Physical Characteristics of the Dual Phase Region in Mixtures of Recycled Polystyrene/Curbside Tailings Materials

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Introduction

Virtually all studies of polymer mixtures made by the processing of virgin polyethylene and polystyrene show that the blends possess poor mechanical properties when compared to the individual components. This is generally attributed to the lack of good interfacial adhesion between the blend components with the result that an applied stress cannot be efficiently transferred between the phases.[1,2]

Recent research, however, has shown that it is possible to fabricate objects that possess strength and utility by the mixing of certain recycled polymeric materials previously thought to be incompatible.[3] By the blending together of polystyrene with the "mixed plastics" (mostly polyolefinic) component of the recycling stream it has been found to be possible to produce materials which behave mechanically and appear morphologically like fiber reinforced composites. Moreover, there exists a unique composition range where the mechanical properties are optimal, and the morphology, as determined by scanning electron microscopy, is interlocked and co-continuous, forming a three dimensional interpenetrating network.

Thermal analysis has revealed that the co- continuous morphology inhibits crystallization in the polyolefinic phase. Annealing the materials does not result in any significant increase in the crystallinity. However, exposure to gamma radiation was found to increase the crystallinity of several samples.

Materials and Processing

The base material used throughout this study is known as New Jersey Curbside Tailings (NJCT). NJCT is defined as the rigid plastic containers (mainly bottles) that remain in the post-consumer plastic waste stream after the more valuable PET soda bottles and the natural HDPE milk and water containers are removed. These materials are obtained from recycling programs in New Jersey which request only PET soda and natural HDPE from households.

The polymeric composition of NJCT was estimated by analyzing a representative batch of materials delivered to the Center for Plastics Recycling Research (CPRR) at Rutgers University. The composition of NJCT is listed in Table 1. They are primarily polyolefinic in nature (88%), with the remaining materials being comprised of a mixture of the common packaging plastics. These estimates were confirmed by an independent study carried out at Rennselaer Polytechnic Institute utilizing a selective dissolution technique.[4] The exact polymeric composition of NJCT could be expected to vary slightly depending upon time of year and geographic location of the collection program.

Two basic forms of NJCT are utilized in this study, the first being a bulk form of NJCT in which the materials are granulated and then processed without any cleaning or separations. From these materials, large cross-section lumber like profiles approximately eight feet long were extruded from the NJCT utilizing an ET/1 extrusion-molding machine.[5] The second form of NJCT used in this study is a refined form in which the raw NJCT were run through the resin recovery pilot plant facility at CPRR and then melt-filtered and pelletized using a counter rotating, non-intermeshing twin screw extruder. The result of this process is a clean, mainly polyolefinic mixture (NJCT as above minus PVC, PS, and PET) of plastic material which can be processed on conventional equipment. This material is referred to as NJCT "Floats".

The NJCT, being mainly polyolefinic, produces products that are relatively flexible and have a low Young's modulus. In order to improve upon the mechanical properties of these materials, polystyrene was blended with both forms of NJCT. Two different polystyrene materials were used to mix with the raw NJCT materials. The first polystyrene was obtained from Mobil Chemical Company's expanded polystyrene regrind operation. This polystyrene will be referred to as "MPS". This post-industrial polystyrene was plant scrap that was initially used to make foamed products and was dandified and pelletized prior to being mixed with the NJCT. The second polystyrene utilized for this research was obtained from Plastics Again Inc., one of the pioneers in the recovery of post-consumer polystyrene. This polystyrene will be referred to as "PPS". The Plastics Again polystyrene was chosen to represent typical, post-consumer, mixed polystyrene. Only the MPS polystyrene was blended with the NJCT Floats.

The specific polystyrene/NJCT compositions (percent by weight) that were fabricated for these experiments are as follows: 0/100, 10/90, 20/80, 30/70, 35/65, 40/60 and 50/50 for the MPS. The formulations for the PPS are the same with the inclusion of a 45/55 mixture.

These mixtures of plastics were blended in 400-500 pound batches and physically premixed in the feed hoppers of the ET/1 for the raw NJCT. To produce samples from the NJCT Floats, the materials were premixed and injection molded into ASTM type "dogbones" utilizing a Newbury 30-ton injection-molding machine.

Dual Phase Co -Continuity

If two polymers are processed under the proper conditions of composition and viscosity, it may be possible to cause the two components to form continuous interlocking phases regardless of miscibility.[6] In this type of dual phase co- continuous structure, the two phases intertwine in such a way that both phases remain continuous throughout the material. This morphology is analogous to that of a sponge soaked in water where both sponge and water form continuous systems.[7] The resulting microstructure in this type of system enables each phase to share in the load bearing capability of the material. This reduces somewhat the need for efficient stress transfer between the phases required for dispersed phase blends.[8] This type of morphology has been observed in many polymer blend systems under the proper conditions.[9]

Previous Results

The following is a brief summary of results that have been obtained for these systems. A more detailed account has been given by Renfree.[10]

The addition of PS into the NJCT materials improves the modulus, yield stress, and the ultimate strength. Figure 1 is a plot of the yield stress versus composition for the three systems tested. Up to the 30% PS composition range, all materials tested show a law of mixtures (proportional) type response in which the property in question is a weighted average of the component properties. In the 30 to 40 percent PS composition range however, the three systems show a positive deviation from the additive response and a relative maximum in the properties.

SEM micrographs indicate that as the polystyrene is incorporated into the NJCT materials that it is drawn into long rods and plates in the direction of flow.[11] The material may therefore be thought of as being similar to a fibrous composite. As the law of mixtures is considered the upper bound for the mechanical properties of a fiber composite, it's not surprising that these materials follow a similar relationship. In the composition range where the mechanical properties are optimal, SEM micrographs indicate that the polystyrene and NJCT (mainly polyethylene) form co-continuous phases which are intermingled or intertwined in such a fashion as to produce an interpenetrating or interlocking of the phases.

Figure 2 shows the plots of viscosity ratio versus composition ratio for the three systems studied. As the viscosity ratio for each system is assumed to be constant throughout the composition range, the plot for each system is therefore parallel to the composition ratio axis of the graph. The darkened symbols represent compositions for which SEM micrographs indicate a dual phase co-continuous morphology is present. The dashed lines in the figure indicate the dual phase region. The width of the dual phase region was determined experimentally from the known dual phase compositions. The shape of the region was chosen arbitrarily since more experiments would have to be carried out in order to define the actual shape of the region. Sample compositions that plot above this region would be expected to have NJCT as the continuous phase while compositions that plot below this region would be expected to have polystyrene as the continuous phase.

Thermal Analysis of NJCT/PS Mixtures

Thermal analysis measurements were performed on representative samples of all of the polymer mixtures reported on in this work. A Perkin-Elmer model DSC-4 Differential Scanning Calorimeter (DSC) was utilized for the measurements. A plot of ΔH, in calories per gram, versus composition is given in Figure 3 for the MPS/NJCT ET/l samples. The ΔH values remain fairly constant for compositions up to 30% MPS. At the 35% composition however, ΔH decreases by 34% from the 100% NJCT value. ΔH increases for the 40% sample and returns to approximately the 100% NJCT value at the 50% composition. A similar response is seen for the other samples tested over their composition ranges. To eliminate the effect of thermal history on the observed behavior of these materials, several of the sample compositions were quenched from the melt while others were annealed for 1 hour and slow-cooled and then retested. No significant change in the heat of fusion values was observed.

It appears from these data that in the 30-40% polystyrene range there is a decrease in the crystallinity of the polyolefinic portion of the samples. This has been verified for the MPS/NJCT ET/1 samples by wide angle X-ray diffractometry as well as positron spectroscopy.[12] This range of compositions corresponds to the range in which the mechanical properties of these materials display unexpectedly improved properties.

The decrease in the crystallinity observed for the co-continuous structures may possibly be explained by considering a simple model. As the material is cooled, the polyethylene will crystallize and the polystyrene will pass through its glass transition. As the polyethylene crystallizes, it will isothermally exhibit a decrease in volume of up to 15%.[13] The polystyrene, however, will not, but will only display a change in the slope of its volume- temperature curve (change in thermal expansion coefficient). The onset of crystallization in the NJCT and the glass transition of the polystyrene occur at approximately the same temperature.[14] As the NJCT begins to crystallize, both polystyrenes have entered their glass transition regions.

As the polyolefin begins to crystallize, the interlocking nature of the system will inhibit the mobility of this phase and prohibit the NJCT from executing the volume change that would occur in an unrestrained condition. This effect may be amplified by the concurrent conversion of the polystyrene to a glass. This restriction of volume contraction and limitation of mobility of the polyethylene molecules may prevent them from being incorporated into the growing crystalline phase. The result of this would be an excess of tie molecules, in various degrees of extension, and a corresponding decrease in the crystallinity of the NJCT phase.

Irradiation Study of NJCT/MPS

If this model has validity, then it would be expected that if it were possible to cause the tie molecules to break, then the crystallinity of the material would increase. By causing the scission of the tie molecules, some of the restriction to mobility would be lifted and the molecules will be better able to present themselves to the growth surfaces of the crystalline lamellae for incorporation into the crystal structure. The net effect would be an increase in the crystallinity of the sample. It is well known that the exposure of polyolefins to ionizing radiation results in chain scission, crosslinking, and the formation of double bonds in the material. These processes are considered to be confined to the amorphous regions in a semi-crystalline polymer.[15]

Ultra high molecular weight polyethylene (UHMW PE) is a material that has a relatively low degree of crystallinity as compared to HDPE. The lower degree of crystallinity is attributed to the low mobility and the large amount of molecular entanglements associated with the very high molecular weight. The entanglement network can be expected to run from one crystalline region to another and therefore may be considered to consist of tie molecules. This is a somewhat analogous situation to that of the PS/NJCT dual phase model.

Studies have been performed on the effects of radiation on the percent crystallinity in both UHMW PE and HDPE.[16,17] The results of these studies indicate that irradiation of these materials produces a pronounced increase in the percent crystallinity for the UHMW PE, on the order of 20%, while the effects are rather small for the conventional HDPE material. This observed increase in the percent crystallinity for the UHMW PE is attributed to the radiation induced chain scission of the tie molecules with the attending increase in the mobility of these molecules allowing their incorporation into the crystal lattice.

Therefore, owing to the similarities between the proposed model and the structure of UHMW PE, samples of the MPS/NJCT materials were exposed to gamma radiation in order to determine if the percent crystallinity could be increased in the samples that displayed decreased crystallinity.

Samples of 100% NJCT, 30%, 35%, and 40% MPS/NJCT produced on the ET/1 extrusion molding machine were exposed to several different doses of cobalt 60 gamma radiation at the University of Virginia's Nuclear Reactor Facility under the direction of Dr. Albert Reynolds of the Department of Nuclear Engineering and Engineering Physics. The exposure was performed at room temperature with an exposure rate of 220 Krads per hour. Total exposures of up to one Mrad were performed.

The 100% NJCT and 30%/70% MPS/NJCT samples were used in this study as controls since these materials did not display the dual phase morphology while the 35% and the 40% MPS samples did display this morphology. It was therefore expected that the first two samples would respond to the irradiation in a similar manner as the HDPE discussed above and show little crystallinity change upon being irradiated. The two samples displaying the dual phase morphology were expected to show an increase in their crystallinity if the model had some physical relevance.

The results of the gamma radiation on the various samples are plotted in Figure 4. This figure is a plot of the heat of fusion versus radiation dose for the four materials tested. The dashed line near the top of the figure represents the heat of fusion for the 100% NJCT sample with no gamma irradiation. As expected, the 100% NJCT and the 30% MPS samples show very little effects due to the irradiation. In fact, instead of the marginal increases in crystallinity found for virgin HDPE reported in references 16 and 17, the materials show a slight decrease in overall crystallinity with exposure to radiation. This decrease amounts to about 3% for both samples at 1 Mrad dose.

The 35% and 40% MPS samples do show a substantial response to being irradiated. The 35% MPS material has had its heat of fusion increased by 20% by the application of 0.2 Mrads of radiation. After this dose, the ΔH_m. for this material remains fairly constant for doses up to the 1 Mrad dose. For the 40% MPS material, the ΔH_m. increases by 5% for the 0.2 Mrad dose and increases again by 10.5% over the non-irradiated material by a 0.4 Mrad dose.

Discussion

It is to be expected that the increase for the 40% MPS material would be less than that for the 35% MPS. The initial decrease in ΔH_m. for the 35% MPS samples was 34% while that for the 40% MPS material was only 15%. This difference may be explained by considering the degree of dual phase co-continuity displayed by each sample. The 35% MPS sample is in the mid-range of the dual phase co-continuous region as indicated in Figure 4 and by SEM micrographs(1B). This composition also corresponds with the relative maximum found in the mechanical property results for this material. The 40% MPS composition, however, is on the edge of the dual phase region in Figure 4 and the mechanical properties do not show optimal values for this composition. It may therefore be surmised that at this composition the MPS has started to become the continuous phase and that the 40% MPS sample is to a lesser degree co-continuous and interlocking. As the restriction to mobility of the polyethylene molecules would be expected to increase as the degree of co-continuity increases, so would the degree of crystallinity be expected to decrease as the degree of co-continuity increased.

The results presented here are not intended as proof of the simple model that was discussed, but rather to illustrate that the model may have some physical significance. The exact nature of the interactions of the phases in the co-continuous structure which result in the reduction of crystallinity in the systems reported on in this work will require more research to elucidate.

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Table 1

Polymeric Composition of NJCT

Polymer	**CPRR Estimates**	**Results from Reference 4**
NDPE [non-milk jug]	80%	75.3%
LDPE	4%	3.5%
Polypropylene	4%	8.1%
Polystyrene	3%	3.3%
PVC	4%	3.4%
PET [non-soda bottle and insolubles]	5%	6.4%

Figure 1
Yield Stress versus Composition for PS/NJCT

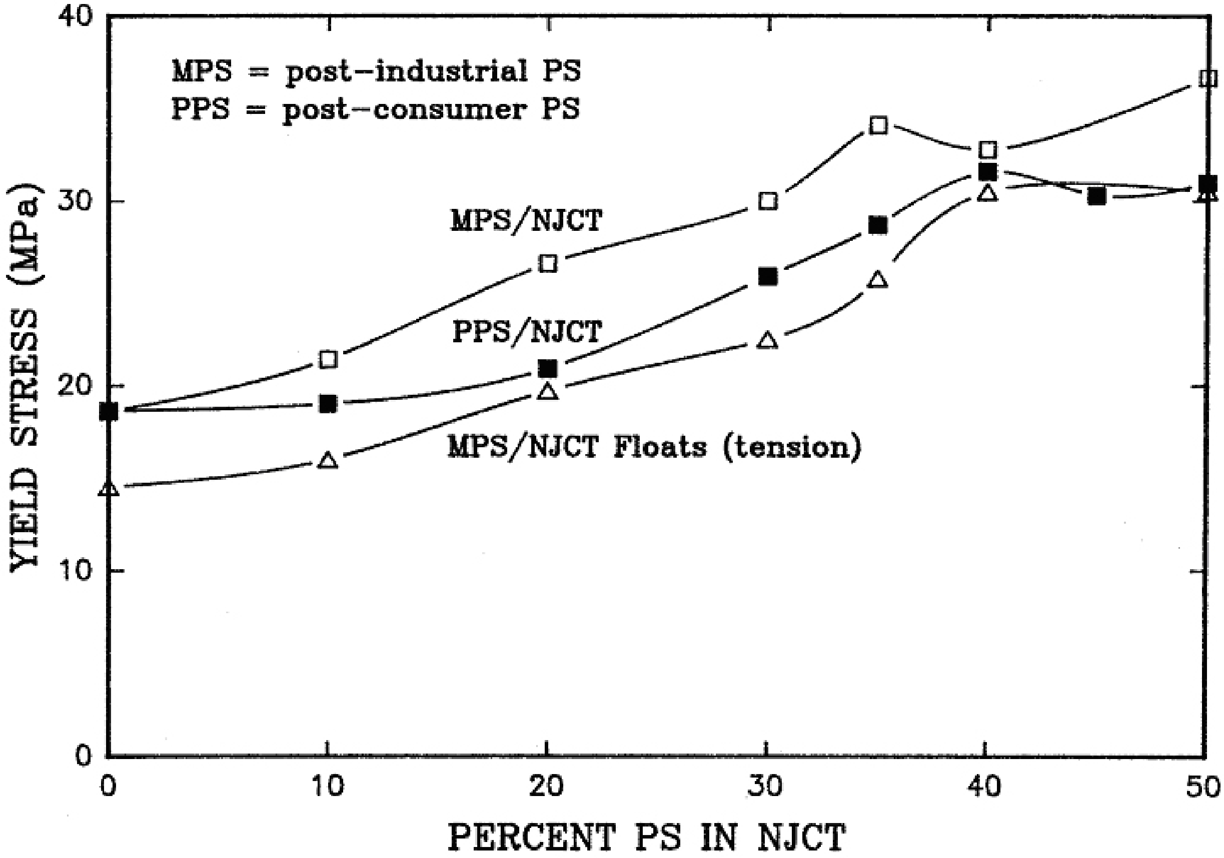


Figure 2
Plot of Viscosity Ratio Versus Composition Ratio for the
Various PS/NJCT Materials indicating the Dual Phase Compositions

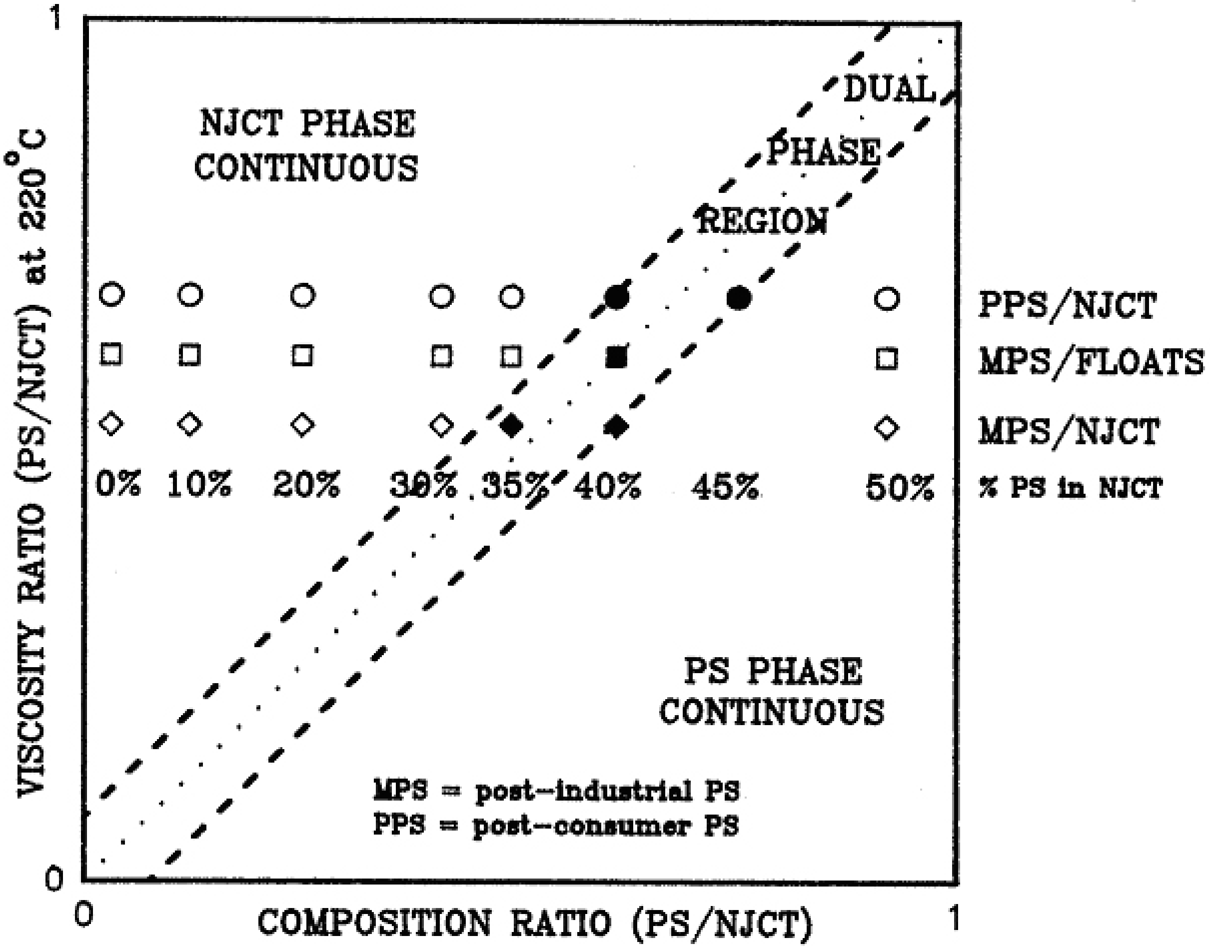


Figure 3
Heat of Fusion Versus Composition for MPS/NJCT

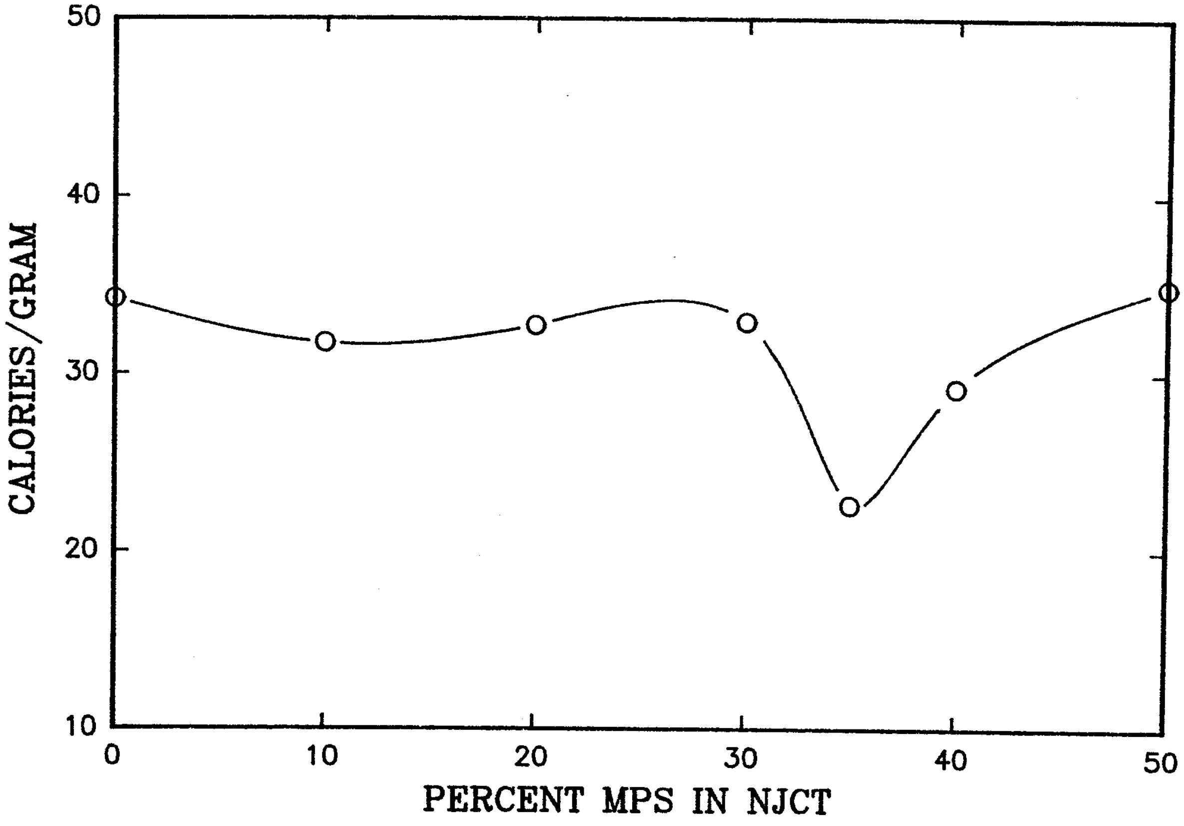
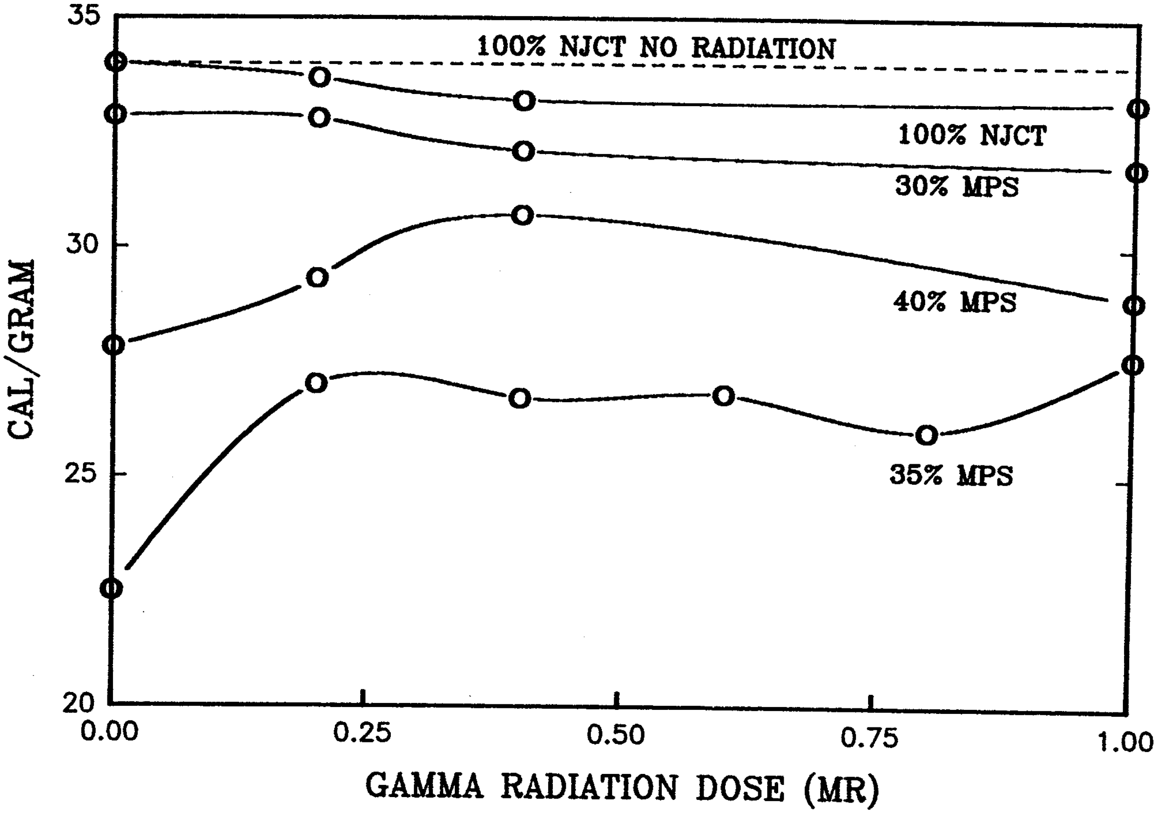


Figure 4
Heat of Fusion Versus Radiation Dose



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