Chelsea Center for Recycling and Economic Development

University of Massachusetts

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Potential End Uses For Polyester Fiber Waste:

A Laboratory Study

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POTENTIAL END USES FOR POLYESTER FIBER WASTE
A LABORATORY STUDY

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Chelsea Center for Recycling and Economic Development
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The Chelsea Center for Recycling and Economic Development, a part of the University of Massachusetts' Center for Environmentally Appropriate Materials, was created by the Commonwealth of Massachusetts in 1995 to create jobs, support recycling efforts, and help the economy and the environment by increasing the use of recyclables by manufacturers. The mission of the Chelsea Center is to develop an infrastructure for a sustainable materials economy in Massachusetts, where businesses will thrive that rely on locally discarded goods as their feedstock and that minimize pressure on the environment by reducing waste, pollution, dependence on virgin materials, and dependence on disposal facilities. Further information can be obtained by writing the Chelsea Center for Recycling and Economic Development, 180 Second Street, Chelsea, MA 02150.

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1. Introduction

In early 2000, the Chelsea Center launched a research project to investigate the potential end uses of a polyester (PET) fiber waste, generated in the manufacture of Polartec® fleece fabrics, made by Malden Mills, of Lawrence, Massachusetts. The Chelsea Center contracted with Plastics Engineering Professor Robert Malloy of UMass Lowell to lead the study. The study was conducted in four phases:

1. Melt Process Feasibility
2. Glass Fiber and Bottle Scrap Additives
3. Fleece/Polycarbonate Blends
4. Solid Stating

During the third phase of the project, with support from the Chelsea Center, Malden Mills hired an intern to look at the marketability of the pellets and molded samples made from the fiber waste.

2. Phase One – Melt Process Feasibility Study

In this first phase the feasibility of melt processing the shear waste and baseline properties were established.

Small-scale extrusion studies were run to establish processing temperatures. Approximately 30 pounds of waste were melt processed for this study. Pre-drying was carried out at 350°F for 12 hours before all melt processing operations. The material could be extruded at temperatures as low as 430°F, however, the extrudate was only partially melted and many fibers appeared to be unmelted. Ultimately, a melt temperature in the range of 530°F was chosen as optimum.

Once this was established, the three bags of material were dried and extruded without additives for in-line strand pelletization. The viscosity of the melt was extremely low and continuous pelletization was not possible with our equipment. Thus, the strands were extruded into a water bath for cooling and eventual off-line "granulation," resulting in a somewhat irregular shape to the granules. The granular material was then redried and injection molded to produce test specimens.

Unmodified PET is never an easy material to mold. It is very fluid and has a small process window. The samples were run in a cold (50°F) mold to keep the PET amorphous, as is the normal practice with unfilled PET. A sharp melting point and low viscosity make PET very tough to mold. However, even using less than optimum small scale molding equipment, relatively good samples were obtained, showing that the material can be molded. The mechanical properties of the molded parts are shown in the following table:

Test Method & Property	
ASTM D638	
Ultimate Tensile Strength	5740 psi, 39.6 Mpa
Ultimate Elongation (%)	3.6
Initial Tensile Modulus	193,000 psi, 1,331.0 MPa
ASTM D256	
Notched Izod Impact Strength (ft.lbs./in.)	0.36
Un-notched Izod Impact Strength (ft.lbs./in.)	3.22

3. Phase Two – Glass Fiber and Bottle Scrap Additives

The following three formulations were evaluated in Phase Two:

Formulation 1: 100% fleece scrap (as a control)
Formulation 2: 75% fleece scrap / 25% clean recycled PET bottle scrap
Formulation 3: 80% fleece scrap / 20% short glass fiber

All formulations were first dried and extruded using a single screw extruder to produce "compounded" material for granulation. The granules were re-dried, injection molded and tested. The properties evaluated included tensile (ASTM D638) and Izod impact (ASTM D256). All materials were molded and tested at the same time in order to minimize testing related variation. The results reported are the average of five replicates.

Formulation 1:
As in Phase One, the control formulation was very low viscosity, stiff and relatively brittle. The material exhibits stiff – brittle behavior with no yield, with properties similar to a general purpose polystyrene. It can be molded, but would have limited application. It is possible that some of the brittleness could be the result of moisture re-absorption before extrusion (due to the high surface to area ratio of the material), since even small amounts of moisture in the granules can have a large effect on the final properties of PET. It could be due to contamination or the low intrinsic viscosity (IV) of the PET scrap to begin with. The IV test results done by UMass Dartmouth (see section on test results test results) have helped in the interpretation of these results. The IV results shown below do indicate that a significant reduction in average molecular weight in going from fiber to granule to molded part. It is likely that better properties could be obtained if better (a fully closed desiccant) drying equipment was used.

Formulation 2:
The purpose of incorporating 25% bottle grade PET was to increase the average IV of the material and hence its properties using a material that should be compatible and inexpensive. Bottle grade PET has a higher IV than fiber grade (though it does lose some IV during processing and the clean, pelletized material used had two heat histories). The compounded extrudate did appear to be slightly more viscous than the control, but no improvement in properties was observed. A fairly

significant increase in break elongation and Izod impact strength was expected, however, the properties of this blend were a little weaker and a little more brittle than the control. (This may actually fall within the overall test error.) Possible reasons for these results may be incompatibility between the fiber and the flake, or the 25% level of flake may not be enough. This warrants additional investigation.

Formulation 3:
There are a number of plastic molding materials on the market based on recycled (bottle grade) PET that are reinforced with short glass fiber. In general, glass fiber is added to stiffen the formulation and increase thermal properties. As a side effect, the addition of glass fibers does reduce ductility. Most recycled PET has enough toughness that the glass fiber formulations are still useful. In this case, the control (unmodified) formulation is already quite brittle, with an ultimate elongation (UE) of only 4.8%. The glass fiber formulation has a very low UE of only 2.8%. It is stiffer (higher modulus), but still very brittle – probably too brittle for most applications.

3.1 Test Results – Phase Two

Test Method & Property	**Formulation**		
	1 100% fleece scrap (control)	**2** 75% fleece scrap 25% clean recycled PET bottle scrap	**3** 80% fleece scrap 20% short glass fiber
ASTM D638			
Ultimate Tensile Strength	6800 psi 46.9 MPa	6630 psi 45.7 MPa	5485 psi 37.8 MPa
Ultimate Elongation (%)	4.8	4.14	2.8
Initial Tensile Modulus	142,000 psi 979.3 MPa	144,000 psi 993.1 MPa	196,000 psi 1,351.7 MPa
ASTM D256			
Notched Izod Impact Strength (ft.lbs./in.)	0.30	0.25	0.63
Un-notched Izod Impact Strength (ft.lbs./in.)	2.90	2.83	2.30

Intrinsic Viscosity Testing – University of Massachusetts Dartmouth

Four configurations of PET fleece waste were sent to UMass Dartmouth for Intrinsic Viscosity (IV) testing – fiber, granule, bar and sheet. Each sample was dissolved in m-cresol in a volumetric flask at 60 C overnight. An Ubbelohde viscometer was then used to measure the flow time of the m-cresol solution of all four samples at 25 C. The following equations were used to obtain the IV (η) of each sample:

Relative viscosity, $\eta_r = \eta/\eta_o = t/t_o$, where t and t_o are the flow time of the sample solution and pure m-cresol liquid under the same conditions, respectively

Specific viscosity, $\eta_{sp} = \eta_r - 1$

Intrinsic viscosity, $\eta = \lim (\eta_{sp}/C)_{c\to o}$, where C is the sample concentration in m-cresol in g/cm^3

Intrinsic Viscosity of PET Fleece Waste

Units	Tested Values				Typical Values	
	Fiber	Granule	Bar	Sheet	Bottle grade	Fiber grade
dl/gr	0.578	0.517	0.397	0.428	0.7	0.58-0.65
(cm^3/g)	57.824	51.653	39.659	42.747	70	58-65

These results show that (i) the IV (or average molecular weight) of the fiber material is quite low relative to the bottle grade PET, and (ii) the IV of the PET decreased as the number of heat histories increased. Some loss in IV is always expected in processing, however, IV reductions of 0.5 - 1.0 dl/g per heat history are more than one should see with proper processing. It is apparent that the method used to dry the fleece scrap and granules was not optimum. The loss in IV, hence the loss in properties, would be minimized if better drying equipment was utilized. Eliminating the intermediate pelletizing process would also help maintain the IV, however, direct processing or product manufacturing using the bulky fleece scrap would be very difficult.

4. Phase Three – Fleece Scrap / Polycarbonate Blends

The following three formulations were injection molded into standard ASTM test bars for testing in Phase Two:

Formulation 4: 100% fleece scrap (as a control)
Formulation 5: 90% fleece with 10% injection molding grade polycarbonate (GE Lexan 141 - 10g/10min MFR)
Formulation 6: 70% fleece with 30% polycarbonate

The molding trials were conducted at barrel temperatures in the 490-520°F range. The extruded and "granulated" material was dried for six hours at 300°F prior to injection molding. The mold temperatures used for injection molding were kept low at 115°F. At this mold temperature and part thickness (3.2 mm), it would appear that the fleece (PET) did not crystallize during molding (i.e. it cooled in the amorphous state). PET is a unique material in this way as it can be molded amorphous or it can crystallize under certain molding conditions (eg., a very thick part with a thick wall {> 4 -5 mm})

The conclusion that the molded fleece is amorphous is based upon several factors. First, the mold shrinkage for the material was very low, only about 0.004-0.005 inch/inch. If it had crystallized it would have shown greater mold shrinkage. After molding, oven heat age testing was done. In one test, the sample was placed in an oven at 100°C, and showed another 0.014 in/in shrinkage (a total of 0.019 in/in including mold shrinkage) after 12 hrs in the oven. The additional shrinkage indicates the heat-aged sample crystallized (as expected) indicating that the unaged molded sample had not.

A second heat age test run at 71°C (160°F) also resulted in shrinkage but at a much slower rate. The first table in the Appendix shows how the sample changed its dimensions over time at 160°F. These dimensional changes would limit the use of this material at temperatures in this range. The material should be stable at temperatures less than 140°F but this should be confirmed.

The last test that shows the amorphous nature of the parts is a differential scanning calorimetry (DSC) test. Unaged (*as molded*) and heat aged (12 hr at 100°C) samples were heated in a DSC instrument. The DSC heat flow - temperature curves are in the Appendix. The *as molded* sample shows a "crystallization" peak at 110°C (heat is given off as it crystallizes), while the heat aged sample does not show the crystallization peak meaning that it had already crystallized in the oven. This is pretty clear evidence that the *as molded* sample is amorphous.

Physical property tests including tensile tests in accordance with ASTM D638, flexural tests in accordance with ASTM D790, and Izod impact tests in accordance with ASTM D 256, were performed on the molded samples. All samples showed rigid type behavior without a yield.

4.1 Test Results – Phase Three

Test Method & Property	**Formulation**		
	4 100% Fleece Scrap	**5** 90% Fleece Scrap 10% Polycarbonate	**6** 70% Fleece Scrap 30% Polycarbonate
ASTM D638			
Ultimate Tensile Strength	5400 psi 37.2 MPa	6040 psi 41.7 MPa	8280 psi 4 1.7 MPa
Ultimate Elongation (%)	4.1	4.7	6.3
ASTM D790			
Initial Flexural Modulus	271,000 psi 1870 MPa	293,000 psi 2020 MPa	302,000 psi 2082 MPa
ASTM D256			
Notched Izod Impact Strength (ft.lbs./in.)	0.4	0.3	0.3
Un-notched Izod Impact Strength (ft.lbs./in.)	3.6	4.3	11.6

The addition of the polycarbonate (a very tough, ductile polymer) did appear to improve the ductility of the fleece as expected, but the results are not dramatic in all cases. The addition of PC did increase the break strain or elongation, and especially the un-notched Izod impact, as well as increasing the strength and stiffness. Overall it had a positive effect, though the effect on heat resistance and heat aging is yet to be determined.

5. Phase Four – Solid Stating

One unique characteristic of condensation polymers (of which PET is an example) is that it is sometimes possible to "build-up" their molecular weight by a process known as "solid stating." Solid stating is the process of heating the polymer in the absence of water in an inert environment or under vacuum. References suggest temperatures in the 150-240°C range. Manufacturers of PET (material suppliers) sometimes do this after polymerization so that they can create higher molecular weight PET from lower molecular weight material. They do it after the pellets have been produced and crystallized. Solid stating involves hours of heating in this controlled environment.

While there is no solid stating equipment at UMass Lowell, it was shown that the fleece scrap molecular weight could be increase using this concept. In the study, samples of extruded/granulated fleece waste were subjected to two thermal treatments. The melt flow rate of the samples was then measured the following the ASTM D1238 (Flow Properties of Polymers Using the Extrusion Plastometer) test protocol.

The control sample was dried in an air circulating oven for 12 hrs @ 140°C. This is fairly typical of drying conditions for PET, even a little longer than normal. The material should have been quite dry after this treatment (remember that residual moisture will react with PET and reduce its molecular weight). The average melt flow rate @280°C / 2.16 kg was 568 gram / 10 minutes.

The second sample of PET was dried in the same way, and then placed in a vacuum oven for an additional 12 hrs @ 180°C (a solid stating type process). The average melt flow rate of this second sample was 296 grams / 10 minutes. This sample had a higher viscosity, indicating either (i) its molecular weight increased, or (ii) possible it was drier than the control sample and did not degrade as much during MFR testing, or (iii) a little of both.

Though this was not an extremely scientific study, it has been done a few times with similar results. The vacuum oven used cannot operate at temperatures over 180°C, and higher temperatures would likely be more effective. It should be noted that solid stating is sometimes done with recycled bottle grade PET to compensate for some of the process related degradation. While solid stating is an additional process, it may be an additional option for the fleece waste.

6. General Comments and Follow-on Thoughts on the Reprocessing of Fleece Waste

All of the formulations, including the control (unmodified) formulation molded well and appear to have "useful" properties. However, there are a number of issues that are important and will need specific attention.

6.1 Residence Time

The properties of the unmodified (control) fleece waste appear to be significantly better for the third run than for the previous two runs. This can be attributed to more experience processing this type of material. It is very certain that the fleece scrap was being degrading during the earlier single screw extrusion / granulation procedure. Excessive residence time due to feeding difficulties was alleviated by learning how to feed the scrap better. The residence time in the extruder for the third run was about 75% less than the earlier runs. The net result is less degradation, and better property retention. Minimizing degradation is everything with PET. Based on this trial, it is possible that the unmodified material may have value without additional additives. Based on our earlier work, I was thinking modification was required. The properties and market study will determine if the unmodified material has a market. Additives are still an option.

6.2 Drying

Drying is the single most critical issue with PET, and is more critical with PET than with any other plastic. Improper drying leads to degradation and a related loss in properties. The moisture level of the PET should be below 0.005%, and the material would need to be dried both before pelletization and before injection molding.

The drying of the shear waste could probably be done inline as part of the feeding process, prior to extrusion. This may be the most significant problem in the pellet making process. Drying is done using low dew point heated air, and since this is a fine, dust-like material, there may be concerns of a possible explosion hazard. It would be wise to contact a dryer vendor early on to determine the feasibility and type of technology available.

Drying at the injection molder will also be a concern. After pelletization, the PET pellets will pick up moisture from the environment. The must be dried prior to molding by the molder using a closed (hopper) drier. Most molders have dryers, but not all standard dryers are suitable for PET, and most molders do not have experience with PET. A molder that plans to use this material need to have good drying equipment (readily available) and must be educated as to the importance of drying PET (since it is far more critical than with any other plastic).

6.3 PET and Injection Molding

The lack of familiarity that manufacturers and molders of injection molded products have with PET may also be a problem in marketing. PET is not commonly used for injection molded products (probably due to a combination of factors including the drying issue and the morphology issue – see below). Therefore, this will not be a simple “virgin to recycle conversion”. A manufacture will need to be willing to change materials from another thermoplastic to the recycled PET. Alternatively, the reuse of this material may be associated with an entirely new product development process (new product and process).

6.4 Morphology

Morphology is a complicated issue, since PET can be amorphous or semi-crystalline. If PET is injection molded at low mold temperatures and the part is less that 3/16” thick, it will cool relatively quickly and remain amorphous. If PET is cooled very slowly (for example a thicker part), it will tend to crystallize. The parts molded for this study did not crystallize as molded, and the mold shrinkage seen is typical of any amorphous plastic. However, if the PET was to get hot after molding, it would begin to crystallize and as a result shrink more. Molded fleece waste parts put in an oven at 100°C did shrink another 0.015 in/in due to crystallization. The crystalline parts are also more brittle, changing the physical properties of the part. The as molded amorphous PET parts have some value, but can only be used in applications where the part temperature does not get too hot. 150°F or 160°F is probably the upper limit before crystallization begins, but this should be tested.

6.5 Color

The dark color will limit the application of the fleece waste. In all the trials the color is a fairly consistent dark blue, almost black. There is little to be done in this regard, but a basic study on the effect of pigments on the color might be of interest.

6.6 Process Line

A compounding line for the material must be designed and/or specified. As stated earlier, the predrying system for the shear waste is the first part of the system, while other concerns include feeding and the method of pelletization. A forced hopper feed into a dual-diameter single-screw extruder is a likely feed option. The very low viscosity of this material and dedicated nature of the line would point in the direction of die face pelletizing, though strand pelletizing is still an option.

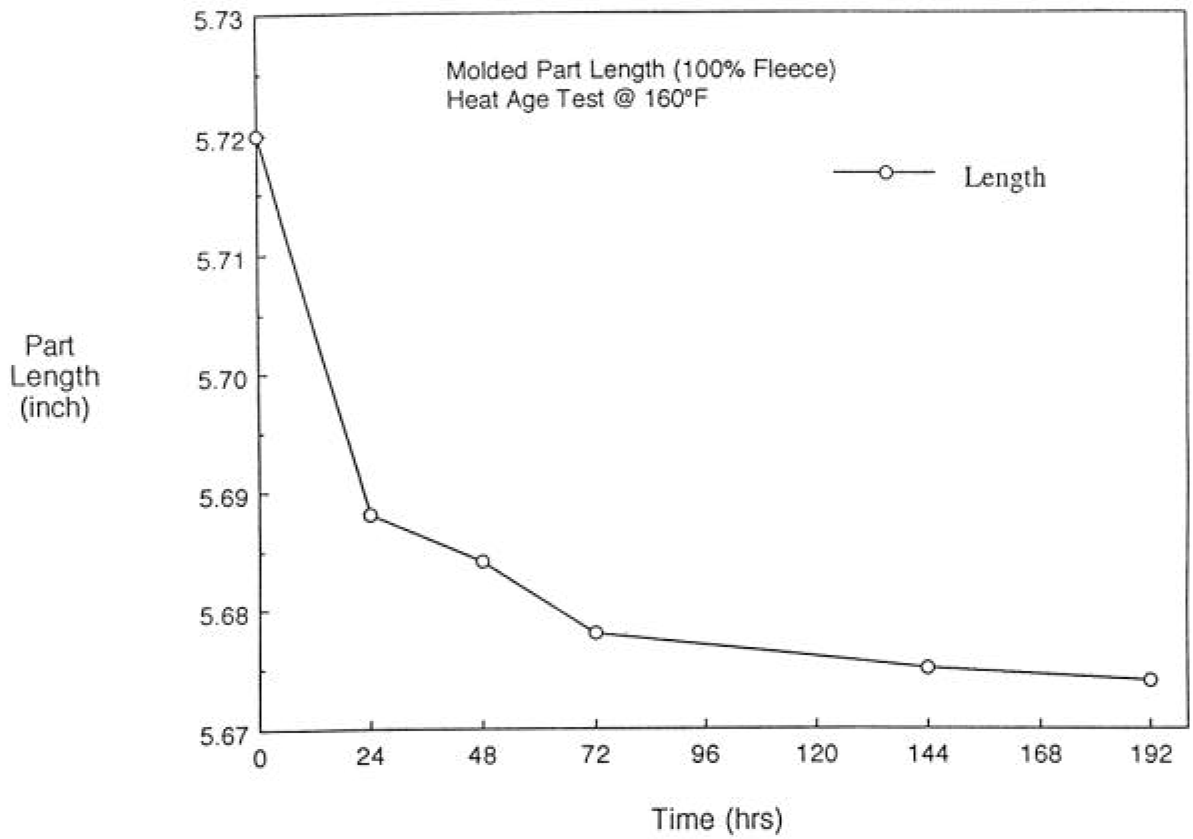
6.7 Contamination

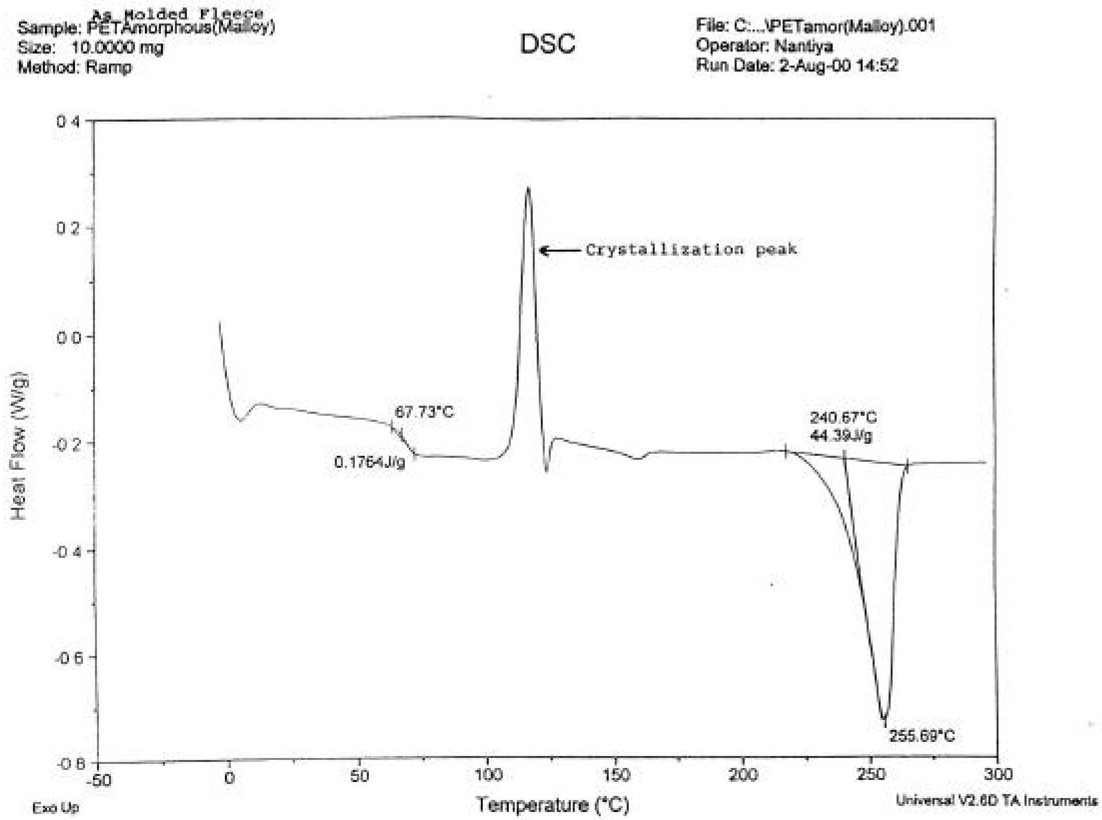
The presence of contamination is also an issue. To date, there have been no particular problems with contamination, however, the purity of the material can be important for both the application and processing. An analysis of the coatings on the incoming fiber could be helpful. Volatile contaminates as well as random solid contaminates could affect mechanical properties of the molded material.

7. ReTern Project

The Chelsea Center provided additional funding for a student intern (ReTern) to analyze the plastics market in order to determine the feasibility of marketing this PET material. The results of the project are promising. The student discovered businesses within the plastics industry that were interested in the shear waste as well as in the pellets. This finding provides Malden Mills with two different opportunities: provide companies with the shear waste at no cost (savings due to avoided disposal costs - $76,035 last year), or invest in the equipment and training to pelletize the material, and find customers willing to pay a fair price. At this time, Malden is waiting for proposals from those interested in the shear waste itself. If this opportunity seems viable and stable, the company will likely move in that direction, rather than making the long-term investment of becoming a pelletizer.

8. Appendix – Heat Aging Tests

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DSC
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Operator: Nantiya
Run Date: 2-Aug-00 14:52
Crystallization peak
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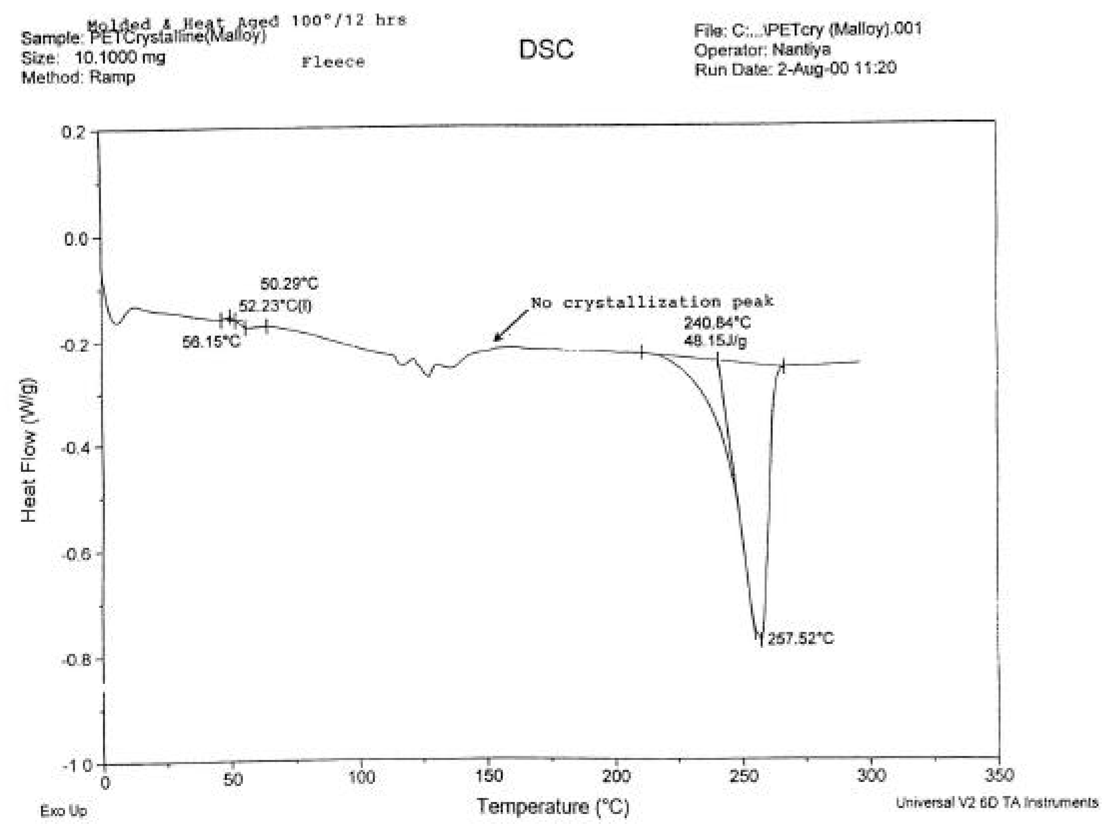
240.67°C
44.39J/g
255.69°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V2.6D TA Instruments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Fleece
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DSC
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No crystallization peak
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48.15J/g
257.52°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V2.6D TA Instruments