RECYCLING OF MARINE PLASTICS DEBRIS THROUGH MELT REPROCESSING: A CASE FOR LOST OR ABANDONED FISHING GEAR

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ABSTRACT

In attempts to offer a technological solution to the marine plastic debris problem, the Polymer Processing Institute in collaboration with the New Jersey Marine Sciences Consortium began in January 1989 a 2-year research program that focuses on the collection, characterization, and subsequent recycling of unusable plastic fishing gear. The present paper contains initial data developed during the first quarter of 1989 (Phase I) on netting containing nylon-6, nylon-6,6, and polypropylene plastics. Molecular weight determination and thermal analysis suggest that none of the nylons are badly degraded; thus, the nets could be reprocessed without difficulties in the recycling extruder. However, the presence of fiber coatings (e.g., "green enamel," "tar") was found to complicate the polymer characterization and to interfere with the recycling process. The fact that these coatings cannot be easily removed suggests that further work is required to determine their possible adverse effects on the processing and product characteristics. The present paper also provides a complete description of the work planned for the two successive phases of the project.

INTRODUCTION

Among the various marine plastic debris items, abandoned or lost fishing gear is a major pollutant adversely affecting marine life and disturbing the ecological equilibrium. Recent estimates of the National Academy of Sciences bring the amount of fishing gear lost in the sea to about 135,000 metric tons/annum (Lautenberg 1987). Many marine species die from entanglement in such plastic debris. It is believed that 30,000

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northern fur seals, *Callorhinus ursinus*, and at least 250,000 birds die each year in nets laid by salmon fishermen, as well as in other debris. The problem appears to become increasingly important as a result of the recent deployment in the North Pacific of huge drifting nets stretching up to 30-50 km (Shabecoff 1989). If these lightweight monofilament nets are discarded or lost, they do not degrade but continue to drift unless retrieved.

The Polymer Processing Institute, in a joint effort with the New Jersey Marine Sciences Consortium (NJMSC), began in January 1989 a 2-year program having as an ultimate goal the development of cost-effective methods for complying with the prohibition of marine pollution. The project is funded by the Saltonstall-Kennedy Act and will attempt to offer a technological solution to the marine plastic debris problem. Its specific objective is to establish incentives for recycling lost or abandoned fishing gear such as nets, lines, and ropes by demonstrating that these materials can be converted into useful products when melt reprocessed.

DESCRIPTION OF THE RESEARCH PROJECT

This project consists of two phases: Phase I, completed in January 1990, concentrates on the collection, on a national level, of discarded fibrous fishing gear, followed by separation, identification, and subsequent chemical and physical characterization of the plastics involved. Preliminary data indicate that the major types of plastics to be recovered are nylon-6, nylon-6,6, and polypropylene (PP), all possibly contaminated or degraded as a result of prolonged exposure in the marine environment. The extent of environmental degradation and its effect on rheological and mechanical properties will dictate the design of the melt reprocessing experiments of the next phase.

In Phase II of the project (to be completed in its second year), various processing methods will be evaluated with the final objective of producing molding materials with properties equivalent or superior to those of virgin resins. Reprocessing will be conducted in a twin-screw extruder and will involve blending of the recovered netting with virgin resin, blending with other recycled resins of different chemical structure, or chemical modification. It is expected that these methods will upgrade the properties of the recovered plastics and produce value-added compounds. At this stage of the project, potential markets for the recycled product will be identified as well as companies interested in establishing facilities for recycling and reprocessing. Based on the analysis of the collection and separation data, the possible financial incentives that will encourage recycling will be estimated.

EXPERIMENTAL RESULTS

Characteristics of Collected Fishing Gear

Samples of used and new fishing nets were supplied by NJMSC. The used samples that were collected during the first quarter of Phase I varied

widely in characteristics such as net mesh size, filament diameter, type of coating, degree of exposure, polymer type, and site of collection. All samples were classified and characterized as shown in Table 1. The majority of the collected nets were relatively clean, with minimum visible gross contamination from either organic or inorganic matter.

Identification of Plastics and Contaminants

The identification of plastics and their contaminants was undertaken in order to establish the proper reprocessing conditions and to minimize any possible adverse effects of the contaminants on processing and long-term polymer stability.

Identification methods used for plastics were infrared (IR) spectroscopy, melting temperature determination, and solubility measurements (the latter only for nylons). The preferred analytical method was IR spectroscopy, since the presence of coatings (e.g., "green dip," "tar") often interfered with the melting temperature and solubility determinations. The IR spectra were obtained on films cast on a AgCl plate from solutions of 90% formic acid (nylons) or hot xylene (polypropylene). Table 2 summarizes the identification results for all plastics. It is shown that nylon-6 and nylon-6,6 are the materials of choice for nets, whereas polypropylene is used for ropes and lines. It is interesting to note that the green-dipped twine in 88-2 contained both nylon-6 and nylon-6,6 fibers; by contrast, the attached repair portion was only nondipped nylon-6,6 fibers.

A thorough analysis and identification of contaminants was not completed at this stage of the project. Some surface elements that were identified by combined scanning electron microscopy and energy dispersive x-ray analysis included silicon and iron on the 88-2 fibers. These could correspond to sand and rust, respectively. Also, the "green dip" on 88-2 and 89-2 and the tar coating of 89-1 contain infusible cross-linked organic materials that turn black (degrade?) when heated near the melting temperature of nylons. The coatings level was not precisely determined. Preliminary thermogravimetric data suggest that the green dip content is at least 3-5%, whereas the tar content is at least 1% of the weight of the fiber.

Separation of Individual Plastics and Removal of Contaminants

Separation of the individual identified plastics present in the nets or the net and line combinations was not considered necessary at this stage of the project, since the proximity in chemical structures and melting points could allow these polymers to be eventually processed as blends (e.g., nylon-6 with nylon-6,6 in sample 88-2, nylon-6 with PP in sample 88-3). Floats, buoys, and lead-containing lines were the only articles that were removed. With respect to contaminant removal, the insolubility of the "green dip" and "tar" coatings in either water or organic solvents appears to preclude their economical separation from the fibers. Also, any water treatment of the fibers by slurrying under agitation does not seem to be beneficial in improving their thermooxidative stability, as certain

Table 1.--Classification and description of used and new fishing gear received in 1988 and first quarter 1989.

Designation	Type or description	Color	Mesh (cm)/ diameter (mm)	Other information
Used				
88-1	Fyke(?) net with braided line attached; ca. 14 kg	Dark brown	Net: 7.5/1.2 Line: --/6.3	Brittle, dusty, badly degraded.
88-2	Trawl net, apparently dipped in green "enamel" and repaired with non-dipped net; ca. 50 kg	Dipped part: green or faded green Repaired part: off-white	8.3-10.5/3	Collected in New Jersey; variable in color, mesh and diameter; tar patches.
88-3	Monofilament gillnet with braided line attached; ca. 10 kg	Net: natural Line: green	Net: 8.3/0.37 Line: --/6.3	Collected in New Jersey.
89-1	Trawl net [30-ft flat otter] dipped in tar; ca. 25 kg	Black	4.5/1.2	Bought in Connecticut; used once per month for 1 year, stored in shed, repaired.
89-2	Trawl net [30-ft flat otter] dipped in green enamel; ca. 25 kg	Light green	3.8/1.2	Bought in Mississippi; used twice per month for 1 year, stored in shed.
New				
89-3-V	Twine net sample	Off-white	3.8/1.6	None.
89-4-V	Multifilament net sample	Light green	12.7/0.8	None.
89-5-V	Braided net sample	Light green	20/2.5	None.
89-6-V	Twine net sample	Blue	3.4/1.6	None.

Table 2.--Identification of polymers (by infrared spectroscopy, and solubility and melting temperature measurements) in used and new fishing gear.

Gear designation	Type of polymers
Used	
88-1	
Net	Not identified
Line	Not identified
88-2	
Green net	Nylon-6 and nylon-6,6
Faded green net	Nylon-6 and nylon-6,6
Repair net	Nylon-6,6
88-3	
Net	Nylon-6
Line	Polypropylene
89-1	
Net	Nylon-6
89-2	
Net	Nylon-6
New	
89-3-V	Nylon-6,6
89-4-V	Nylon-6
89-5-V	Polypropylene
89-6-V	Polypropylene

experiments showed. Thus, the only treatment prior to characterization was the removal of loose surface debris by air jetting.

Characterization of the Recovered Nylon Plastics

The characterization of the recovered plastics could provide valuable information on the extent of their degradation and their thermooxidative stability during reprocessing.

Table 3 summarizes the intrinsic viscosity and molecular weight data of all nylon polymers including three virgin materials in pellet form. Since the exact molecular weight of a fiber prior to exposure is not known, the extent of degradation can be only approximated. Thus, by comparing the intrinsic viscosities of the recovered polymers with those in the new nets and certain virgin pellets, one can conclude that with the possible exception of the "88-2 faded green" none of the other used nets showed extensive degradation of molecular weight. Thermal analysis (Table 4) by differential scanning calorimetry (DSC) and thermal stability investigations (Table 5) by thermogravimetry (TGA) tend to support the above conclusion. Differences in fusion and crystallization behavior between the fibers in the used or new net and the commercial pellets reflect largely the presence of

Table 3.--Intrinsic viscosity and molecular weight of nylon polymers: comparison of used and new fishing nets with commercial polymer pellets.

Sample designation	Intrinsic viscosity η^a(dl/g)	Molecular weight (M_v) Nylon-6	Nylon-6,6
	Used nets		
88-2			
Green	1.45	[b]43,840 or	21,480
Faded green	1.07	[b]30,380 or	14,140
Repair	1.31		18,710
88-3	1.52	46,520	
89-1	1.42	42,660	
89-2	1.31	38,840	
	New nets		
89-3-V	1.44		21,460
89-4-V	1.61	50,090	
	Pellets		
Zytel 101-F	1.16		15,760
Capron 8207-F	1.47	44,730	
Capron BHS-D	1.70	53,440	

[a]η = Measured in 90% formic acid solution at 25°C.
[b]Figures given refer to the individual polymers since both nylons are present in these nets in unknown ratios.

Table 4.--Thermal analysis (differential scanning calorimetry (DSC)) of nylon polymers: comparison of used and new fishing nets with commercial polymer pellets. Note: Heating, cooling, and reheating at 20°C/min; fusion data on second heating.

Polymer	Fusion temperature onset/maximum (°C)	Heat of fusion (cal/g)	Crystallization temperature onset/maximum (°C)	Heat of crystallization (cal/g)
		Nylon-6		
Used nets				
88-2				
Green	211/222	10.7	187/181	-12.1
Faded green	212/223	10.9	187/182	-12.4
88-3	202/215	10.4	173/164	-11.4
89-1	208/221	8.3	181/174	-10.4
89-2	195/200	10.2	184/176	-12.0
New nets				
89-4-V	205/220	9.9	186/171	-12.1
Pellets				
Capron 8207-F	209/222	12.8	180/168	-13.4
Capron BHS-D	212/226	11.4	172/163	-10.7
		Nylon-6,6		
Used nets				
88-2				
Repair	253/263	16.2	231/227	-12.7
New nets				
89-3-V	250/259	11.8	229/222	-12.9
Pellets				
Zytel 101-F	256/265	11.3	226/214	-14.0

coatings, rather than extensive polymer degradation. For example, coatings and contaminants or their residues appear to act as nucleating agents, as evidenced by the higher crystallization temperatures of the polymers in all the coated used and new nets. Also, extensive weight losses in TGA are probably associated with the early decomposition of the coatings and contaminants and not with that of the degraded polymer itself (with the possible exception of the "88-2 faded green" sample). Table 5 also shows that the thermal stability of the samples is practically independent of the type of test atmosphere (nitrogen versus oxygen).

Table 5.--Thermal stability (thermogravimetry (TGA)) of nylon polymers: comparison of used and new fishing nets with commercial polymer pellets.

Polymer	Standard TGA[a]				Isothermal TGA[a]		
	Onset decomposition temperature (°C)		Temperature at 10% weight retention (°C)		Isothermal temperature (°C)	Weight % decrease after 15 min	
	Nitrogen	Oxygen[b]	Nitrogen	Oxygen[b]		Nitrogen	Oxygen
Nylon-6							
Used nets							
88-2							
Green	429	NM	560	NM	225	4.03	4.84
Faded green	396	NM	673	NM	230	1.35	1.48
88-3	445	NM	513	NM	225	0.33	0.42
89-1	459	NM	519	NM	230	0.91	1.06
89-2	426	NM	525	NM	230	2.71	3.49
New nets							
89-4-V	459	NM	513	NM	230	0.26	0.38
Pellets							
Capron 8207-F	466	453	513	497	225	0.25	0.25
Capron BHS-D	471	NM	506	NM	230	0.62	0.67
Nylon-6,6							
Used nets							
88-2							
Repair	449	NM	530	NM	270	1.18	4.31
New nets							
89-3-V	451	NM	514	NM	270	1.23	1.75
Pellets							
Zytel 101-F	439	436	503	512	270	0.33	0.58

[a]Standard TGA at 40°C/min; in isothermal TGA temperature reached withn 2 min.

[b]NM indicates not measured.

Experiments on Net Size Reduction and Extrusion Reprocessing

Attempts to chop net 88-2 into smaller pieces in a laboratory granulator were not successful even in the presence of dry ice. However, it was possible to feed continuously the same net into the hopper of a single-screw extruder and produce an extrudate that could be pelletized. The extrudate was black in color, presumably as a result of the decomposition of the fiber coating. Further experiments are under way in order to produce solid particles with dimensions suitable for feeding in polymer processing machinery such as extruders or injection molding machines.

CONCLUSIONS

The identification results on samples of unusable fishing gear collected during the first quarter of 1989 indicate that the major plastic involved are nylon-6, nylon-6,6, and to a lesser extent polypropylene. Th initial characterization results of the exposed nylons are encouraging: it appears that none of the nylons are badly degraded in terms of reduced molecular weight or loss of thermooxidative stability. This could mean satisfactory processing characteristics during remelting of the net in the recycling extruder. The presence of fiber coatings that cannot be easily removed tends to complicate not only identification and characterization, but also the reprocessing behavior of the nylon nets. Our future efforts will include the complete analysis and characterization of typical commercial fiber coatings for a better understanding of their effects on processing. Other research areas addressed during this phase of the project include the full characterization of the collected exposed polypropylene gear and the investigation of net size reduction methods.

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