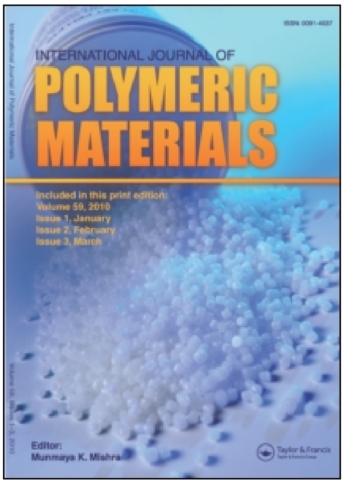

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Recycling the Mixed Plastics Fraction from Junked Autos IV. Pyrolysis Products of Polymer Wastes as Melt Flow Improvers and Compatibilizing Agents

Cornelia Vasile[ab]; Sumsak Woramongconcha[a]; Rudolph D. Deanin[a]; Abdelkader Chaala[ac]; Christian Roy[ac]
[a] Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, USA [b] "P. Poni" Institute of Macromolecular Chemistry, IASI, Romania [c] Chemical Engineering Department, Laval University, Quebec, Canada

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Recycling the Mixed Plastics Fraction from Junked Autos
IV. Pyrolysis Products of Polymer Wastes as Melt Flow Improvers and Compatibilizing Agents

CORNELIA VASILE[a,b], SUMSAK WORAMONGCONCHA[a],
RUDOLPH D. DEANIN[a], ABDELKADER CHAALA[a,c] and
CHRISTIAN ROY[a,c]

[a]*University of Massachusetts Lowell, Department of Plastics Engineering, 01854, Lowell USA;* [b]*Permanent Address, "P. Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, Ro. 6600 IASI, Romania;* [c]*Laval University, Chemical Engineering Department, Quebec, G1K 7P4, Canada*

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A procedure for recycling the light auto fluff has been proposed. In order to improve the melting flow and the characteristics of materials various pyrolysis waxes from other polymer waste have been employed.

Keywords: Recycling; plastics; autos; pyrolysis products

INTRODUCTION

Between 10 and 11 millions automobiles are shredded every year in North America. A large quantity of steel is recovered from the crushing operation. The automobiles carcasses are generally introduced into the shredding process through a hammermill. This operation pulverizes the carcass into small pieces. The heavier pieces fall through the mill onto a conveyer belt while the lighter fraction is recovered in a cyclone. This light fraction is known as automobile shredder residue.

Automobile shredder residue (A.S.R.), commonly known as fluff, is composed of components such as rolled steel, cast iron, forging, light metals, plastics, rubber, glass, paint and other materials such as wood, fibrous substances and leather. These residues are not biodegradable and are severely controlled in many countries. At present, plastic part and trims such as dashboard, door interiors, etc., represent approximately 100 Kg of each car.

As car makers continue to increase the amount of plastics they use in car parts, efforts to recover and recycle auto plastics are incresingly being made worldwide. The majority of automotive plastics is landfilled. Increasing public pressure is forcing the automotive and related industries to find new ways to divert the plastics away from disposal and into productive uses. Especially, the amount of automotive shredder residue produced by shredding operations has been steadily increasing as a result of the growing use of plastic components in automobiles [1].

Several recovery options to eliminate the disposal problems associated with this trend are summarized in Table I.

Recycling seems to be the most suitable method if the compatibility problems can be solved. In the case of the "light fluff" an improved thermoplastic flow is also required.

In our previous paper [2], several melt flow improvers as atactic polypropylene, polyethylene wax, linear low density polyethylene, etc. were tested in the recycling of the light fluff by injection molding.

This paper reports on the use of the pyrolysis products resulted from mixed plastic wastes as melt flow improvers for light auto fluff.

TABLE I Comparison of Polymer Waste Management Technologies

Technology	*Advantages*	*Disadvantages*
Recyle	Good Material Use	Compatibility problems Separation
Landfill	No Separation	Toxicity Lost Resources Space
Incineration	Energy Generation No Separation	Toxic Gases Location Lost Resources

2. EXPERIMENTAL

2.1. Materials

We investigated the light auto fluff of an Italian auto shredder which generally corresponds to the plastic part used by Italian automotive industry. According to the literature data [3] it contains a mixture of variable quantities of plastics, rubber, fibers and dirt.

The light autofluff sample tested in this study was essentially composed of plastic materials, free of large metallic scraps. The main plastic components are: polypropylene (PP), polyethylene (high density polyethylene HDPE), polyurethanes, ABS, nylons, unsaturated polyesters and polyvinyl chloride. This plastic fraction was ground two times in a Thomas Willey Laboratory mill Model 4 and washed with water to eliminate the dirt. For the second grinding a sieve of 2 mm was employed. The purified fraction had the following elemental composition: 68 wt % C, 11.02 wt % H, 2.01 wt % N, 6.62 wt % Cl, 0.41 wt % S, 10.98 wt % uncombustible residue – Table II. From this 10 wt % were acetone – extractible. This extracted part could contain a plasticizer, PVC and ABS because it had the following elemental composition: 74.5 wt % C; 10.71 wt % H; 1.95 wt % N; 11.34 wt % Cl and 0.64 wt % S. In its IR spectrum the presence of C—Cl bonds has been evidenced – Figure 1.

As melt flow improvers we tested three waxy pyrolysis products obtained from various polymer waste and pyrolysis conditions. Two waxes were obtained by vacuum pyrolysis of the electric cable wastes. The waste was pyrolyzed at a reduced total pressure of 20 KPa and at a temperature of 450°C (842 F) [4]. The pyrolytic wax was trapped at -15 (59 F) and -72°C (161.6 F). These samples were purified by repeated washing with acetone which solves and eliminates the low molecular compounds and some impurities. So two kinds of waxes were obtained corresponding to the above-mentioned cooling temperatures. They were labelled as "HARD" and respectively "SOFT" wax.

The unpurified hard and soft waxes were earlier characterized by FT-IR and NMR spectroscopic techniques [4]. It was reported that both waxes consist primarily of long and less branched-chain paraffins along with small amounts of long chain fatty acids and their corre-

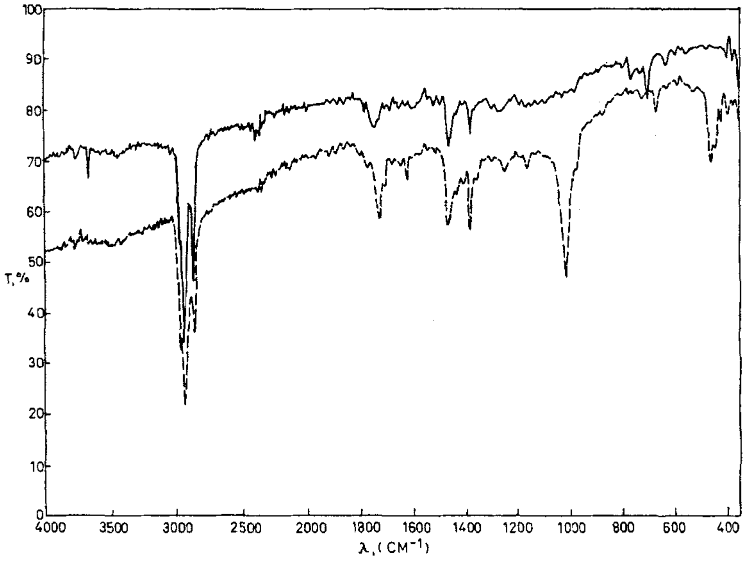

FIGURE 1 IR – spectra of acetone-extracted light auto fluff (------) and acetone soluble fraction (————).

sponding esters. In addition, unsaturates of the type $RCH{=}CH_2$, $RCH{=}CHR'$ and $RR'C{=}CH_2$ were observed. The amount of olefinic compounds in the soft wax was found to be relatively higher as compared to the hard wax and no aromatic hydrocarbons were detected. The NMR spectra of these waxes, revealed that the peak positions in the spectra are almost identical, however, the relative intensities are different. The ^1H-NMR and ^{13}C-NMR spectra suggest that the average length of the n-alkyl chains is about 21 for the soft wax and 26 for the hard wax. Therefore, the presence of high molecular weight hydrocarbons allows the wax to be potentially used as melt flow improvers and compatibilizing agents.

The third wax was obtained by pyrolysis of the disposable syringes at the normal pressure and the same pyrolysis temperature (450°C) [5]. It was subjected to the maleation reaction, resulting a content of grafted maleic anhydride of about 0.2 moles/100 g sample; the average nuber molecular weight was ~ 20 000. It consists in large fragments of polyethylene and polypropylene [6]. This wax was labelled as MAL.

TABLE II Characteristics of the Auto Fluff and Pyrolytic Waxes Used as Melt Flow Improvers

Sample	*Softening Point (°C)**	*Elemental Composition (%)* *C*	*H*	*N*	*O*	*S*	*Halogen*	*Uncombustible residue*
Auto Fluff	depends on composition see Figure 3.	68	11.02	2.01	6.96	0.41	6.62	10.98
SOFT	60–67	83.34	13.38	0	2.83	0.018	0.012	0
HARD	65–72	85.79	14.02	0.01	0.18	0.024	0.014	0
MAL	50–55	77.74	13.58	0	8.98	–	0.05	0

*By DSC method.

The waxes differ by softening point and elemental composition as it results from the data of the Table II. For details concerning their characteristics see refs. 4 and 6.

2.2. Preparation of the Light Auto Fluff/Pyrolytic Wax Mixtures

Before mixing both the light auto fluff and waxes were dried in an air circulating oven at 90°C for 5 hours in order to eliminate moisture.

A preliminary manual mixing at 70–80°C (158–176°F) has been performed. The quantity of incorporated wax in the shredded auto fluff varied between 5 and 10 wt %. After that, the final mixing was achieved on the Microprocessor Controlled Haake-Buchler Torque Rheometer System 40 at an average temperature of 198–200°C (388–392°F), 32 rpm, 6 minutes. Normally 40 g of mixture was used per test. Additions were complete in less than a minute.

The second procedure consisted of mixing on a two-roll-mill in the following conditions: front roll 190°C (388°F) rear roll 200°C (392°F), speed 10 rpm, friction 1.6 N1/N2, torque 10 Nm, shear rate 20 $\sec^{-1}$, time 2 min. The quantity of the waxes incorporated in the mixture by this procedure was 8 wt %. When the time was reached, the sample was removed with the cutting tool and taken off to cool down. This was pressed in a square aluminium frame with rectangular bar, tensile bar and circular mold. The temperature was 200°C (392°F) for 3 minutes after preheating 5 minutes.

The processing characteristics were tested by means of a Haake-Buchler Rheometer and a Tinius Olsen Extrusion (Piston) Plastometer (according to ASTM D 1238–86, condition 190/5 or 235/ 2.16 Kg). The melt index apparatus was operated at isothermal conditions.

2.3. Characterization Methods

DSC curves were recorded on a Du Pont 2000 TA instrument using a heating rate of 20°C/min (68°F/min), temperature range from −50 to 200°C (−58 to 392°F). Two or three runs were performed for each sample. Mechanical and electrical properties of the blends were tested in the following conditions:

- For *impact strength* a specimen was held as a vertical cantilever beam and was broken by a single swing of the pendulum with the of initial contact at a fixed distance from the specimen clamp and from the center line of notch.
- The *Izod test*, mehod A (ASTM D 256) was used. The load of pendulum was 0.9 Kg (2 lbs) and the notched specimens were tested (at least five samples) in the same conditions. The average impact strength was recorded.

Flexural strength and flexural modulus were measured by the three-point loading system utilizing two center loading on a simply supported beam (ASTM D 790, Test Method I, procedure A). Set load 90.7 Kg (200 lb), crosshead speed 5.1 cm/min (2.00 in/min) and span length 10.2 cm (4.00 in). The temperature and humidity were 25°C (77°F) and 50 % respectively. All data were recorded by computer acquisition connected to testing machine.

Tensile strength and tensile modulus. The tensile properties of plastics in the form of standard dumbbell-shaped test specimen were determined under condition (ASTM D 638, Type 1, specimen dimensions for thickness). Set load was 90.7 Kg (200 lbf), crosshead speed 0.508 Kg/min (0.200 in/min) and gage length 10.2 cm (4.00 in). The temperature and humidity were 25°C (77°F) and 50 % respectively. All data were recorded from computer acquisition connected to testing machine.

Volume resistivity. The current is read from the electrometer under a power supply voltage 500 volts to the circular specimen. The full scale current range is the range switch setting times the multiplier switch setting. The volume resistivity of a material is the ratio of the potential parallel to current in the material to the current density ($\rho = 3.53$ V/Ti I), where ρ = volume resistivity of the sample, in ohm. inches, V is the applied voltage from the power supply, in volts, Ti is the average thickness of the sample in inches and I is the current reading from the electrometer, in amperes.

Heat deflection temperature (*HDT*). The specimen is placed in the grips attached to the fixed and movable members. It is then immersed into the bath at a temperature of approximately 20°C (68°F) below the temperature at which the specimen is expected to begin to deform. A stress of 1.78 MPa (264 psi) is applied. Five minutes after applying the load, the pointer is adjusted to zero and the oil heated at 2.0–0.2°C/min (35.6–3.56°F/min). The temperature was recorded when it reached the HDT. The above procedures were repeated using the same material under a stress of 0.455 MPa (66 psi) (ASTM D 638).

3. RESULTS AND DISCUSSION

The light auto fluff without waxes could not be processed on Haake Buchler Rheometer or tested on Tinius Olsen extrusion Plastometer. The auto fluff/wax blends had similar curves both in the torque and totalized torque values – Figure 2.

The data obtained by means of Tinius Olsen extrusion plastometer are given in the Table III.

In both working conditions used at all concentrations, the values obtained with the three waxes were similar. The incorporation of waxes increases the flow rate and density, decreasing viscosity. However, this depends on the characteristics of the wax incorporated. The SOFT wax was found to be the most effective in enhancing the flow rate. On the other hand, the HARD wax influenced much more on the viscosity and density of the blends. The MAL wax was less effective. It can be concluded that the pyrolytic waxes acted as melt flow improvers, without important differences regarding the type of the wax.

The sheet obtained on the basis of these blends had satisfactory mechanical and good dielectric properties as it results from Table IV.

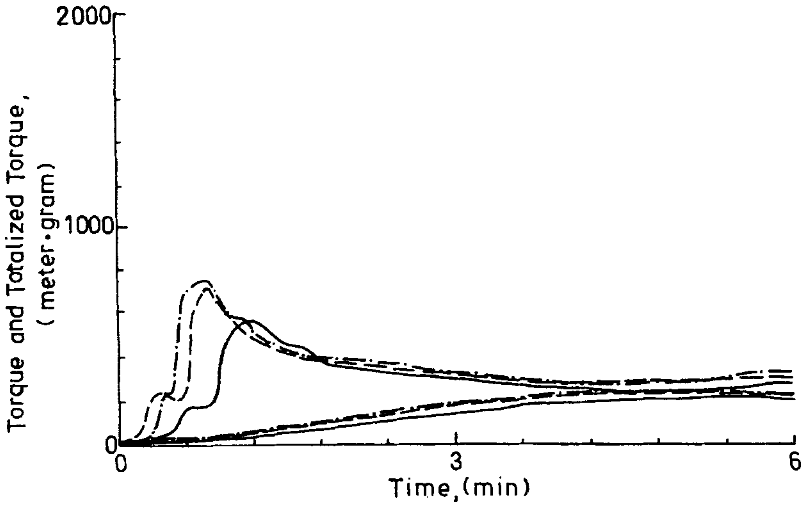

FIGURE 2 Torque – time plot for the mixture light auto fluff with 8 wt % HARD (———) and 11 wt % SOFT (–·–·–) or MAL (-------) wax.

TABLE III Extrusion (piston) Plastometer data for fluff auto/pyrolytic wax blends

Characteristic	*HARD*	*SOFT*	*MAL*
	5 wt%, Condition 235/2.16		
Shear Stress (Pa)	19587	19587	19587
Shear Rate (sec^{-1})	23050	28174	28114
Viscosity (Poise)	8490	6950	6960
Density (g/cm^3)	0.695	0.666	0.644
Flow Rate (g/10 min)	9.605	10.432	9.908
	5 wt%, Condition 190/5		
Shear Stress (Pa)	45341	45341	45341
Shear Rate (sec^{-1})	12584	15382	14013
Viscosity (Poise)	36000	29470	32350
Density (g/cm^3)	0.859	0.824	0.876
Flow Rate (g/10 min)	6.898	6.933	6.715
	11 wt%, Condition 190/5		
Shear Stress (Pa)	45341	45341	45341
Shear Rate (sec^{-1})	27920	32492	24180
Viscosity (Poise)	16239	13950	18750
Density (g/cm^3)	0.865	0.862	0.880
Flow Rate (g/10 min)	13.24	15.32	11.65

TABLE IV Mechanical and Dielectric Properties of the Auto Fluff/Pyrolytic Wax Blends*

Property	*Value*
Notched Izod Impact Kg/cm (ft.lb/inch)	*5.44 (1.26) complete break*
Flexural Properties	
Load at yeild max N (lbf)	6.05 (1.36)
Stres at yield MPa (psi)	7.2 (1044.4)
Strain at yield cm/cm (in/in)	0.041 (0.041)
Modulus MPa (psi)	6.2 10^2 (89, 260)
Tensile Properties	
Stress at Max Load MPa (psi)	48 (6,964)
Strain at Max Load, cm/cm (in/in)	0.044 (0.44)
% Strain at Max Load %	4.4
Stress at Ultimate MPa (psi)	4.8 (695.3)
Strain at Ultimate cm/cm (in/in)	0.044 (0.044)
Modulus MPa (psi)	3.23.10^2 (46, 933)
Volume resistivity ohm.cm (ohm. inches)	3.4 10^{15} (8.748 10^{13})
5. Heat deflection temperature	
0.455 MPa (66 psi)	64°C
1.82 MPa (264 psi)	49°C

*All values are average of at least five determinations.

DSC curves were very useful both to identify several components of the light auto fluff and also to appreciate the effect of the pyrolytic wax incorporation.

The curve in Figure 3 present two melting peaks which can be attributes to the HDPE and (PP) and also three or four glass transition temperatures at 42; 73; 96 and 107.3°C [7, 8]. These glass temperatures could be attributed to the following components of autofluff as polyurethanes, thermoplastic polyesters (PET has Tg = 67°C, and PBT has Tg of 22–43°C), polyoxymethylene has Tg of 13°C, polyvinylchloride has Tg of 80°C, and ABS [8] has Tg > 100°C. Knowing from literature [7] the melting heat for HDPE of ~ 287 j/g and 209 j/g for IPP; it is possible to estimate the quantity of the first two mentioned polymers from the investigated light auto fluff. This would give erroneous values if the wax is compatible with polyolefins, the wax generally decreases the melting heat and temperature. The average values obtained was of ~ 13 wt % HDPE and about ~ 2–3 wt % IPP in

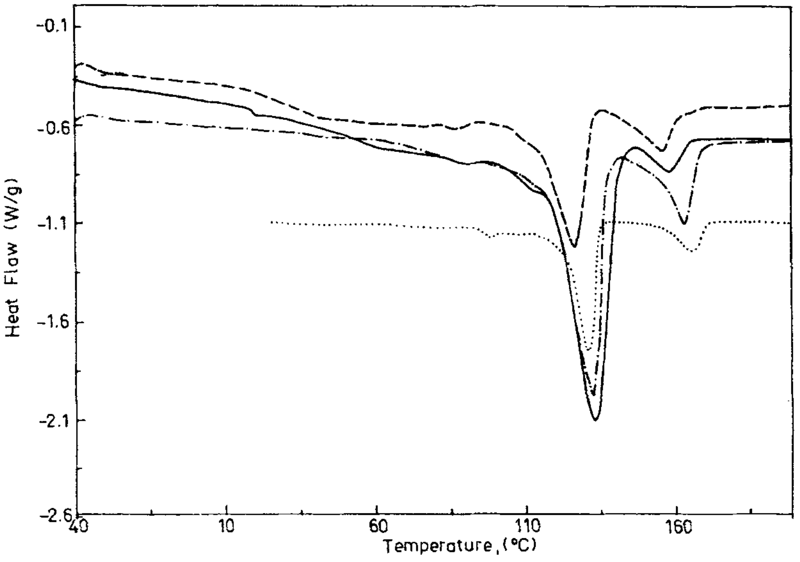

FIGURE 3 DSC curves of the mixtures of light auto fluff with (———) HARD; (–·–·–) SOFT and (-------) MAL pyrolytic waxes and (–·–·–) auto fluff after acetone extraction.

accordance with some literature data [3]. The determination was performed on the auto fluff after extraction with acetone.

The maleated pyrolytic wax decreased both the melting temperature from 133 to 126°C and the melting heat from 39 *j*/g to 21 *j*/g for the peak corresponding to HDPE. SOFT and HARD waxes also reduced the second melting temperature but to a lesser extent as compared to MAL addition. Therefore, it can be concluded that MAL contributed more than the other two pyrolytic waxes to the formulation of the mixture with auto fluff. Figure 3 also showed that the second melting temperature corresponding to the polypropylene melting temperature was decreased on addition of MAL wax. This last wax showed a better compatibility with polymer components of auto fluff. The second melting temperature was also decreased by the incorporation of the maleated wax from 163 to 156°C, but the melting heat was less influenced. The scattering of DSC results could be due to the inhomogeneity of the samples that influenced also the sampling operation for the DSC analysis.

CONCLUSION

The use of pyrolytic waxes obtained by vacuum and atmospheric pyrolyses of cable wastes and disposable syringes improved the processing characteristics of the light autofluff studied. The viscosity, the melting temperature and the melting heat of the blends were reduced. Pyrolytic waxes also assured the obtainment of the materials with satisfactory mechanical and electrical properties.

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