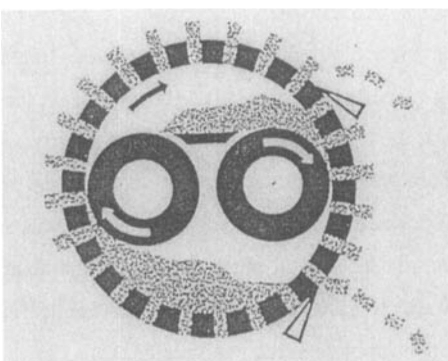

Fig. 4 Granulation with a pellet press

The frictional heat melts the material, which is pressed into the matrix through a large number of 60-mm long bored channels. On the outer side of the matrix, the material, which has now assumed the form of a hank, is cut by fitted knives to a defined length, by means of which a pourable material is created.

As shown above, carpet-floor scraps vary too strongly in type and in their composition from one manufacturer to another and over the time to be economically separated into all components. Flowable granulates have been produced with the pellet press. Statistical analysis of the input carpet-floor scrap as well as market analyses revealed that the scrap contains between 0.15 and 0.3 % of zinc. This is far above the 0.1 % required by the specification of the steel industry. Because of its high carbonate content, which can be incorporated into the produced cement, the carpet-floor scrap was passed on to cement works for partly chemical and partly thermal recycling (Ref. 11). On the other hand, flocked polystyrene foils mentioned above are processed to granulates which fulfil the specifications for use in blast furnaces (Ref. 12).

Synthetic materials from electrical appliances have been studied as well. The input materials were polystyrene fraction from refrigerators, styrene-butadiene copolymers and polystyrene from TV rear parts and a mixture of plastics from household ware (Ref. 14). Basically, these plastics are suitable for raw material recycling. A determining factor for the selection of the type of raw material recycling is the content of chlorine-containing flame-retardant additives. Here, market research and statistical analyses revealed that the chlorine content from the flame-retardant depends on the type as well as on the local origin of the scrap. Mixtures of the three types of plastics have chlorine contents well below the specification required by the raw material recycling industry.

Such heterogeneous mixtures of plastics are also found in mixed packing waste. Granulated, these scraps fit a raw material recycling (Ref. 15).

CONCLUSIONS

Composites containing plastics can be recycled as materials by separating components if the composites are not too heterogeneous and are well defined in their composition as shown on examples of wire scrap, beverage packs and medicinal blister packs. In the case of very heterogeneous composite scrap like carpet-floor scrap or scrap from electronic devices, which changes from manufacturer to manufacturer and also over the time, producing granulates with specifications satisfying the requirements of the appropriate industrial chemical processes is the method of choice.

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