

D. Compatibilization/Compounding Evaluation of Recovered Polymers

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Participants:

This project is conducted as part of a Cooperative Research and Development Agreement (CRADA) among Argonne, USCAR's Vehicle Recycling Partnership¹, and the Plastics Division (formerly the American Plastics Council) of the American Chemistry Council.

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Objectives

- Evaluate the market opportunity for polymers recovered from shredder residue.
- Identify limitations associated with the reuse of the materials as recovered and determine the need for post-processing technology to upgrade the recovered materials to meet the requirements of the market.

Approach

- Specify standard protocols for material testing, content characterization, and performance properties.
- Determine properties of recovered polymers.
- Conduct blending and pelletizing trials of the recovered polymers.
- Conduct mold trials using recovered polymers.

Accomplishments During this Reporting Period (FY 2006)

- Determined the physical properties of the 70% filled acrylonitrile-butadiene-styrene (ABS) fraction .

- Determined the physical properties of two blends of the 70% filled ABS fraction with virgin ABS (10% recovered/90% virgin and 25% recovered/75% virgin).

Prior Accomplishments

FY 2005

- Midland Compounding developed a protocol for evaluating the physical properties of recovered plastics.
- Compiled a physical properties database for virgin plastics.
- Determined physical properties of the PP/PE product recovered from the Argonne froth-flotation process and from the polypropylene/polyethylene (PP/PE) fraction recovered by the Salyp process.
- Pelletized 1000 pounds of a blend of the Argonne recovered PP/PE product.
- Conducted mold trials of the recovered PP/PE product.

Future Direction

FY 2007 activities will focus on:

- Determine physical properties of the upgraded filled ABS fraction.
- Determine physical properties of the upgraded unfilled ABS and PS recovered from the unfilled ABS/PS concentrate.
- Determine physical properties of the 85% PC-ABS/PC alloy.
- Pelletize a blend of recovered filled ABS with virgin ABS and compare the properties of the blend with the properties of the virgin material.

Summary

The objectives of this project are (1) to characterize the properties of potentially recyclable automotive materials and (2) to confirm the technical and economic feasibility of using those materials in value-added applications.

The project will initially focus on establishing the properties of polymeric materials that are recovered as part of the Post-Shred Materials Recovery Technology Development project (see 7.E).

Regardless of the effectiveness of any automotive-materials recovery technology, the materials that will be recovered will be on average 10–15 years old and derived from different sources (automobiles, home appliances and others). In this project, the performance properties of recovered polymers will be compared vis-à-vis new or virgin materials to establish a database of the properties of recovered automotive polymers. At present, there are few data about the physical properties of polymers recovered from post-consumer durable goods. Absent such data, it is unlikely that sustainable applications for

recycled materials will be either identified or developed.

Physical properties testing has been conducted by Midland Compounding, Inc. Midland also conducts composition testing, the results of which are compared with the results of compositional analysis done on recovered materials by Argonne.

Blending and pelletizing of the PP/PE recovered from shredder residue by Argonne has been tested by Palmer Plastics, Inc. More blending and compounding tests will be done, as required, to achieve the desired performance properties of the recovered materials for target applications.

Mold trials using the recovered PP/PE were also done by MG V Enterprises. More molding tests are planned to confirm the technical and economic feasibility of using recycled polymers in specific applications.

Three additional companies — Collins and Aikman Corporation, Enviro-Plas Corporation, and Mayco Plastics, Inc. — have agreed to evaluate, compound,

and run mold trials by using recovered materials, subject to the physical properties of the recovered materials.

Polymer Physical Properties and Materials Composition Analysis

Typically, 10-lb samples of recovered materials are used to define physical properties and to characterize the composition of the material.

To quantify the physical properties of the recovered material, a sample is extruded on a single-screw extruder, melt-screened through a 40-mesh screen, molded into American Society for Testing and Materials (ASTM) test bars and plaques, and tested. The molded parts and a random selection of regrind chips from each sample are evaluated for material identification by using infrared spectroscopy.

Common physical properties that are measured for each sample include the following:

- Melt flow rate (MFR),
- Izod impact,
- Flexural modulus,
- Tensile strength at yield,
- Tensile strength at rupture,
- Elongation at rupture,
- Deflection temperature under load (DTUL),
- Gardner impact, and
- Specific gravity (SG).

Physical Properties and Composition of the Recovered PP/PE

The physical properties of PP/PE recovered from different shredder residues by Argonne and by Salyp were determined for several samples. The results for the Argonne materials are given in Table 1.

Properties of commercially-available PP and PE virgin resins and for PP from dismantled automobiles are presented in Table 2 for comparison. The Izod impact of the recovered material is about three times that of the virgin resins, while the tensile strength of the recovered material is lower than the tensile strength of the virgin resins by about 30%. This phenomenon may be attributed, at least in part, to the presence of thermoplastic olefins (TPO) and rubber in the recovered material, which act as impact modifiers. Recovered samples 8, 9,

and 10 listed in Table 1 contained about 2% rubber, while samples 1 through 7 contained about 4% rubber.

The results for the more than 20 PP/PE samples recovered by Salyp from different European and U.S. shredder residues are given in Table 3. The properties of the Salyp recovered PP/PE are equivalent to the properties of the Argonne-recovered PP/PE.

Physical Properties and Composition of the Recovered Filled ABS

Filled ABS recovered by the Argonne froth-fotation process followed by removal of the rubber by the Argonne dry mechanical process contained 70% filled ABS (specific gravity greater than 1.07 and less than 1.1), 1.5% PS, 8% PPO, 3% rubber, 3% PP, 7% nylon and 7.5% others. The physical properties of this recovered filled ABS were determined. The results are given in Table 4 and are compared with properties of a commercially-available virgin ABS. Table 4 also shows the properties of two blends of the recovered ABS with virgin ABS (25% recovered/75% virgin and 10% recovered/90% virgin). Interestingly, except for elongation at rupture and Gardner impact, the properties of the blends were very close to the properties of the virgin material. Operating condition to upgrade the recovered filled ABS to over 90% has been determined. Properties of the upgraded material will also be established.

Polymer Physical Properties Database

A physical properties database has been compiled so that the physical properties of the recovered polymers can be compared with general purpose virgin polymers.

General purpose physical properties have been compiled for the following plastics:

- ABS,
- Nylon (6 cast, 6/6 extruded, 30% glass filled),
- PPO [polyphenylene oxide] (unfilled, 30% glass filled),
- Polycarbonate

Table 1. Properties of PP/PE recovered by Argonne from different shredder residues.

Property	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Average
MFR, g/10min, 230°C, 2.16 kg	10.5	14.9	7.7	10.1	11.4	7.2	8.7	7.2	8.7	7.2	9.4
Izod impact, ft-lb/in., 73°F	12.3	10.5	11.9	10.8	9	10.7	13.2	1.7	2.8	3.3	8.6
Flex mod., 1% secant, 1,000 psi	83	73	89	84	82	101	112	126	127	113	99.0
Tensile strength at yield, 1,000 psi	2.6	2.2	2.7	2.6	2.4	2.8	3.1	3.4	3.3	3.1	2.8
Tensile strength at rupture, 1,000 psi	0.8	1.2	2.1	1.9	1.4	2.5	2.0	3.1	3.1	2.9	2.1
Elongation at yield, %	23.0	20.8	21.1	22.8	20.6	20.6	17.1	**	**	**	24.3
Elongation at rupture, %	132	78	233	154	82	251	229	12	14	13	119.8
DTUL, 66 psi, °F	131	131	134	134	138	147	155	**	171	160	145
Gardner impact, 73°F, in.-lb	104	88	136	96	56	144	184	20	32	40	90.0
SG, g/cc	0.94	0.95	0.94	0.95	0.94	0.93	0.93	0.94	0.94	0.94	0.94

** Not tested

Table 2. Comparison of recovered PP/PE with commercial grades of PP & PE (Boedeker) (<http://www.boedeker.com/mtable.htm>), unless specified otherwise.

Property	PP-Homo Polymer	PP-Co Polymer	PP-FR	Standard PP-Co	LDPE	HDPE
MFR, (g/10 min), 230°C	0.5-136*					
Izod impact, ft-lb/in.	1.9	7.5	0.65	0.7	No Break	3
Flex Mod, 1,000 psi	180	160	145	120	200	125
Tensile Strength, 1,000 psi	4.8	4.8	4.3	5.2	2.0	4.6
Elongation, %	12	23	28	600	600	900
DTUL, °F @66 psi	210	173	106	210	110	--
SG, g/cc	0.905	0.897	0.988	0.90	0.92	0.95
Gardner impact, 73°F, in.-lb	0.9-22*					

* Data from http://www.ed-cam.com/materials/propylene_molded.asp. Ranges are for with and without additives.**Table 3.** Properties of PP/PE recovered by Salyp from different shredder residues.

Property	Salyp Data
MFR, (g/10 min), 230°C	2.3–4.6
Izod impact, (ft-lb/in.) 73°F	4.7–13.3
Flex mod., 1%, secant, 1,000 psi	81.7–116.5
Tensile strength at yield, 1,000 psi	2.4–2.9
Tensile strength at rupture, 1,000 psi	2.2–2.8
Elongation at rupture, %	19–57
DTUL, 66 psi, °F	150–169
Gardner impact, 73°F, in.-lb	190–240
Specific Gravity, g/cc	0.93

Table 4. Properties of recovered filled ABS, virgin ABS and blends of the two materials.

Property	Recovered Filled ABS	Virgin ABS (342 EZ)	90%Virgin/ 10% Recovered	75% Virgin/ 25% Recovered
MFR, g/10min, 230C, 3.8 kg	3.9	6.5	7.6	6.4
Izod Impact, ft.lbs./in., 73F	0.9	3.8	3.0	2.6
Flex Mod, 1% secant, ksi	324	296	299	302
Tensile strength at yield, psi	4982	5546	5392	5312
Tensile strength at rupture, psi	4956	4459	4544	4930
Elongation at rupture, %	2	56	9	6
DTUL, 264 psi, °F	162	165	166	164
Gardner Impact, 73F, in.lbs.	0	>320	32	8
SG, g/cc	1.08	1.05	1.05	1.06

- Polyethylene, low-density polyethylene [LDPE], high-density polyethylene [HDPE], ultra-high-molecular-weight [UHMW] polyethylene,
- Polypropylene,
- Polystyrene (general purpose, high impact), and
- Polyvinyl chloride (PVC).

The VRP had previously compiled physical properties data on selected polymers that were recovered during the U.S. field trials. These materials were recovered by disassembly. The data from these polymers are included in the database so that the physical properties of materials recovered by disassembly can be compared with those of materials that are recovered from post-shred operations, Table 5 (“USCAR U.S. Field Trial for Automotive Polymers Recycling,” by W.W. Gallmeyer, C.M. Duranceau, R. L. Williams and G.R. Winslow, SAE Paper # 2003-01-0645, 2003).

Table 5 gives the properties of PP dismantled from automobiles as part of the USCAR U.S. field trial. The recovered PP was reported to have a specific gravity of 0.915 and it is made of 99.2% PP, 0.4% PE and 0.4% ABS. The differences in the properties of the dismantled PP and the PP/PE recovered from shredder residue are also compared in Table 5.

The differences are not significant and do not affect the usefulness of the material. For example the specific gravity of the material recovered at Argonne is about 0.94 compare to 0.915 for the dismantled material. The MFR reflects the largest difference: 17 for one of the two samples of the dismantled flakes versus about 9.4 for the material recovered from shredder residue. The USCAR study also found that the properties of the dismantled PP responded as expected when additives were added to the PP. For example, the Izod increased from less than 2 ft-lb/in.

Table 5. Properties of PP Dismantled of Cars as Part of the USCAR U.S. Trial. (SAE Paper # 2003-01-0645, “USCAR U.S. Field Trial for Automotive Polymers Recycling,” by W.W. Gallmeyer, C.M. Duranceau, R.L. Williams and G.R. Winslow).

Property	Recovered, Extruded	Recovered Flakes, Sample #1	Average Properties of Recovered PP/PE*
MFR, (g/10 min), 230°C	19.9	17	9.4
Izod impact (ft-lb/in.) 73°F	1.8	1.8	8.6
Flx. Mod., 1%, secant, 1,000 psi	136.9	131.9	99
Tensile Strength at Yield, 1,000 psi	3.130	3.136	2.8
Elongation at Yield, %	19	18	24.3
Tensile Strength at Rupture, 1000 psi	2.388	2.384	2.1
Elongation at Rupture, %	59	60	119.8
DTUL, °F	129.7	136.5	145

* From Table 1

to about 11 when 10% of an impact modifier was added, and to about 14 when 20% were added (USCAR U.S. Field Trial for Automotive Polymers Recycling: Interim Findings”, by W. W. Orr, SAE Paper # 2000-01-0735, 2000).

Blending and Pelletizing of Recovered PP/PE

250 lbs. of PP/PE recovered by Argonne were blended with 750 lbs. of supplemental PP copolymer regrind for 15 minutes. The blended material was then run through an extruder and pelletized. The general appearance of the final pellet was excellent (Figure 1). Properties of the recovered material used in blending and the properties of the regrind and of the resulting pellets are shown in Table 6. Standard pelletizing conditions were used. Barrel heats were set from 365°F at the rear barrel zone and increased progressively to 390°F at the front, with six heat zones in between. Screen-changer and breaker-plate heats were set at 405°F, and die heats were set at 395°F. Melt temperature was recorded as 460°F, and drive load and screw speed were set at 60% and 67.5% of the maximum values, respectively. Material output was recorded as 1,400 lb/h. Extra-fine screen packs were used (20/20/20/60/100/20 mesh screens) to remove impurities because this was the first time this material has been tried.

In addition, while screen changes are typically performed at pressure differences between 500 psi and 1,000 psi, in this test, changes were performed when the pressure exceeded 500 psi to safeguard against puncturing a screen pack and losing material. Because extra-fine screen packs were used in the test, screen changes were required approximately every five minutes. The results indicated that the recovered PP/PE can be blended with other olefinic regrind and pelletized by using standard processes and equipment.

Mold Trials

Three types of auto parts were molded by MGV Enterprises by using Argonne-recovered PP/PE from shredder residue: knee bolsters, battery trays, and steering column covers (Figure 2). A standard molding machine was used in these trails. No changes to the standard conditions were required to run the recovered material. The limited testing done on the recovered PP/PE fraction shows that quality products, including auto parts, may be produced from the recovered materials. Additives and/or modifiers may be added to meet the specifications of some products.



Figure 1. Pelletized PP/PE product recovered from shredder residue.

Table 6. Properties of recovered PP/PE when mixed with regrind.

Property	Argonne, As Recovered Sample 9 (see Table 1)	Regrind As Is	Pelletized Blend
MFR (g/10 min), 230°C	8.7	3.1	9.2
Izod impact (ft-lb/in.) 73°F	2.8	13.6	10.4
Flex mod., 1%, secant, 1,000 psi	127	157	136
Tensile strength at yield, 1,000 psi	3.3	3.7	3.4
Tensile strength at rupture, 1,000 psi	3.1	2.9	2.3
Elongation at rupture, %	14	125	57
DTUL, 66 psi, °F	171	197	176
Gardner impact, 73°F, in.-lb	32	>320	132
SG, g/cc	0.94	0.91	0.92

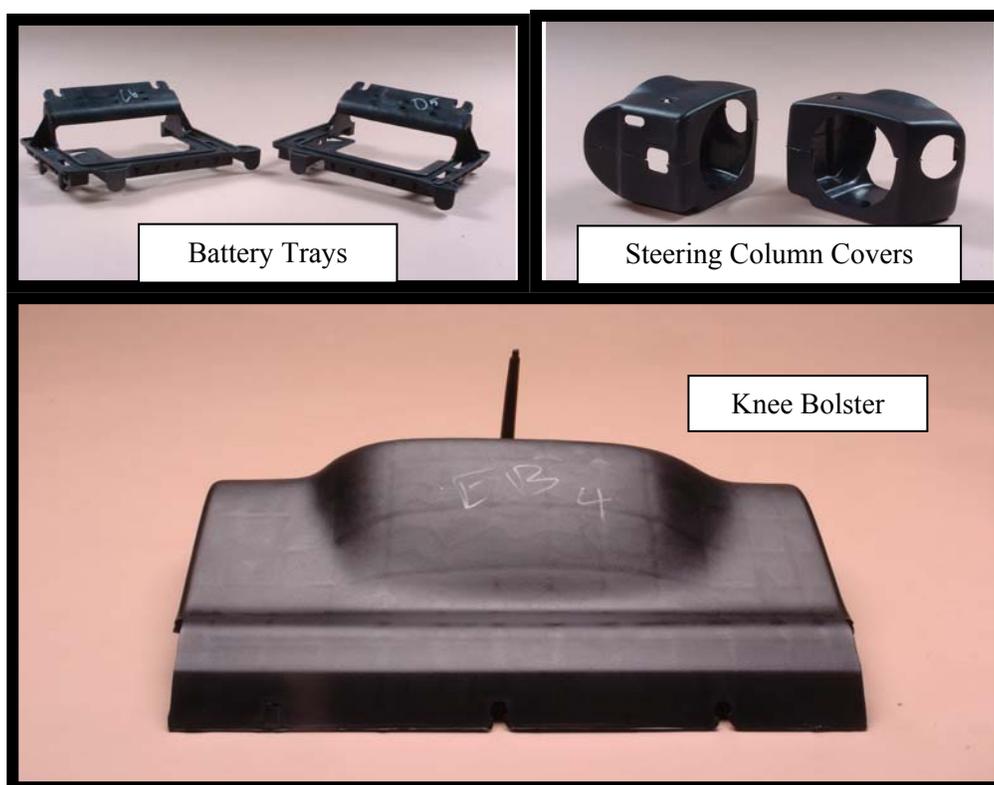


Figure 2. Auto parts molded from PP/PE recovered from shredder residue.

Recovered Rubber/Plastics Material

A mixed-rubber fraction with about 20% by weight mixed plastics was recovered. A sample of the recovered material was sent for testing by the “TireCycle” process used for recycling rubber. Preliminary tests done on the recovered material indicated that it may be suitable for making construction products, such as roofing shingles. The

presence of the plastics in the mixed-rubber material appeared to improve its overall properties, especially its stiffness.

¹ One of the formal consortia of the United States Council for Automotive Research (USCAR) set up by the “Big Three” traditionally U.S.-based automakers to conduct joint pre-competitive research and development.