"A Method of Estimating by Infrared Spectroscopy the Relative Abundance of Polymeric Components in Complex Polymer Blends"

by

Charles Cannon Edwards

ABSTRACT

In this Honors Thesis, I describe a method created by Profesor Van Ness and myself which effectively differentiates regions of unique polymer composition within comingled products. My goals are two fold. First, in order to provide the necessary background knowlege for another student to efficiently continue work on this project I discuss the foundations of our project, outline basic infrared spectroscopy techniques and describe the evaluation of spectra. Second, I describe our method in detail and discuss the results acheived through it with regard to the MCC5SIB blend.

Introduction

As our society commits itself in the coming years to recycling a greater proportion of plastics from the solid waste stream, the need to develop useful recycled materials will increase. Because of the expensive nature of sorting different types of post-consumer plastic wastes, recycled plastic blends are often the most cost effective recycled plastic materials. One obstacle to the development of blends with attractive physical properties is the inherent incompatibility of most polymer combinations. While such blends are made from an evenly mixed feedstock of multiple polymers, the resultant recycled product often is not uniform in composition. Distinct regions within a blend have a relative composition of polymers different than that of the blend as a whole. The physical properties of the blend are affected by such migrations in ways that we can not explain unless the nature of the migration is known. In order to efficiently design composite polymer materials the nature of polymer migrations in a recycled blend must be understood.

My research over the past two years with Professor Van Ness has culminated in our development of a method by which we can detect changes in relative polymer composition in different regions of a plastic blend. Our method is very inexpensive, quick, and produces semi-quantitative results. All other available methods involve equipment considerably more expensive than an infrared spectrophotometer, and many are less accurate. We have tested this method on one particular blend which contains

primarely polyethylene terephthalate and high density polyethylene. The blend, on which we have focused our study, is one of a family of blends consisting of resins derived from a mixture of plastic post-consumer waste. This mixture represents to a first approximation the plastics recovered from curbside collections wherein all clean plastic bottles are collected. We refer to products and blends made from this feedstock as "Model Cities" materials. We have demonstrated that our method is capable of detecting changes in the relative composition of this blend.

Before we can analyze a blend with our method, we must know the identity and have an estimate of the relative abundance of each of the constituent polymers. Our analysis involves a comparison of the infrared spectra of films cut from the designated blend with the infrared spectra of the most prevalent constituent polymers in their pure form. The spectra of pure polymers are distinguished by multiple peaks of a size and location standard for that polymer. A peak in the spectrum of one polymer may not even exist in that of another polymer. We compiled and edited a list of regions containing major peaks for each spectra of the pure polymers we knew to exist in the blend. We then calculated the areas under these peaks for each of the pure spectra and for the spectrum of the blend. For each spectrum we calculated the relative area under each peak compared to the total area under all the designated peaks. A comparison of the relative areas under the specific peaks in the pure

spectra with those of the sample spectra provides a means to calculate the relative abundance of a polymer constituent within a specific region of a blend.

Before I describe the specific aspects of our method, I will first characterize the nature of plastics, and the technique of infrared spectroscopy. I do so with two goals in mind. I wish to familiarize the reader with the terms and concepts necessary to understand the details of our method. I also hope that by providing background material on infrared spectroscopy and my work with plastics that the person continuing on with my research will efficiently be able to continue where I have left off.

Chapter 2
An Overview of Polymers

The constituent polymers of most recycled blends belong to a class called thermoplastics. Thermoplastics are characterized by long chain structure and a low branching ratio. The individual chains do not link with each other chemically, but instead, they intertwine to form a cohesive mass, sometimes crystalline in character. When thermoplastics are heated, the chains are able to move around rather uninhibited relative to each other. In a heated condition, the material takes on almost a liquid character such that it can be easily molded to any shape. Upon cooling, long chains regain their rigidity, and the molded shape is retained.[1]

The Model Cities blend and other recycled plastic blends that our project will consider are composed of primarily three types of polymers. Other polymers and a compatibilizer in the blends are present only in meager proportions. Their presence does not influence in any significant way the infrared spectra of the composite. For this reason my description of polymers and their infrared spectra will focus specificly on high density polyethylene (HDPE), polystyrene (PS) and polyethylene terephthalate (PET).

A polymer is defined as a single molecule with a molecular weights of one thousand to ten million built up by the repetition of small simple chemical units called monomers. The manufacture of polymers, therefore, takes place in two stages. First, the monomer unit must be either collected or produced. Second, the

separate monomers are added successively end to end to form a chain molecule in a process termed 'polymerization'. To use PE as an example:

First Stage

Obtain $CH_2=CH_2$ as a gas found naturally
ethylene

2nd Stage

$$CH_2=CH_2 + CH_2=CH_2 + CH_2=CH_2 + \ldots \xrightarrow{\text{polymerization}}$$

n molecules of ethylene

$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

polyethylene

In the polymerization of ethylene, the double bond is opened and one of the electrons which had been shared between the two carbons moves so as to be shared by one of the original carbons with a carbon atom from a different ethylene molecule. Carbon atoms are not stable unless they share eight valence electrons at any given time. The addition of an ethylene molecule to a chain always leaves the end carbon with only seven electrons in its outer orbital: two in the covalent bond with the adjacent carbon, two shared with each hydrogen and one unbonded. This electrophilic carbon, in turn, promotes the cleaving of the double bond in another ethylene molecule.

This process inevitably continues until one of two circumstances arise: 1) the reaction progresses until it reaches equilibrium - no more unreacted ethylene is present, or 2) in the

polymerization process, an impurity such as a stray proton or a methane (CH3) group may become bonded to the chain ending carbon rather than another ethylene molecule.[2] If the polymerization reaction is carried out with few impurities present, the resultant chains can be very long. These highly regular chains usually take up the low-energy zig-zag form shown in figure 2.1.

Figure 2.1[3]

Real examples of polymers do not exist without defect structures. This is not surprising if one views polymerization as a sequence of reactions which has to be repeated perfectly many thousands of times. One imperfection in polyethylene is called 'branching'. Figure 2.2 demonstrates the effect of branching in which side chains extend from the main polymer backbone.

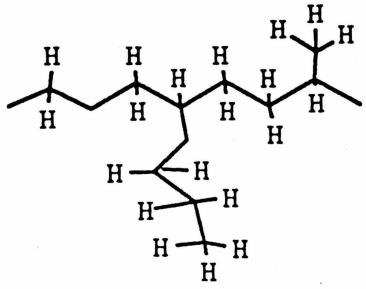


Figure 2.2

The branches present in PE consist of either methyl groups or short methylene sequences terminated by a methyl group.[4]

Below the melting point, polymer molecules may come together to form a crystalline structure, or they may intertwine into what is referred to as an amorphous region. Not all polymers are

capable of crystallizing. One of the essential features of a polymer for crystallization is symmetry. This is clearly achieved in linear PE, as it has no regular branches which would disrupt the individual chains from coming together and achieving the lowest energy level. The occasional branching of PE does not prohibit the crystallization of the sections of the molecule between the branch points.[5]

In crystallization from the melt, PE chains frequently become a part of a microcrystalline polymer called a spherulite. Microtomed sections of crystalline PE show that the internal structure of sphereulites is radially symmetric. Their diameter can grow to over one micron. The spherulite grows by crystalline fibers attaching to a nucleus and filling in the amorphous space between them with either more crystal fibers or cross linking (Exhibit 2.1 shows an artists depiction of this process). The size of a sphereulite depends to a great degree on the cooling rate of the melt. If the melt cools slowly, fewer nucleation sites arise, and the average radius increases.[6] In polarized light, these structures, shown in Figure 2.3, appear as a Maltese Cross caused by birefringence effects.

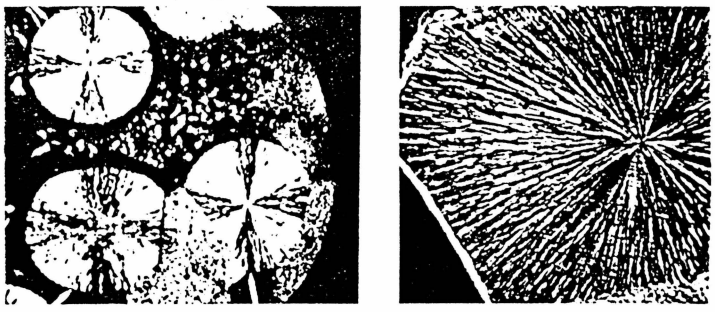


Figure 2.3[7]

The cross appears because the sphereulites behave as crystals with radial optical symmetry, and in this case there are four extinction positions.

Sphereulites are produced when the overall crystallization rate is the same in all directions in space. Directionally dependant crystallization rates produce a different morphology of crystal called "shish-kebab" structures as shown in Figure 2.4.

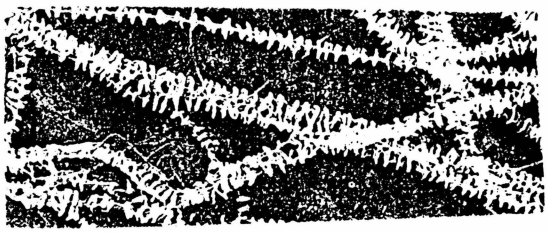


Figure 2.4

Shish-kebab structures are formed by equiaxial growth and main chain orientation in the direction of stress. At higher stresses, the crystallization is obviously induced by a continuous series or row of nuclei arranged along the direction of flow.[8]

As I have just described many levels of PE crystalline order, it is important to recall that no solid polymer can be completely crystalline. Polyethylene is divided into two categories based on its percent crystallinity. Low density polyethylene (LDPE) is 40-60% crystalline and high density polyethylene (HDPE) is 60-80% crystalline. Low density polyethylene is more flexible, transparent, and has a greater branching ratio than HDPE. The level of crystallinity in LDPE is achieved through high pressure polymerization, 1000-3000

atmospheres. The polymerization of HDPE involves the use of catalysts in addition to application of extreme pressure.[9] By the polymerization of PE under other conditions of temperature, pressure and catalyst, a range of polymers can be manufactured including oils, greases, and soft waxes.[10]

In addition to HDPE and LDPE, polystyrene is an abundant component in the blends which we analyze. The monomer unit of PS, shown in Figure 2.5, is identical to that of PE with one important exception. The structure of a styrene monomer is an ethylene molecule with a benzene side group. The polymerization process of PS is identical to that of PE. The benzene side group is very stable and remains a spectator throughout the process.

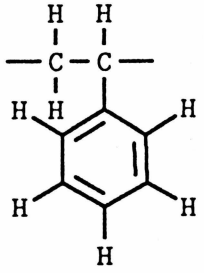


Figure 2.5

The PS chain is very similar to that of PE with one significant alteration. Every other carbon along the chain is bonded to one hydrogen and one benzene side group. The size of this side group and its high electron density limit the interactions between PS chains, and affect the relative orientation of neighboring monomer units. Although the benzene ring has a neutral charge, its concentration of electrons repel one benzene side group from its immediate benzene neighbors. The

summation of these repulsive forces among the side groups produces a spiral orientation of the groups along the length of the chain. This configuration represents the lowest energy state for a single chain and is the form assumed by the solid state of polystyrene.

While the benzene side group itself is not reactive, its presence does significantly affect the morphology of solid polystyrene. The large size of the benzene side groups and their spiral orientation along the length of the chain make the crystallization of PS very difficult. The carbon atom in the benzene ring farthest from the main chain is estimated to be 3.879 angstroms away from the chain backbone, whereas the length of the bond between a carbon on the chain and one of its constituent hydrogens is only 1.062 angstroms.[11] If PS does achieve some degree of crystallinity, its form resembles that of a closed zipper. In order for PS to achieve a significant degree of crystallinity, the temperature of the liquid polymer must remain near its melting point for a prohibitively long duration. In plastic molding processes, the cooling period is usually only a matter of minutes. While this time interval is sufficient for PE to achieve a large proportion of crystallinity, only small intervals along the whole PS chains are able to align with portions of other chains. The zipper-like structure of sporadic crystalline regions along neighboring PS chains significantly limit relative chain mobility. An important result of polystyrene's limitation of intra-chain mobility is that the

solid state of PS, though amorphous, is characterized by significant rigidity.

Polyethylene terephthalate, the most common form of polyester, is more complicated than the two polymers which I have previously discussed. Its monomer unit, shown in Figure 2.6, contains four different functional groups: para-benzene, ester, carbonyl and aliphatic.

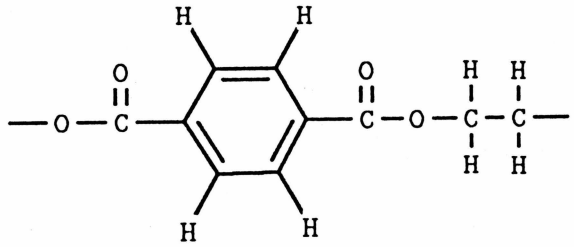


Figure 2.6

The polymerization process for PET does not involve the cleaving of a double bond as is the case with PS and PE. The monomer unit, ethylene terephthalate is unstable, and therefore, its production must be carried out simultaneously with the polymerization reaction. As this synthesis is quite complicated and not necessary to the understanding of our project, I will not describe it here.

Unlike PS, the nature of PET is very amenable to crystallization. The carbonyl side groups of PET do not extend from the main chain to the degree that benzene does in PS. The length of the C=O bond is 1.22 angstroms, less than one third the distance occupied by the benzene side group in PS.[12] The narrow nature of the PET chain and the multiple locations of high

electron density in each monomer encourage high levels of crystallinity in PET.

Contrary to this evidence, PET left to cool without any special treatment immediately after its manufacture produces an amorphous solid. However, when tensile stress is applied to a PET sample as it is being quenched, the rate of crystallization increases. Crystallization takes place during the stretching process. The resultant crystals are very stiff and do not melt when the stress is removed.[13]

The tensile strength of PET film is about 25,000 psi, twice that of aluminum and almost equal to that of mild steel.[14] Polyethylene terephthalate is an attractive material for, among other uses, soda bottles because of its toughness and relatively low cost of manufacture.

Chapter 3
Infrared Spectroscopy

Our samples are composed of atoms bound together by chemical bonds. To a first approximation, the force required to make a small change in the length of a bond or a small change in the angle between two bonds is proportional to the change produced. Molecules, therefore, consist of a set of coupled harmonic oscillators. If a molecule is disturbed from its equilibrium state it will vibrate in such a way that the motion can be considered to be the superposition of a number of simple harmonic vibrations.[15] The modes of vibration of a given chemical bond can take on one of three forms: stretches, bends or rotations. Figure 3.1 shows these three modes for a portion of a PE chain.

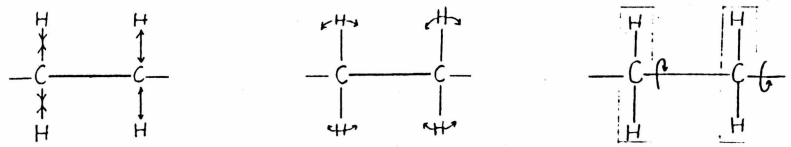


Figure 3.1[16]

Each mode of vibration for a particular bond has a unique fundamental frequency. The stretch mode is usually the highest energy vibration, followed by the bend mode. The energy associated with the rotational mode of vibration is often so low that it is not resolved in the infrared spectrum.

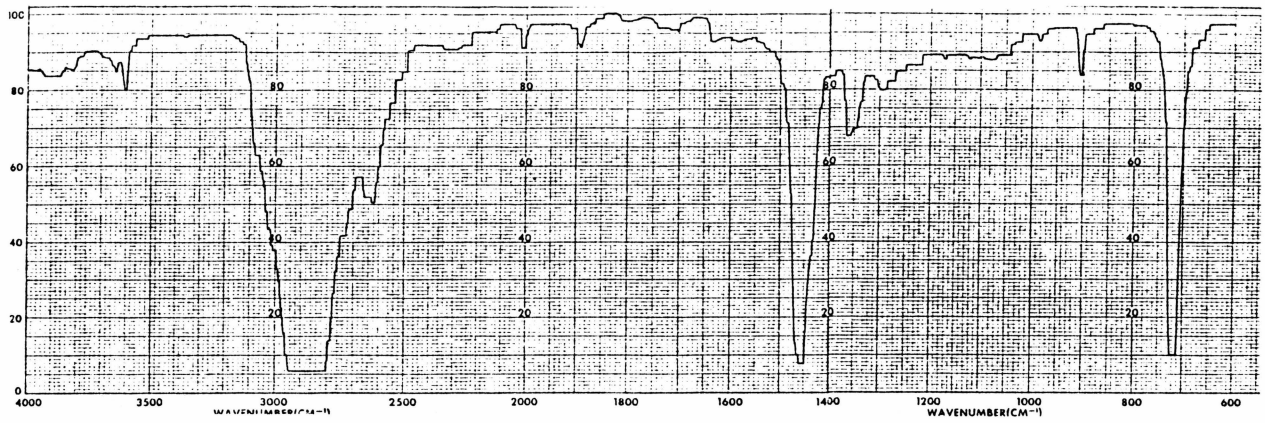
An infrared spectrophotometer obtains a spectrum of a film by directing a portion of the infrared spectrum at the film and then recording what fraction of the light at each wave number the sample absorbs. Transmittance readings at different frequencies provide specific details about the characteristics of the sample.

If the frequency of infrared light directed at a sample is identical to one of the normal modes of vibration for a chemical bond in the sample, the bond will absorb a portion of the light. Under such a scenario, between two and ten calories, per mole of affected chemical bonds, are absorbed by a film, and subsequently given off in the form of heat. The frequency at which any peak in the absorption spectra appears is, therefore, also one of the normal modes of vibration for the molecules in the sample.[17] As the three polymers which I have described in detail share many similarities in their chemical composition, many peaks in the Model Cities spectra are contributed to by multiple component polymers.

In order to understand the spectra of a polymer blend, one must first become familiar with the spectra of each component polymer in its pure state. As each type of chemical bond in a PE molecule is also present in PS and PET, so do the peaks characteristic of a PE spectra also appear in the other two spectra. All of the chemical bonds in a PS molecule are also represented in the structure of PET, and likewise each peak in the PS spectrum also exists in the PET spectrum. In order to simplify the explanation of the pure spectrum of PE, PS and PET, I will describe the pure spectra of each polymer individually from most simple to most complex.

There are three regions of intense absorption in the infrared spectra of PE. They are centered near 2920, 1470 and 725 cm-1 as in Figure 3.2 below. The first two are associated

with the internal modes of vibration of the CH2 groups, while the third is due to the rotational mode of vibration along the carbon backbone.



(A Pure PE Spectra)
Figure 3.2

The most prominent band in the PE spectrum, centered at 2900 cm-1, is assigned to C-H stretching. In less crystalline, pure samples, the edges of the peak often extend up to 3100 cm-1 and as low as 2500 cm-1. The wave number at which the absorption occurs indicates the type of carbon to which the hydrogen is attached.[18] Portions of PE chains under strain cause the absorption by C-H stretching at wave numbers above 3000 cm-1. A common source of chain sequences under strain exist at the point in which a individual chain folds back upon itself in a crystalline or semicrystalline state.

Absorption at the wave numbers between 3000 and 3250 cm-1 in the C-H stretch band result from a bond between hydrogen and an unsaturated carbon. This functional group in a PE sample exists in the form of either unreacted ethylene, or partially degraded PE in the sample. The most intense absorption in the C-H stretch

peak occurs near 2900 cm-1 with the support of two other weak peaks at 2912 and 2932. These two peaks are inevitably overlapped by the large C-H stretching peak. Their presence is caused by overtones of the 1463/1473 cm-1 doublet which corresponds with the (CH2)-(CH2) stretching fundamental.[19]

The C-H bending mode characteristic of PE appears near 1400 cm-1. The higher energy peak centered at 1470 cm-1 corresponds C-H bending in methylene, CH2. This peak often overlaps a portion of its close neighbor peak, 1360 cm-1 which corresponds to C-H bending in methyl groups. In PE, the ratio of methylene to methyl groups depends on the amount of branching and the average molecular weight. The proportion of methyl groups in a PE sample has a direct impact on the degree of crystallinity in the sample. The ratio of the area under these two peaks can, therefore, be used to provide an indication of the relative crystallinity of the sample.[20]

The vibration of the C-C bond in PE is reflected by the large peak centered at 725 cm-1. The deformation of the bond is commonly described as 'rotational' or 'rocking'. This motion may roughly be described as a twisting of the CH2 group about the -C-C- skeletal axis. In solid PE, this peak is usually appears as a doublet structure. At room temperature, the doublet consists of two peaks, one at 720 cm-1 and the other at about 730 cm-1. This doublet serves as another valuable source for measuring the relative crystallinity of a PE sample. The peak at 720 cm-1 is linked to vibrations within the crystalline portion of the

sample. In all PE spectra, the higher wave number component has the greater level of absorption. In very crystalline HDPE samples, the intensity of the lower peak is almost equal to that of the dominant peak. In LDPE the relative intensity of the lower band falls off significantly. In molten PE samples, the doublet structure is not resolved at all.[21]

The benzene ring side group present in PS greatly complicates the polymer's spectra. The high electron density of this ring affects the other adjacent bonds in the monomer unit. The influence of the unsaturated ring on the infrared spectra of PS is to increase the fundamental energy of vibration of many of the neighboring bonds. A spectra of a pure PS film is shown in Figure 3.3 below.

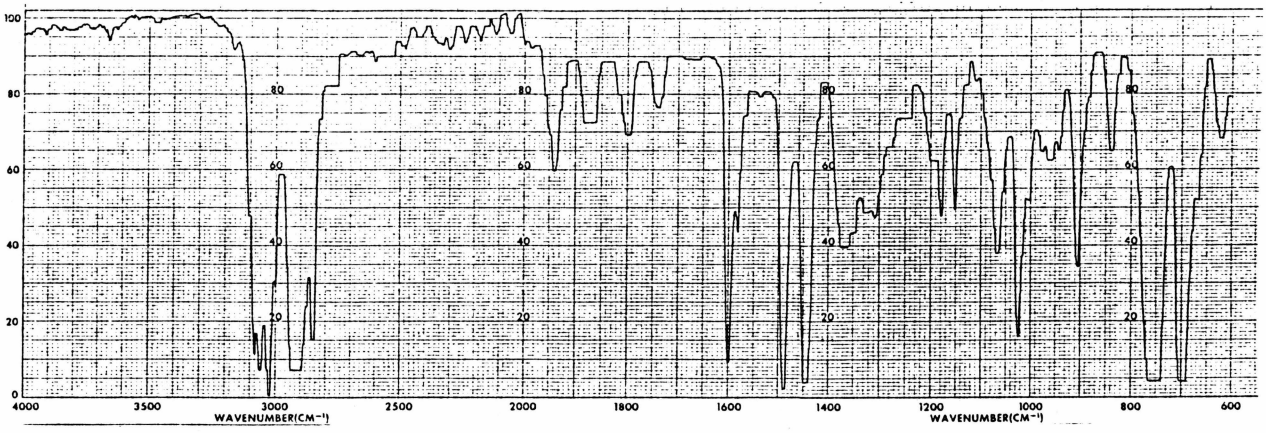


Figure 3.3

On the benzene ring, three types of C-H bonds exist. Of the five aromatic hydrogens in each monomer unit of PS, two pairs are symmetrically situated and the remaining hydrogen is unique in its position farthest from the main chain. These three distinct groups each have different fundamental modes of vibration. The

hydrogen bonded to the carbon, which retains the benzene side group, is also significantly affected by the double bond character of the ring. Both the complex nature of the forces in PS, and the lack of symmetry in the molecule cause the PS spectra to be quite complicated.

The bond most affected by the ring unsaturation is the C-H bond coming off of the benzene ring. This bond absorbs at greater wave numbers than we would expect if we ignored the double bond character of the ring. This same effect is felt to a limited degree by the C-H bond shared by the carbon which has the benzene side group. The stretching vibration of these C-H bonds occur always at wave numbers greater than 3000 cm-1.

Two types of bending vibrations exist for the C-H bonds within the benzene ring. The in-plane vibrations occur between 1300 and 1000 cm-1. These bands are rarely useful, however, because other, stronger absorptions in the same region overlap them. We use the out-of-plane vibrations, between 900 and 690 cm-1, to assign the position of substituents on an aromatic ring. The monosubstituted nature of benzene in PS always gives a strong absorption near 690 cm-1. If this band is ever absent from the spectra of an aromatic compound, than we know conclusively that no monosubstituted rings are present. A second stronger band corresponding to out-of-plane bending also appears near 750 cm-1.

As the aliphatic backbone of PS is very similar to that of PE, each of the peaks in PE's spectra are also reflected in the spectra of PS. On this basis, we assign the stretching modes of

CH2 along the chain backbone to a large peak around 2900 cm-1. The peak at 1450 cm-1 corresponds to the bending mode of CH2. The location of this peak is almost identical with the same absorption in the PE spectra, 1460 cm-1. The aromatic ring significantly affects the fundamental frequencies of vibration of the C-C main chain bond in PS. As a result the peak corresponding to the rocking vibration exists at higher wave numbers in the PS spectra than it does in PE. The location of the C-C rocking peak is coincident with the peaks assigned to in-plane bending.[22]

The C=C bond does absorb infrared light in the form of a stretching vibration between 1600 and 1425 cm-1. Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single bond character (through resonance as shown below), and thus a lower frequency of vibration.

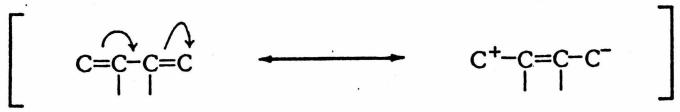


Figure 3.4[23]

With several conjugated double bonds, the number of C=C absorptions often corresponds with to the number of conjugated double bonds.[24] Three large peaks centered at 1430, 1480, and 1595 cm-1 reflect the presence of the three conjugated double in the benzene side group of PS. The last significant feature of a PS spectra is the presence of four distinct peaks between 2000

and 1700 cm-1. These peaks are a result of combination and overtone absorptions. The number and locations of these peaks are characteristic of a monosubstituted aromatic ring. These peaks in addition to the C-H out-of-plane bending region, 900-690 cm-1, serve as 'fingerprints' as to the type of aromatic substitution present in the sample.[25]

My description of the spectra of PS, though intentionally incomplete, does demonstrate that reasonably complete assignments for all the peaks are possible for a polymer with a repeat unit as large as that of PS. Ethylene terephthalate is larger and more complex than styrene, and therefore, its spectra, shown in Figure 3.5 below, is more complicated and perhaps confused than the other two spectra which I have already presented.

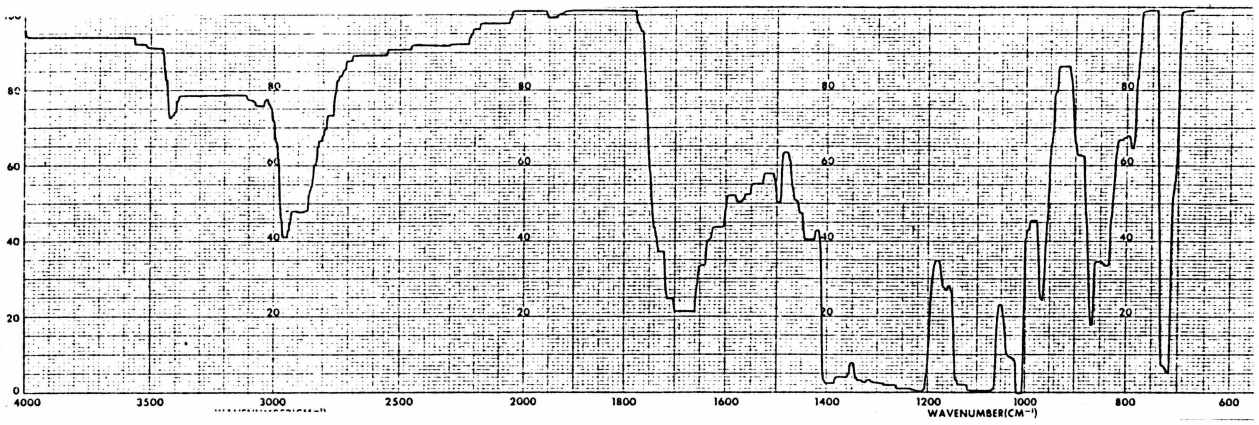


Figure 3.5

The vibrational spectrum of PET is more complex than that of PS for two reasons: 1)PET contains oxygen and 2)PET is partially crystalline, and thus the intensities of several peaks depend of the crystalline / amorphous ratio. The interpretation of the PET spectra is most clear if we examine the contribution of two

symmetric parts of the monomer unit individually. The two subunits, shown in Figure 3.6[26], demonstrate symmetry, and contain different functional groups.

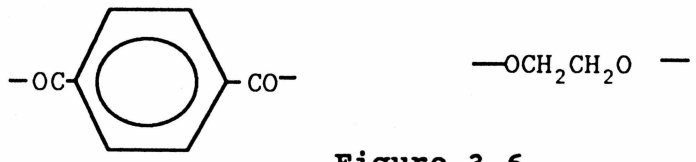
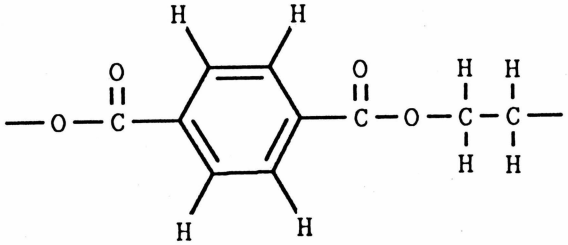


Figure 3.6

The subunit which contains benzene is bisubstituted in the para position by two carbonyl groups. The second subunit is an ethylene molecule with ether linkages on both ends. These C-O units are part of an ester linkage in the polymer.

As PET contains all the functional groups of PS, every vibrational mode present in PS also exists in PET and is likewise reflected in its spectrum. The stretching vibration of the aromatic C-H bonds absorb in the same location as the corresponding vibration in PS. However, the presence of oxygen adjacent to the aliphatic C-H bonds leads to a shift in the C-H stretching frequencies. The center of the C-H stretching peak in PET is approximately 2960 versus a center of 2900 cm-1 in PE.[27] In PS, the benzene contains three conjugated double bonds. In PET, the benzene has as its immediate neighbors two carbonyls whose double bonds are part of a conjugated bond resonance form, shown in Figure 3.7. It is therefore, possible for a resonance form of PET to have either four or five conjugated double bonds.



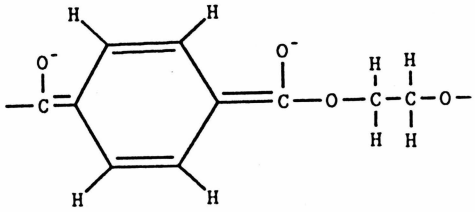


Figure 3.4 A **Figure 3.4 B**

This conjugation affects the vibrations of the benzene ring and those of its neighboring carbonyl groups.

The stretching vibrations for all the possible resonance forms of conjugated carbon/carbon double bonds are resolved into one large, or multiple, weak peaks in the region between 1400 and 1600 cm-1. In most films, the peaks either appear as small bumps or they fade into the background noise.

The most stable resonance form of the conjugated double bonds is shown in figure 3.4 A. The C=O bond has a stretching vibration slightly higher in energy than that of the C=C bond. The C=O stretching peak is centered at 1705 cm-1. This carbonyl stretching peak is the most important peak in the PET spectra for three reasons: 1)It is always present as a large, single peak 2)It does not overlap with any other major peak in the PET spectrum and 3)No other polymers which we consider have a major absorbance peak in the same location.

Another significant feature of the PET spectrum is manifested in the strong and broad C-O stretching vibrations which appear between 1300 and 1000 cm-1. This type of vibration

involves two different types of carbons in PET. The (C=O)-O stretch exists at 1263 cm-1. The (CH2)-O stretch often occurs as a doublet at 1100 and 1120 cm-1. Whether or not this doublet reflects the crystalline / amorphous content of the sample is a subject of current investigation.[28] The two or more peaks caused by C-O stretching are contributed to and / or obscured by aromatic out-of-plane C-H bending vibrations which absorb in the identical region. Polyethylene terephthalate samples typically absorb a tremendous amount of light in this region. The resultant peaks overlap to such an extent that they often can not be distinguished as individual peaks.

As PET has many different functional groups, its spectra resembles that of a polymer blend. The absorbencies by specific groups overlap with the peaks created by other functional groups. As a result, unless a film containing PET is very thin, multiple peaks become so large that an accurate analysis of the PET spectrum becomes impossible.

Chapter 4
The Infrared Spectra of a Polymer Blend

The Model Cities blend which we consider in our analysis is composed of retrievable post consumer plastics in the proportion that they exist in the solid waste stream. High Density Polyethylene and PET are the major components of the Model Cities blends that we have analyzed. The percent composition of the Model Cities blend is listed in Appendix 4.1. The polyolefin component of the blend includes PE, PP and a portion of the films which are composed hydrogen substituted carbon chains. The polyolefin components, of which HDPE is by far the most abundant, all have very similar spectra. Our analysis of the relative abundance of PET to PE inevitably, therefore, includes the other polyolefins as a portion of the PE component. Table 4.2 lists the relative abundance of the Model Cities Blend in which all the polyolefins are considered to be one component.

Other polymers in the blend, polystyrene and polyvinyl chloride, exist in such a small proportion that they do not significantly affect the morphology of the blend. We have, therefore, chosen to ignore them in our analysis.

Studies that Professor Van Ness made in the summer and fall of 1991 on a specific Model Cities blend, called MCC5SIB, aroused his suspicions that the distribution of component polymers within the blend is not homogeneous. Electron micrograph pictures the MCC5SIA blend show a band between 150 and 400 microns below the sample surface in which regions of PET are more defined than other zones within the sample. In an effort to confirm his

suspicion Professor Van Ness decided that we would investigate a method by which the infrared spectrophotometer could provide insight into the relative composition of the region in question.

For a polymer without polar sidegroups, like PE, intramolecular interactions are weak. A great majority of the peaks in the infrared spectrum of PE can be attributed to the fundamental harmonic frequencies of an isolated single chain rather than the crystal. A smaller number of features in the spectrum correspond to vibrations of various defect structures or end groups.[29]

The natural frequency of vibration of a polar bond depends to a small degree on the attractive, repulsive and stearic forces felt by the bonded atoms. The same polar bond in different compounds or crystalline structures is influenced by different forces. For example, a C=O bond absorbs specifically at 1735 cm-1 for a ketone whereas the same bond in an aldehyde absorbs at 1720 cm-1. Crystallinity also has a significant effect on the types of vibrations possible in a polymer chain. The vibrations of a molecule in a crystal lattice are altered by any polar groups that are in the direct vicinity. The vibrations of such a molecule are also limited by the confining nature of crystalline structures. The peaks in the spectra of a crystalline, apolar, sample tend to be more narrow and defined than those of a noncrystalline and / or polar polymer sample. In the spectra of a apolar, crystalline sample, a large peak will often be resolved into doublets. One peak corresponds to a specific vibration in

the crystalline regions of the sample, and the other to that in the amorphous regions.

The bonds between atoms in a largely amorphous sample are influenced by many different intermolecular forces. Such forces in a pure crystalline sample, however, are limited, and influence each monomer in the crystal to the same degree. The range of absorption corresponding to a specific vibration in a pure crystalline sample, therefore, spans far fewer wave numbers than the range of wave numbers corresponding to the same vibration in an amorphous sample. The breadth of a particular peak corresponding to a vibration in an amorphous region of the sample may even overlap the peak corresponding to the same vibration in the crystalline regions of the sample.

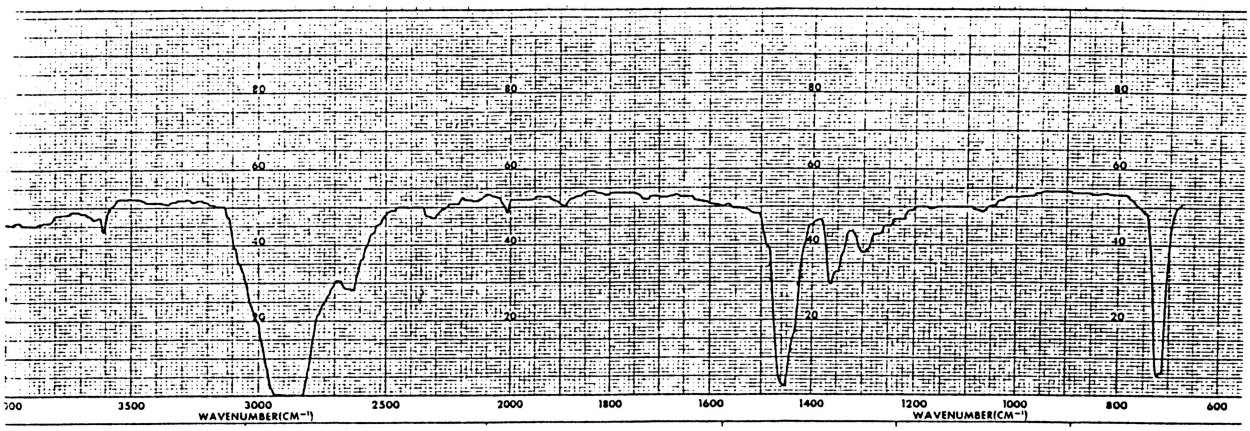
In the Model Cities series, the types of intermolecular forces which affect any given chemical bond are numerous and diverse. In such an environment, the range of the frequencies of vibration for a specific type of chemical bond is considerably broader than those of the same bond in a pure, crystalline sample. An unfortunate effect of broad peaks in the spectra of a mostly amorphous polymer blend is that large peaks corresponding to a given vibration often overlap small neighboring peaks corresponding to a completely different vibration. The overlapping nature of important peaks complicates the interpretation of the infrared spectra of most polymer blends.

All of the major peaks in a Model Cities spectra can be assigned to the fundamental frequency of vibration for a specific

chemical bond prevalent within the sample. Smaller peaks can be attributed to one of three categories. Many types of polymers present in the blend in small proportion may contain chemical bonds which are not present in any of the most prevalent components of the blend. For example, the carbon-chlorine bond is dominant in the spectra of pure polyvinyl chloride, PVC. Because PVC comprises only 2 percent of a Modes Cities blend, the contribution of the carbon-chlorine bond, not present in PET, PE, nor PS, manifests itself in only a minor peak in the blend's spectra. Small peaks in a spectra which can not be attributed directly to any one chemical bond can often be attributed to Fermi resonance. Absorption at a given wave number can be the result of the fractioning of the energy to two lower frequencies which are absorbed by the sample.[30] For example, a small peak could result in a Model Cities spectra at approximately 2185 cm-1 due to the characteristic PE peaks at 735 and 1450 cm-1. The third potential cause of a minor peak is a contaminant in the sample. Examples of contaminants in the MCC5SIB blend include water, dirt, catalysts and compatibalizers remnant from the polymer's processing.

The spectra of recycled polymer blends have significant background absorption in addition to the absorption outlined by major and minor peaks. Background absorption is defined as the area in a spectrum between zero percent absorbance and an imaginary line connecting the points of the spectrum with the least absorbance. This imaginary line is called the baseline.

Background absorption has four main causes: 1)the overlapping of large peaks, 2)extraneous absorption as a function of the extra thick nature of a sample, 3)light reflection and scattering due to a rough film surface and 4)an abundance impurities in the sample including catalysts, additives, dyes and other impurities not removed during the recycling process. The overlapping of major peaks is the cause of a low baseline in regions of the spectra where we know there to be standard modes of vibration characteristic of the sample. The particularly thick nature of a film is usually the cause of a uniformly low baseline. Light of any frequency can only permeate so many layers of atoms. The thickness of a film is a potential cause of absorption in regions of a spectra which do not correspond to any vibrations with in the sample. Figure 4.3 is a spectra of PET which has a constant amount of background absorption due to the unusual thickness of the film.



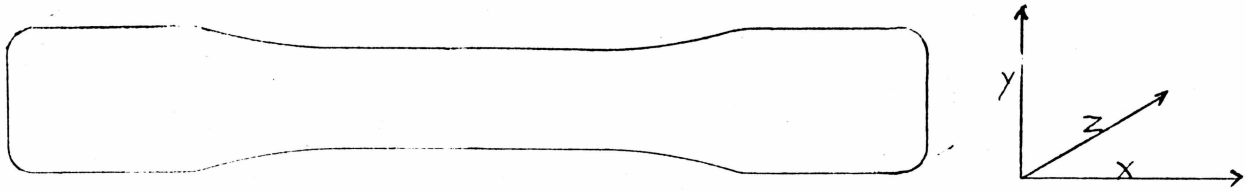
(spectra of a film, 125 microns thick PE film)
Figure 4.3

Many spectra that we analyze have background absorption present throughout, but to different degrees of severity. We are not

sure what the cause of this discriminating background absorbance is. Background absorbance of any variety is a hinderance to the analysis of spectra. In the **Chapter Five** I describe a manner through which we are able to eliminate the effects of background absorption, and thereby attain accurate measurements of the areas outlined by specific peaks.

Chapter 5
A Project Description and Sample Preparation

The blend that we have analyzed with our method is manufactured from molded pelets. The Center for Plastics Recycling Research at Rutgers collected postconsumer plactics, and pelletized the resultant composite resin. The Polymer Precessing Institute at Castle Point, New Jersey, then manufactured samples from these pellets. The individual samples were molded into an odd shape which resembles a flattened dogbone. Dogbone samples are approximately three millimeters thick and fifteen centimeters in length. Figure 5.1 shows a true size outline of the dog bone sample with a corresponding three dimensional axis to which I will refer for the remainder of this chapter.



(3-D drawing of dogbone w/ axis: X=length; Y=width Z=thicknes)
Figure 5.1

Dr. Van Ness gained an indication of differences in the samples' morphology through electron micrograph pictures of their cross sections. He cooled the samples to the temperature of liquid nitrogen and then fractured them by impact, producing fracture surfaces alternately perpendicular and paralell to the long axis of the dogbone.

Electron micrograph pictures of cross sections of MCC5SIB dogbones, fractured at different locations along the X axis of the sample, often demonstrate a region of unique morphology between 150 and 500 microns under the sample's surface. At the corners and ends of the sample, these regions exhibit greater thickness. This type of morphology does not exist in other regions of the sample. The distinguishing feature of this peculiar region is the morphology of the PE / PET interaction. The PE and PET exist as slabs stacked upon each other. Neighboring slabs of like composition share multiple 'bridge' structures between them, giving the appearance of three dimensional continuity for both the PE and PET phases. Although the size of the slabs are minute, and the intra-slab connections mostly nonvisible, the connections provide the region with unique physical properties. We refer to this band, present within the surface throughout the blend, as a cocontinuous region. Exhibits 5.1 is a copy of an electron micrograph picture which demonstrates the presence of the cocontinuous region.

In the surface and inner regions of the sample, the PET exists as discrete units within a background of PE. An analogous composition to that of the surface and central portion of the MCC5SIB blend is that of cherry jello. According to this analogy, the gelatin represents the PE and the cherries represent the PET. The cherries, like the PET, are separate, independent species. The properties of the jello mixture are, therefore, controlled by the continuous gelatin region. Exhibits 5.2 and

5.3 are electron micrograph pictures which contrast the morphology present within the cocontinuous region to that of the center region of the MCC5SIB blend.

The essence of my project is to determine whether the change in morphology of the MCC5SIB blend, visible from 150 to 500 microns below the dogbone surface, also coincides with a variation in composition. Our method of testing this hypothesis is quite direct and involves only four major steps. 1)We cut films, between eighty and one hundred microns thick, from our sample, at specific 100 micron graduations. 2)We obtain an infrared spectra of each film using a Perkin Elmer spectrophotometer Model 3100. 3)We adjust the spectra to eliminate the effects of background absorption. 4)We calculate the areas outlined by specific peaks in each spectrum. An analysis of the films, one at a time, reveals the relative change in the sample's composition as a function of depth, if one exists at all.

Our film production technique, though very elementary in design is the most distinguishing aspect of the method. The individual films must come from a specific one hundred micron thick region of the sample below the sample surface and parallel to the X axis. The length and width limitations of each film are less demanding. The films must be at least one inch long and 3/16 of an inch wide in order to fill the sample window of the spectrophotometer. In order to attain films with the appropriate length and width, we are bound by the small size of the dogbone

samples to mill films only from the X-Y plane of the dogbone. We mill the films from the central portion of the X-Y plane. A complete series of films from each one hundred micron depth in the sample accurately represents the composition of the sample as a whole.

A single dogbone sample is used to produce multiple films. We cut each dogbone perpendicular to its X axis into one-and-a-half inch segments with a band saw. This division produces four segments: two which include the ends of the dogbone and two thinner samples from the middle of the dogbone.

Rather than cutting our films directly from the sample, we extract unwanted sample away from both sides of the region of concern. Before we cut unwanted material from the film, we secure the sample segment with a series of vises. A small aluminum 'C' shaped vise with two adjustable allen bolts holds the sample. We insert a brass plate between the bottom of the sample and the bottom of the vise. The brass plate provides support for the sample, especially when much of the sample bulk is milled away. The plate also serves to keep the sample perpendicular to the vise and to the milling blade. We then insert the aluminum vise / sample / brass plate unit, shown in Figure 5.2, into another vise which is a fixture on the mill's carriage.

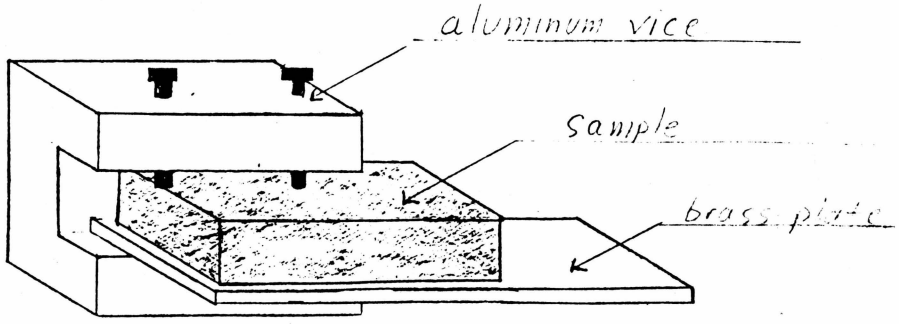


Figure 5.2

Because the aluminum vise is 'square', the pressure provided by the carriage vise aligns the unit vertically. The sample segment is thus fixed flat against the mill carriage with the X-Y plane of the sample perpendicular to the mill blade.

The location of the mill carriage relative to the lowest point of the mill blade can be changed in three dimensions by three calibrated adjustment wheels. When aligning the sample along its Y axis relative to the blade, we leave approximately a two millimeter border between the edge of the blade, opposite the aluminum vise, and the edge of the sample. This border serves two important purposes. The outer five hundred microns of the sample contain the cocontinuous region of the sample parallel to the X-Z plane of the sample. By excluding material of this region from our films, we insure that any cocontinuous material in the film is specific only to the X-Y plane. The second function of the border is to stabilize to the film during the milling process.

We do not need to know the dogbone's thickness when we manufacture a surface film. After aligning the carriage, we cut a single channel in the sample until, at the trough, the sample

is only a few hundred microns thick. At this point, we advance the carriage in the X direction until the center of the blade is about an inch in beyond the edge of the sample. We then raise the carriage until the spinning blade first makes contact with the brass plate. We store this location as a 'zero' on the calibrated Z axis adjustment wheel. We then turn the wheel until it the calibrations on the wheel read 4.0 thousandths of an inch, the equivalent of one hundred microns. One final run of the mill blade though the channel should produce a film of approximately the correct thickness.

The milling procedures for films representing the inner regions of a sample are somewhat more complex. The thickness of the sample must be measured by a micrometer. We mount the sample using two vises in the manner already described. We then calibrate the milling machine relative to the mounted sample by lowering the active milling blade until it just begins to make contact with the sample's surface. We store this location in the as a 'zero' on the Z dimension adjustment wheel. Rather than cutting a channel into the sample, we cut away material from the entire X - Y plane that is showing. We make multiple passes, at each increment along the Z axis, with the milling blade, at different Y dimensions, so that the entire X-Y surface showing remains coplanar. We cut away sample material in this manner until the Z axis adjustment wheel indicates that the location of the blade is one or two thousandths of an inch above the region from which we desire a film. Before proceeding with the cutting,

we remove the sample from the jig, and measure its thickness to confirm the reading of the Z axis calibration wheel. After we complete any further milling necessary to reach the desired region in the sample, we remove the sample from the aluminum vise, turn it over and reassemble the sample / aluminum vise / unit without the brass plate. As we secure the unit in the carriage vise, we place the brass plate between the sample and the carriage vise. At this point, the remaining cut is made in a channel, rather than as a plane. The proceedures for completing the milling of the film are identical to those of a surface film.

Skewed sample seating, a non uniform brass plate, or of the mill's calibration can cause the resultant sample thickness to be different than expected. Either holes will be cut through the sample, or the sample will be destroyed if the sample is not laying firmly against the brass plate. When the cutting is complete, we remove the aluminum vise and sample unit from the carriage vise. Before we remove the aluminum vise, we check the thickness of the film with a micrometer. As the diameter of most micrometer extension arms is greater than 3/16 of an inch, we must cut off a portion of the border to the side of the film before we can obtain a reading. If the film width is greater than two hundred microns than we reinsert the unit into the carriage vise and cut away more of the blend. Otherwise, we extract the film from its two thicker borders by cutting along the samples two interfaces with a razor blade. We then further narrow the film's thickness by sanding it from the appropriate

surface.

We have experimented extensively with different methods of sanding. Our latest method produces the thinnest films with the least amount of film tearing. We hold one end of the film against a wood block with a vise. We then patiently sand the film with 180 to 280 wt carbide paper using minimal downward pressure. Once we obtain a half inch portion of the film with a consistent thickness of one hundred microns of less, then film is ready for scanning.

The unique aspect of this method of sample preparation is its simplicity and practical nature. It is very efficient, inexpensive and precise. An experienced operator can mill a film less than one hundred microns thick from a exact region within a sample every twenty minutes. The only expenses involved with this method of sample preparation are include the occasional purchase of sandpaper and saw blade, and any remaining depreciation of the milling machine which was built in 1941.

Chapter 6
The Infrared Spectrophotometer

The infrared spectrophotometer, termed the I.R., serves three very necessary roles in our method. We use the spectraphotometer and its requisite computer to acquire the spectra of a given film. Before we determine the areas outlined by specific peaks in the spectrum, we must adapt the spectrum, using Perkin Elmer software, to a standard form. Once the spectra is completely justified, we can easily determine the area outlined by specific peaks using a typed command on the I.R. acecessory computer. We repeat these three processes for each film that we analyze.

Our I.R. is a standard transmission unit. Its design and use are both quite straightforward. The I.R. produces two beams of light and directs them at two corresponding light sensors. The two beams are directed across an open field, six inches in width. The light production / receptor couple at the rear of the machine serves as the control for each scan. The anterior couple is identical to the control except for the fact that a film often interupts the light beam. Both light producers emit the same amount of light. A portion of the light emitted by both light producers is absorbed by the air before it reaches its corresponding light sensor. In order to eliminate the effects of light absorbance due to air, the I.R. considers the amount of light measured by the control light receptor to be the standard. The absorbance at each wave number is measured as the difference in transmission between the near and far couples. Our I.R.

repeats this calibration and subsequent measurment at each wave number in its spectrum, 4000 to 602 cm-1.

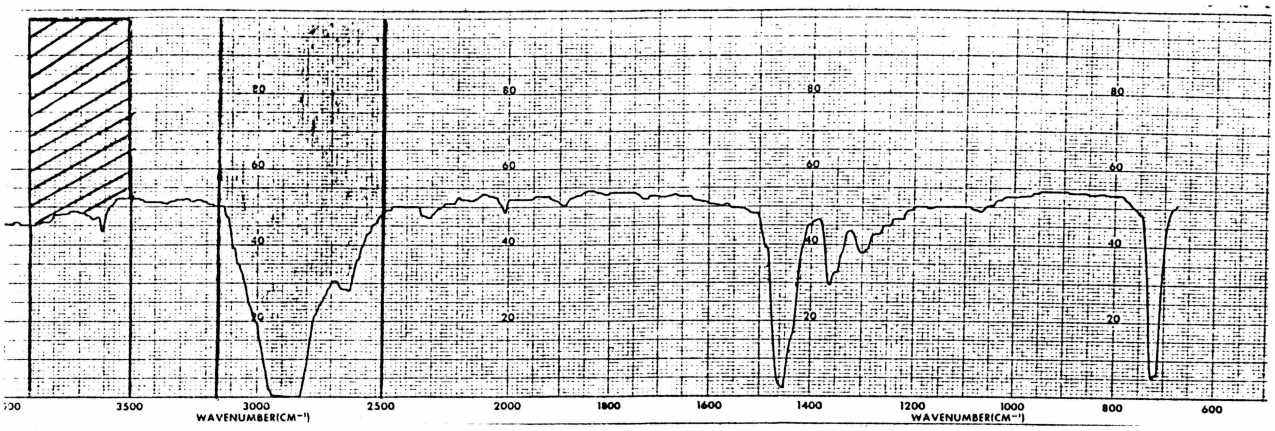
The process of obtaining a spectrum, described above, is completely automated after the necessary software is loaded and the film mounted. I include all necessary instructions concerning the use of the Perkin Elmer software and key stroke commands as an adendum at the conclusion of the paper. We mount each film by centering it over a rectangular hole cut in the middle of a metal plate. We afix the film to this location with low-adhesive tape. The dimensions of this rectangle, approximately 3/16" by 3/4", are slightly greater than those of the window through which the beam of light must pass in order to reach the light sensor. We then mount the metal plate on a pair of brackets bordering the window. A properly mounted film completely blocks the light beam in its passage to the light sensor. The area of film considered in any scan is, therefore, less than 9/64 of a square inch.

After the sample is mounted, the operator of the I.R. must choose whether to run a three minute or a twelve minute scan. The choice is indicated by pressing the apropriate button on the spectraphotometer. During the three minute scan, the I.R. changes the wave number of light emmited approximately two times per second. This time interval is often too short for minor vibrations to become completely activated. A three minute scan does not provide the detail acquired through a twelve minute scan. A three minute scan does bring out definate trends in a

spectra that are sufficient for a quick analysis. By increasing the length of time that a sample is in contact with each wave number of light, minor vibrations become more completely resolved. The additional definition provided by a twelve minute scan increases the accuracy of the resultant spectrum. We have found that the difference in in spectra quality provided by the two scan lengths is not significant unless the film is very smooth. The additional accuracy provided by the longer scan is in general not worth the additional scan time, unless the analysis needs to be precise.

As a the spectrophotometer conducts a scan, the computer stores the percent of light absorbed at each wave number in its memory. We save all good scans and their subsequent revisions to disk for future reference. Before we calculate the areas outlined by certain peaks, we must eliminate the effect of backround absorption on the spectrum. In order to acheive this goal, we first assign a constant baseline to the spectrum. We then raise the spectrum uniformly until the baseline is collinear with zero percent absorbance. At this point, we calculate the area of specific peaks with an automatic keystroke command. We make these adjustments on the accessory computer.

Background absorption affects make the determination of the areas under specific peaks in a spectrum very difficult. In Figure 6.1, for example, common sense tells us that we can not include the area of the shaded column, between 3150 and 2750 cm-1, in the area of the peak corresponding to C-H stretching.



(Unaltered Floats spectrum)
Figure 6.1

To include the shaded area in the area of the C-H stretching peak would by inference mean that the hatched area between 3900 and 3500 cm-1 is also caused by a specific mode of vibration within the sample. As we know that no such vibration exists in pure PET, this inference can not be true, and likewise, the shaded area can not be included as a contribution to the C-H stretching peak.

In order to accurately determine the areas of the peaks, in the spectrum shown in Figure 6.1, we must first assign a baseline to the spectrum. The baseline, in this example, should lie paralell to the X axis and collinear with the horizontal portion of the spectrum, intersecting the Y axis at aproximately fifty three percent absorbance. A result of this method is that the baseline serves as the ceiling for each peak rather than the imaginary line at zero absorbance.

The *area* command availible on the accessory computer automaticly uses zero percent absorbance as its baseline. In order to conform to this structure, we must shift our spectrum up

so that our designated baseline is collinear with the zero absorbance. We add a constant, via the *add* command, to the Y coordinate of each absorbance value in the spectrum. The value of the constant is the difference in percent absorbance between our assigned baseline and zero percent absorbance. Figure 6.2 is a plot of a PE, floats, spectrum before and after we raised it. We assigned a baseline to the spectrum at fifty six percent absorbance. We then uniformly added forty four percent absorbance to the spectrum in order to raise it to zero absorbance.

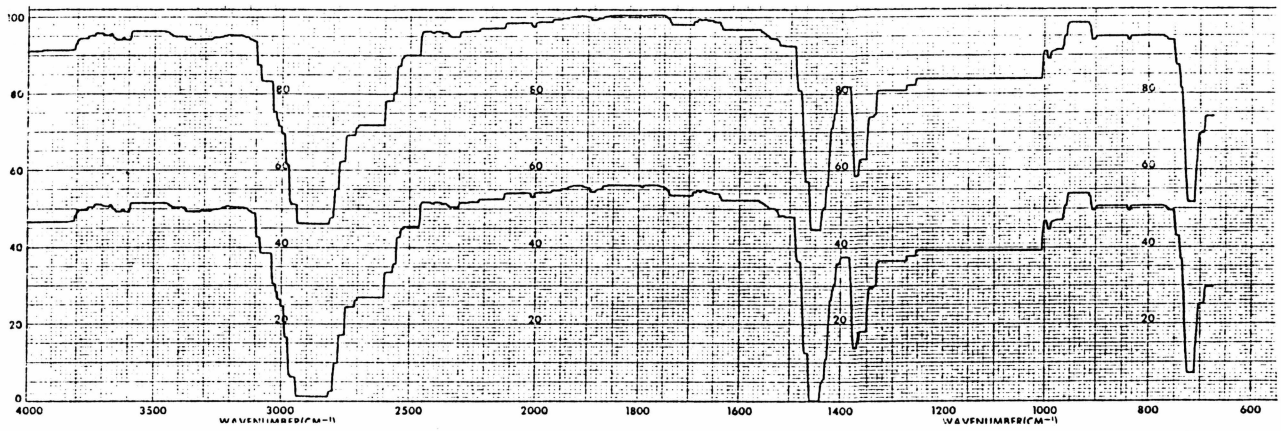


Figure 6.2

The areas obtained by this method should not be affected by backround absorption assuming that the our designated baseline accurately traces the regions where vibrations standard to the sample do not produce peaks.

The process of eliminating the effects of backround absorption is more complex for spectra which do not have a linear or horizontal baseline. Bower and Maddams have offered a solution to this problem through what they term the 'pseudo-

baseline method'[31]. In applying the 'pseudo-baseline method', the analyst designates specific endpoints for the multiple baselines which he wishes to apply to the spectrum. These endpoints must satisfy four criteria: 1)They must lie on the spectra. 2)They must represent different regions of the spectra. 3)The endpoints must correspond to a minimal absorbance. 4)They must be unaffected by the the absorption of nearby peaks which we specificly know to correspond to vibrations common to the sample. The analyst connects these endpoints, in a manner demonstrated by Figure 6.3, so that each peak in the spectra is capped by a segment of a pseudo-baseline.

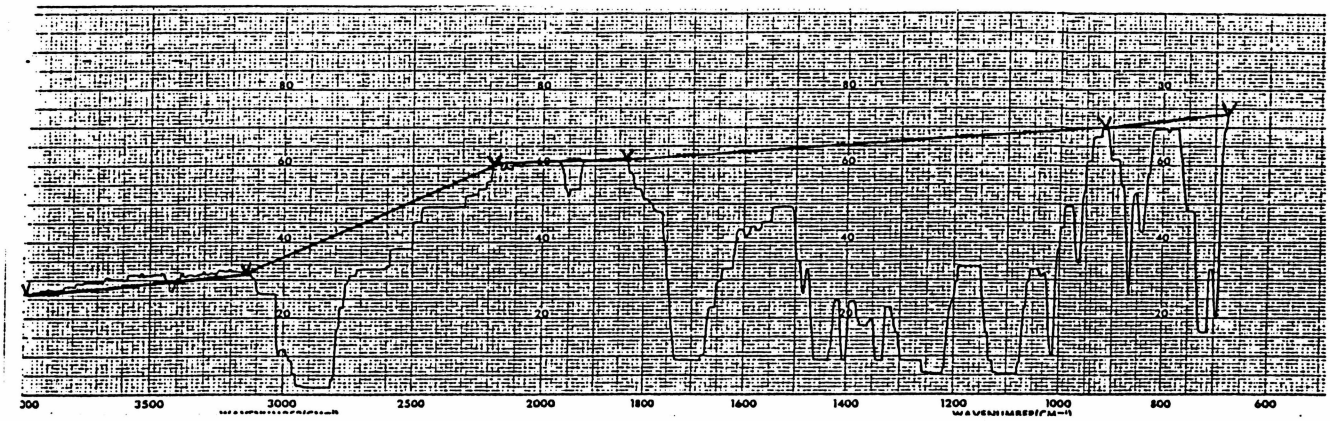


Figure 6.3

We are able to determine the areas under peaks in the spectra analyzed by the 'pseudo-baseline method' either mechanically or by using a computer. The simplest and usually the fastest way of determining the areas is by the well known cut-and-weigh method. According to this method, we carefully cut out the area outlined by a specific peak, and weigh the extracted paper on an analytical balance. Once all the desired peaks of a spectra have been cut and weighed, the relative weight, a

unitless term, of each peak is easily calculated. As we assume the paper to be of a uniform density, the relative area of each peak, therefore, is equal to its relative weight. That we do not, by the cut-and-weigh method, obtain the absolute area for each peak in the spectra is inconsequential because relative area is our basis for comparing like peaks from different spectra. Chapter Seven will explain the comparison of different spectra in detail.

In order to use the *area* command on a spectra analyzed by the pseudo-baseline method', we must first alter the spectrum so that the multiple pseudo-baselines become collinear. A good approximation of a colinear baseline can be acheived using the *flat* command on the accessory computer. This process involves the raising of some peaks and the rotation of others.
We apply the *flat* command multiple times to spectra to which we have assigned multiple pseudo-baselines. Each time we apply the 'flat' commamd we make two points in the spectrum collinear. We input contiguous points which we earlier designated through the 'pseudo-baseline method' as values for the two points used by the *flat* command. We repeat the *flat* command using different combinations of points until a collinear baseline is attained. Once the spectrum's baseline is horizontal and collinear, we elevate the spectra to zero percent absorbance in same manner that I described earlier. Figures 6.4 through 6.8 provide a summary of the multiple stages involved in the 'pseudo-baseline method' and 'flat' command. Figure 6.4 is a spectra of a film

milled from the MCC5SIB blend 600 microns below the surface. The pseudo-baselines are drawn in also to help illustrate the flattening process.

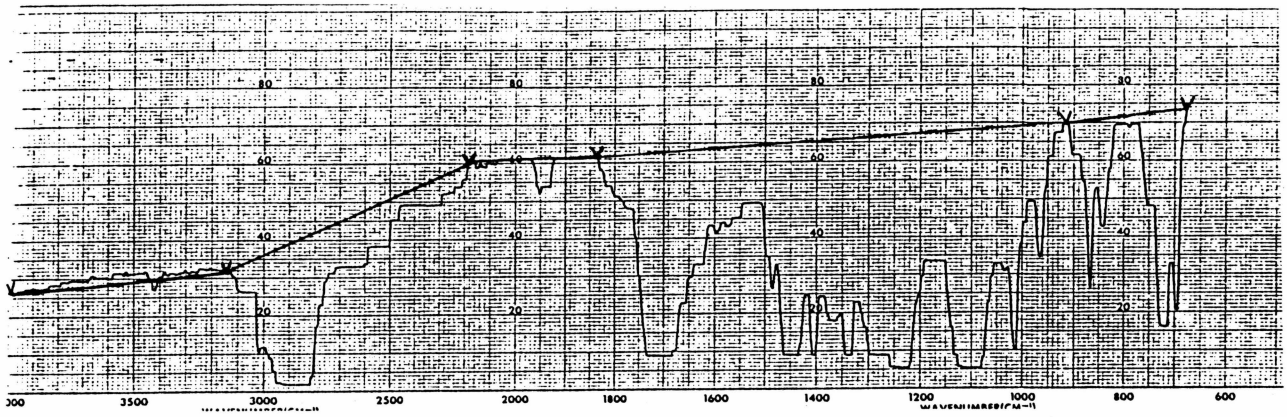
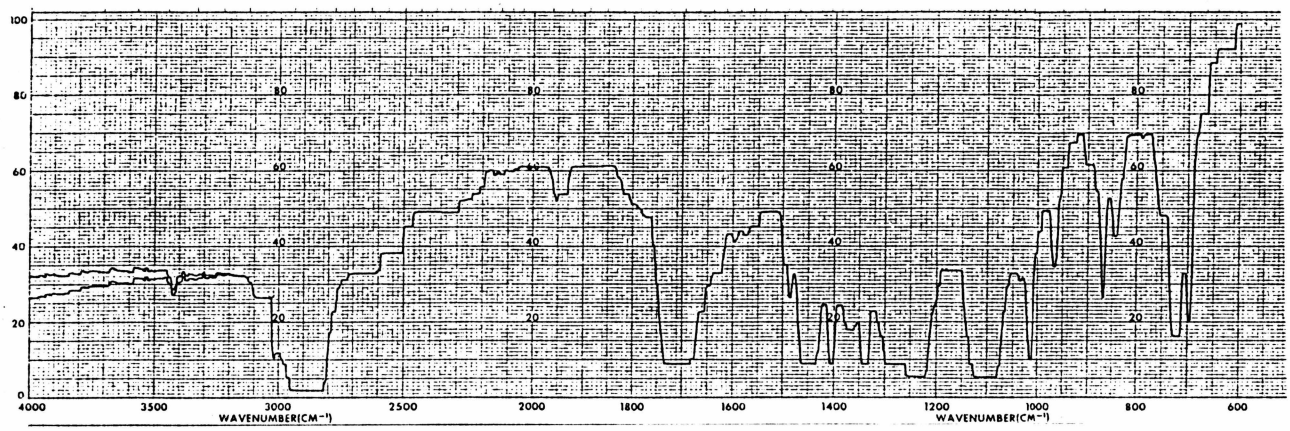
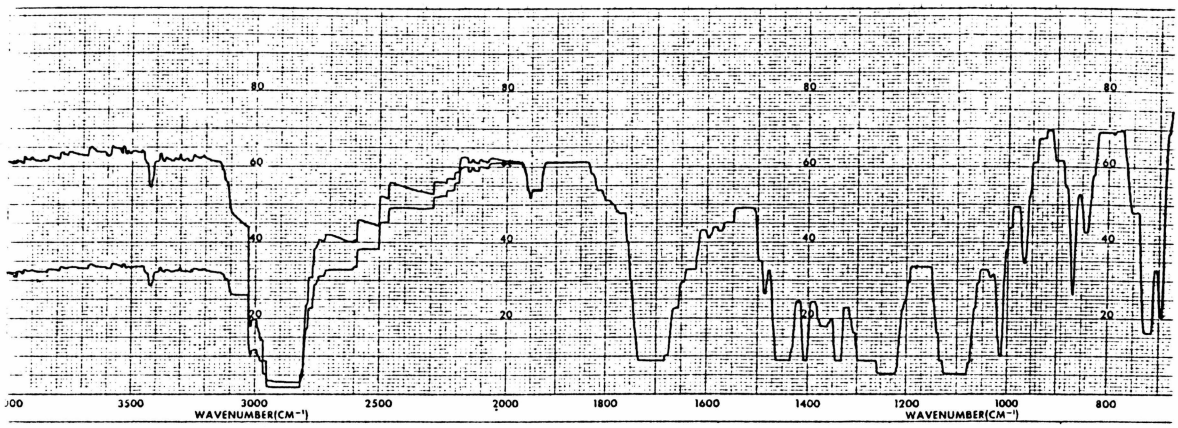


Figure 6.4



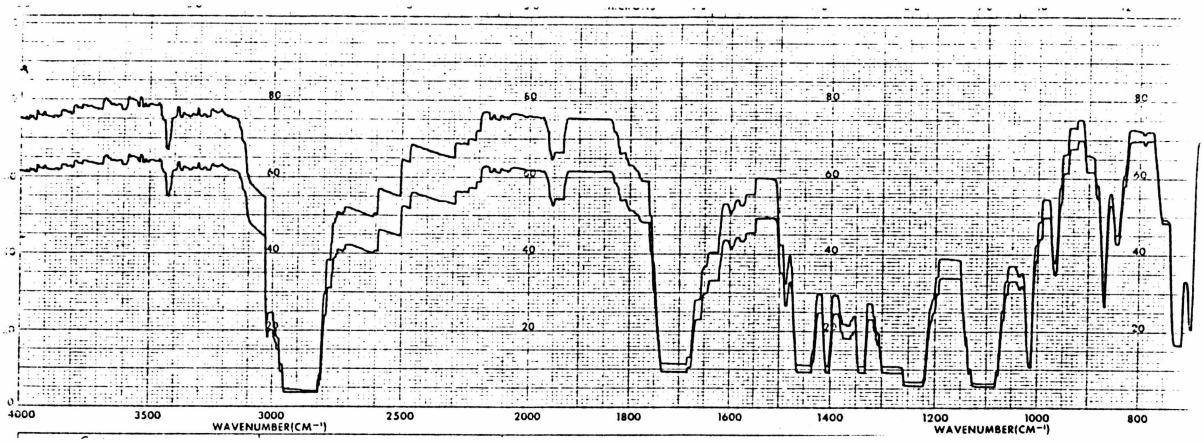
(The spectra in Figure 6.4 before and after the *flat* command is applied to 4000 and 3150 cm-1)

Figure 6.5



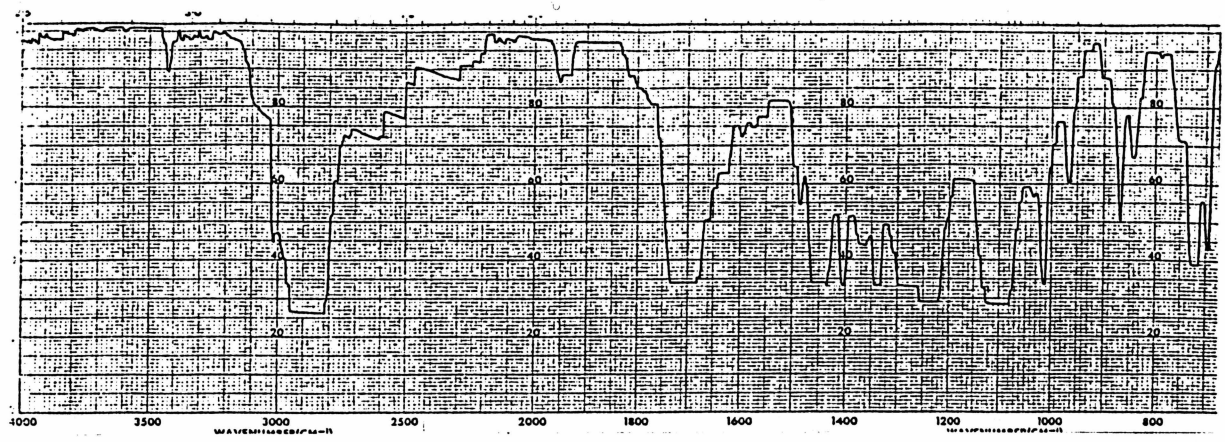
(The same spectra shown in Fig.6.5 before and after *flat* is applied to 4000 and 3150 cm-1)

Figure 6.6



(The same spectra shown in Fig. 6.6 before and after *flat* is applied to 1850 and 675 cm-1)

Figure 6.7



(The same spectra shown in Fig 6.7 raised uniformly by twenty percent)
Figure 6.8

The various methods of spectra manipulation that I have described all involve a significant amount of personal judgement, and thus a great potential for error. The choice of pseudo-baselines is clearly somewhat arbitrary. This source of error is complemented by the subsequent imprecise nature of either the cut-and-weigh method or the use of the *flat* command. Different methods of eliminating backround absorption with the *flat* command produce different relative area values. In order to be consistant we apply the *flat* command according to the method described above to each of our pure and sample spectra. Manipulation of spectra is the phase of our method which is most prone to error. Nevertheless, if the individual steps in the phase are made carefully, ever mindful of the nature of backround absorption, our method can give useful semiquantitative results.[32]

Chapter Seven
Analysis of Spectra

Our analysis of films uses the spectra of pure polymer species as a basis for the film's characterization. In my research I have chosen only to investigate the relative changes in PE and PET composition as a function of depth in the sample. We first characterize the relative area values for specific peaks in pure PE and PET samples. A comparison of these values with the relative sizes of the same peaks in a film's spectra provide a means quantify the relative abundance of PE and PET in a given film.

The pure PE and PET samples which we characterize serve as standards for future analyses. As standards for the like polymer within the blend, it is important to choose a pure sample which absorb infrared light in its major peaks to the same proportion as its respective polymer component within the blend. In determining what sample to use as a standard, we considered crystaline content, processing conditions, dyes, and composition.

An ideal standard for our method, considering the derivation of the samples, is a sample composed of only the PE or PET portion of the MCC5SIB blend which is processed under the same conditions as the blend. A difficulty in attaining such a sample is the separation of a single polymer component, without contamination, from the feedstock. A simple method of separation exists for PE. Polyethylene, both HDPE and LDPE, is one of only a few polymers which floats in its solid, nonaerorated form. In the recycling process, plastic debris is

shredded and cut into tiny flakes and then cleaned before it is melted. The feedstock for our PE standard was obtained by placing a batch of plastic flakes in water, and skimming off those which floated. Samples made of only the PE component of blends are termed 'floats'.

None of the physical properties of PET are unique enough to serve as a basis for its separation from the feedstock. Isolation of PET though float and skim processes in liquids of varying densities is in theory possible, but has not been pursued by The Center of Plastics Recycling Research. Since no sample with a composition identical to that of the PET component of the blend is availible, we attempted to find a material which closely approximated the composition of the PET component of the blend. The PET component of postconsumer plastic waste is a primarily a product of soda bottles and, to a minor extent, fibers.[33] In an effort to produce the hypothetical spectra of the PET component, we obtained the spectra of films cut from multiple soda bottles of different color, size and manufacturer. Any catalysts, copolymers of other impurities present in the soda bottles increase the accuracy of our analysis, as they are also present in the PET component of the blend. From these spectra we measure the relative sizes of certain major peaks. We then calculate from these values, the average relative area of each peak. Table 7.1 shows the average relative area outlined by specific peaks for PET and PE. The PET values reported in Table 7.1 are the average of like values from six different PET spectra. The

relative areas for PE, in Table 7.1, are the average of like values obtained from two floats' spectra. We consider the values reported in Figure 7.1 to best represent the relative contribution of PET and PE to specific peaks in the blend's spectra.

Relative area outlined by the A_n

|Peaks in Pure PE and PET Spectra

	3000-2750	1775-1600	1320-1185	1150-1050
Pure PET	13.4%	14.8%	40.5%	31.3%
Pure PE	89.2%	1.2%	5.9%	3.7%

Table 7.1

We used three criteria to limit the infrared spectrum into the regions listed in Table 7.1. First, we obtained a list of all the major peaks present in the spectra of pure PE and PET. We deleted from this list any peaks which were contributed to by any polymer in the blend except PE and PET in a significant proportion. An example of a prominent peak which we chose to delete based on this second criterion is present in the PET spectrum between 3025 and 3200 cm-1. This peak corresponds to aromatic C-H stretching and is also present in the PS spectrum. Because vibrations in PS contribute significantly to this peak,

and our analysis does not include PS, we deleted it from the list. We also eliminated from the list any peaks which are contributed to by PE and PET in a similar proportion. Such a peak exists in the blend's spectrum between 1500 and 1320 cm-1. This peak corresponds to C-H bending in methylene, a vibration which is prevalent in PE and PET. Other peaks which we eliminated for the same reason are located between 910 and 810 cm-1 , and between 775 and 675 cm-1.

In our analysis of films, we calculate the areas outlined within the regions listed in table 7.1. When analyzing a film of a particular merit of significance, we often scan the film multiple times in different locations and orientations. The relative areas of the peaks fluctuate to a small degree as a function of where, on the film, the infrared beam is focused, and how the sample is oriented. An average of the relative areas outlined by a single peak in multiple spectra provides the best indication of the true value.

The peaks present in the blend's spectrum which we use in our analysis correspond primarely to either PE or PET. By comparing the relative absorption within each defined region of the pure samples' spectra, we can determine whether vibrations within PE or PET are the major contributers to each of the defined regions of the blend's spectra. Polyethylene is responsible for most of the absorption between 3000 and 2500 cm-1 in the blend's spectra. We consider only the area outlined by the peak between 3000 and 2750 cm-1 in our analysis. We limit

our consideration of the C-H stretching peak to these wave numbers in order to reduce the influence of absorption by impurities on our analysis. As the range of our consideration, centered on the C-H stretching peak at 2920 cm-1, increases, so does the contribution of absorbance caused by impurities. We assign the region from 3000 to 2750 cm-1 to PE because it occupies more relative area in the pure PE spectrum then in that of PET. Similar reasoning is the basis for our assignment of the remaining regions, 1775-1600 cm-1, 1320-1185 cm-1 and 1150-1050 cm-1, to PET.

For simplicity we refer to the area outlined by each defined region with a 'A' followed by a subscript denoting the location of the region. The subscripts are integers from one to four, with A_1 representing the region from 3000 - 2500 cm-1 and A_4 representing 1150 - 1050 cm-1. When we refer to the sum of the areas in each of the four regions for a given spectrum we use the notation: ΣA_n.

We characterize the pure PE and PET spectra by determining the ratio of A_1, the PE peak, to ΣA_n and the ratio of $A_2 + A_3 + A_4$, the PET peaks, to ΣA_n for the two pure spectra. We use the leter 'Z' to identify to these ratios. We attatch a superscript to the 'Z' in order to identifiy what type of peak or peaks serve(s) as the numerator of the ratio. We also qualify the 'Z' term with a subscript in order to identify what type of spectra is considered. For example the term Z_{PE}^{PET}, identifies the

fraction of An which is outlined by A_2, A_3 and A_4 for a pure PE spectrum. The Z values for our pure spectra are listed in Table 7.2 below.

Z_{PET}^{PET}	0.0866
Z_{PET}^{PE}	0.0134
Z_{PE}^{PET}	0.108
A_{PE}^{PE}	0.892

Table 7.2

We also determine comperable Z values from the spectra of blend films. Our method of calculating the two Z values for films is identical to that for the pure samples. We do, however, alter the notation of the Z values corresponding to blends. We use a question mark for the subscript of the Z, as we are uncertain of the films composition.

Both PE and PET contribute to each of the A_n peaks in a blend's spectrum. If we call the relative contribution of PET to one of the A_n peaks X, then the relative contribution of PE is, therefore, (1-X). In our analysis of a film, we decide abritrarly to use Z_{PET}^{PET} and Z_{PE}^{PET} as standards in our determination, rather than Z_{PET}^{PE} and Z_{PE}^{PE}. If the second pair is used as standards, the outcome is the same. Our basic formula for determining the relative composition of a film is the

following:

$$Z_{?}^{PET}=Z_{PET}^{PET}X+Z_{PE}^{PET}*(1-X)$$

Once the $Z_{?}^{PET}$ value is determined, the equation can be solved for X by simple algebra.

Chapter 8
Results and Discussion

Our analysis of the MCC5SIB blend according to this method confirms that the cocontinuous region conatins a greater relative composition of PET than the remainder of the sample. Now that our method of film preparation is refined, the process of spectra manipulation better understood, and standard Z values are calculated for PE and PET, analysis of other blends should be very efficient.

In an effort to define, with precision, what if any region in the MCC5SIB blend is PET enriched, we made milled films at every one hundred micron depth for the first five hundred microns below the X - Y surface. We also milled films from the following regions in the center of the blend: 1000 - 1100, and 1500-1600 microns below the surface. If either Professor Van Ness had seen a region of curious morphology in the electron micrograph pictures of the central region of the blend, or if my selective films from this region provided unpredicted results, I would have focused my analysis to a greater extent on the central region of the sample.

These films were prepared according to the method that I have described with one exception. We eliminated the effects of backround absorption from their resultant spectra by a method which has subsequently been refined. This change in spectra manipulation alters the relative abundance of PET to PE ratio slightly, in a uniform nature. The trend demonstrated by the

results reported below is also reflected by our most current method of analysis. The relative areas outlined by the A_n peaks, corresponding to films from different depths in the blend, are listed in Table 8.1 below.

Distance Below the Surface	Relative Area Outlined by the Following Peaks			
	3000-2750	1775-1600	1320-1185	1150-1050
0 - 100 microns	49.7%	9.3	18.0%	13.0%
100 - 200	43.8	18.4	23.3	14.6
200 - 300	44.5	20.3	20.6	14.5
300 - 400	46.1	18.1	21.0	14.8
400 - 500	49.2	18.6	18.0	14.3
500 - 600	50.7	17.0	17.4	14.9
1000 - 1100	54.1	17.6	16.5	11.8
1500 - 1600	52.9	17.4	17.6	12.2

Table 8.1

From this raw data, one can see that there is less relative absorbance in the 3000 - 2750 cm-1 range, near the surface of the sample. From this data we calculated the necessary Z values and the relative PET to PE + PET ratio, shown in Table 8.2, for each spectra.

Depth in the Sample	0-100	100-200	200-300	300-400	400-500	500-600	1000-1100	1500-1600
$Z_?^{PET}$	.503	.562	.554	.539	.507	.493	.460	.471
PET/ (PE+PET)	36.0	41.7	41.0	39.5	36.4	35.0	31.7	32.9

Table 8.2

These results are only semiquantitative in nature. The PET to (PE + PET) ratios determined by our method do not mimic the ratio of polymer abundance, reported by the Center for Plastics Recycling Research and reported in Tables 4.1 and 4.2. They reflect a trend in changing relative polymer composition within the MCC5SIB blend, but do not provide an accurate measurement of the exact proportion of PET and PE in the blend. Exhibit 8.1 demonstrates this trend as a graph with the relative amount of PET to PE as a function of the distance beneath the sample surface.

Future work on this project includes a calibration of the results produced by our method to their true value. Such a calibration will not alter the method as I have presented it. The calibration will, however, permit the absolute comparison of PET to (PET + PE) ratios for different samples and blends. Analyses of similar blends processed under different conditions and with different compatiblizers will also be a major focus in

the near future.

Footnotes

1.Crompton,T.P.; p.2

2.Whitney,G.; Class Lecture

3.Bower and Maddams,p.13

4.Bower and Maddams; p.246

5.Joffe,Z.p.4

6.Keith and Padden; p.4

7.Birley;p.20

8.Elias, Hans-Georg;p.397

9.Bilmeyer;p.365

10.Richards;p.371

11.Corey,F.A.;p.136

12.Corey,F.A.;p.210

13.Billmeyer;p.326

14.Billmeyer;p.414

15.Bower and Maddams;p.30

16.Bower; Maddams;p.78

17.Bower and Maddams;p.2

18.Pavia et.al.;p.33

19.Bower;Maddams;p.167

20.Stein; Sutherland;p.1993

21.Stein; Sutherland;p.1993

22.Bower; Maddams;p.199

23.Pavia et.al.;p.35

24.Pavia et.al;p.35

25.Pavia et.al.;p.40

26.Bower; Maddams;p.201

27.Bower; Maddams;p.203

28.Bower; Maddams;p.203

29.Richards;p.375

30.Bower, Maddams;p.167

31.Bower; Maddams;p.38

32.Bower;Maddams;p.38

33.Xanthos; Nosker; Van Ness;p.2

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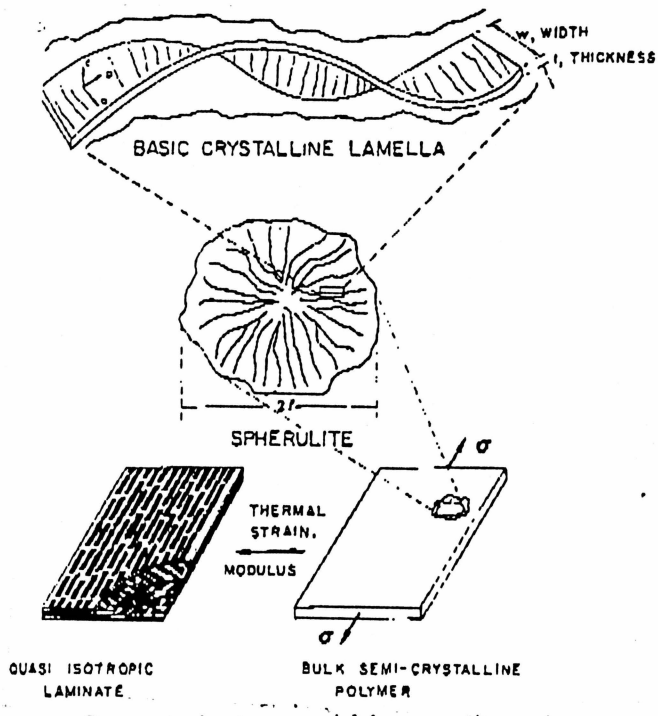


Composite laminate model for crystalline polymers.

Exhibit 2.1

Table 4.1
Composition of the Model Cities blend

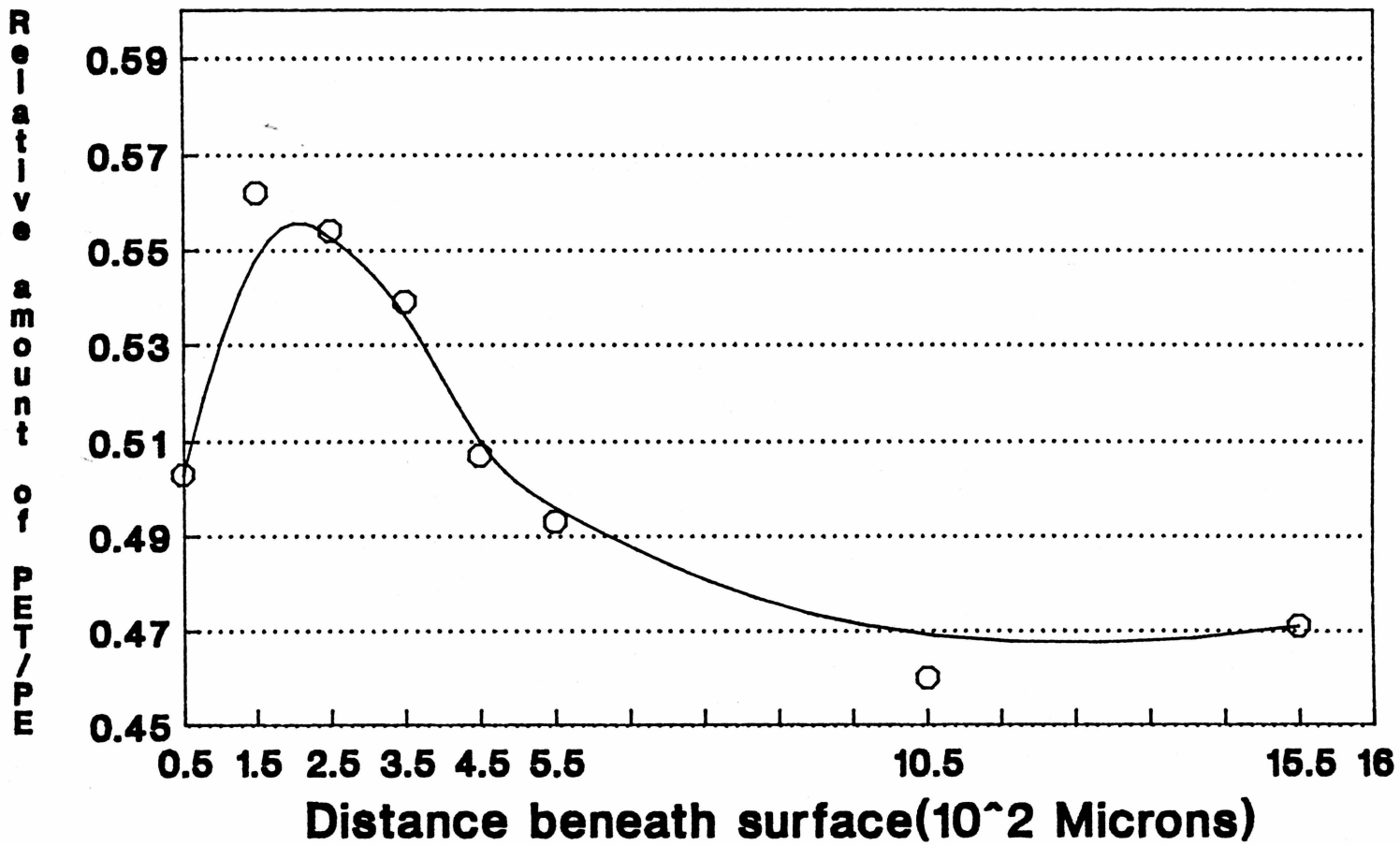
Type of Polymer	% Abundance
PET	27%
Natural HDPE	20%
Colored HDPE	21%
Assorted films	15%
PS	9%
Compatibilizer	5%
PVC	2%
PP	1%

Table 4.2
Composition of the Model Cities blend
(considering all aliphatic polymers
to be a single component)*

Type of Polymer	% Abundance
Aliphatic polymers	56%
PET	27%
PS	9%
Compatibilizer	5%
PVC	1%
Films	2%

*note: over 90% of the films is PE

Relative Amount of PET/PE in MCC5SIB as a Function of Depth



As determined by infrared spectroscopy

Instructions for the I R

Use of Computer and Instrument

-Make sure CDS13 disk is in drive o
-turn on computer (back Right) and spectrophotometer (side right). Do not put anything into the beam until display on spectrophotometer reads 4000
-don't enter date, press 'return'
-at the Petos prompt, type CDS13, press 'return'
-press 'mode ' option key
-at mode prompt, type 'w'; press return

To Make a Scan

-place sample, already mounted on the aluminum plate, on the brackets. Place pen in holder. Check the paper alignment (see Chart Paper below)
-press 'scan' function key
-enter directory (x,y or z) into which you want to place the spectra (it does not matter which)
-the computer will show the dimensions of the scan
-press the 'tab' key until the cursor is on top of the 200
-type 600 to change the lower limit of the scan from 200 to 600
-press return
- at 'are you ready' prompt, press return

To Stop a Scan

-press the 'break' button on the keyboard, or the yellow scan button on the spectrophotometer

To Save a Scan

-once a scan is completed, the spectra may be saved to disk by pressing the 'save' button on the keyboard
-place a formatted disk in drive 1 to which you wish the spectra to be saved
-at the x,y or z prompt, enter the directory which contains the spectra and press 'return'
-when the cursor appears over a shaded line, enter a five character or less title for the spectra
-press the 'tab' button and type a description of the spectra in less than twenty five characters. press 'return' when the description has been entered

To Retrieve a Scan

-place the disk which contains the desired spectra in drive 1
-press the 'retrieve' button
-enter a directory, x,y or z, into which you would like to import the spectra
-press 'return'
-press the 'view' button to see the spectra which has been retrieved

To Calculate the Area Outlined by a Peak

-press the 'area' button

-enter the directory which contains the spectra which you wish to analyze
-enter the two wave numbers which border the region for which you wish to obtain an area
-after a brief pause, the computer will display the parameters of the determination on one line, and two numbers on the next.
-the value on the left edge of the line refers to the area outlined by the spectra in the designated region and limited by zero absorbance. (we use this value in our analysis)
-the value on the right of the second line refers to the area outlined by the spectra in the designated region, and limited by a line which connects the spectra at the two wave numbers entered.

Clear Screen

-press 'clr scrn' twice to clear spectra
-press 'clear' key once to clear spectra

Chart Paper

CHART PAPER
-if the chart paper is not aligned so that the pen is at the edge of the paper numbered 4000, you will need to adjust it. (adjustments are done at the instrument, not at the computer.
-adjust the chart paper by pressing 'chart' and then pressing the parameter keys until the pen is aligned at 4000.

Other Useful Commands and their Functions

'Mult'- enlarges or shrinks a spectrum uniformly by a designated factor

'Add" - raises a spectrum by an inputted value

'Sub' - lowers a spectrum by an inputted value

'Plot'- plots a spectrum which is currently in one of the three directories

'Flat'- flattens the entire spectrum, or portions of the spectrum as directed by the operator (for more detail, see Chapter 6)

'Aute'- automaticly enlarges a spectrum so that its peak of greatest absorbance will be at zero transmittance, and the highest point on the baseline will lie at one hundred percent transmittance. this command is used in conjunction with the 'view' and 'plot' commands only. to make use of the 'aute' command:
-press 'view' or 'plot'
-press the space bar
-type the directory which contains the spectrum followed by a comma
-type 'aute' and press 'return'

CATALOGUE OF SPECTRA PERTINENT TO
THE PROJECT OF IDENTIFYING THE DIFFERENCES IN
POLYMER COMPOSITION WITHIN A POLYMER BLEND
RECYCLED PLASTIC SAMPLE

*=good
**=very good

COMPILED BY CHARLES EDWARDS 4/6/1992

FILE NAME	SAMPLE THICKNESS	DESCRIPTION OF SPECTRA	DATE	QUALITY
CCE23	100	T-20 3/16" CUT	12/12/92	*
CCE24	125	T-20A 3/16" CUT	12/12/92	*
CCE25	120	T-20 600 UNDER	1/10/92	*
CCE26	125	T-20 125 UNDER	1/10/92	*
CCE27	90	T-20 600 UNDER	1/10/92	**
CCR28	90	T-20 125 UNDER	1/10/92	
CCE29		TRASH		
CCE30	110	MCC5SIB 0-110	1/21/92	*
CCE31	110	MCC5SIB 100	1/21/92	*
CCE32	110	MCC5SIB 400	1/21/92	**
CCE33	110	MCC5SIB 300	1/21/92	*
CCE34	110	MCC5SIB 200	1/21/92	*
CCE35	110	MCC5SIB 500	1/21/92	*
CCE36	110	MCC5SIB 600	1/21/92	*
CCE37	110	MCC5SIB 1000 under	2/5/923	**
CCE38	110	MCC5SIB 1500	2/10/92	**
CCE39	150	PURE HDPE 90% CRYSTALINE	2/10/92	**
CCE42	120	PURE HDPE	1/25/92	*
CCE43		FLOAT	1/25/92	*
CCE44		FLOAT,LIGHT GREEN,COLD PROCESSED	2/28/92	*
CCE45	100	PET FROM SODA BOTTLE	3/13/92	-
CCE46		MCC5SIA 100-200	3/13/92	*
CCE47	120	PET SODA BOTTLE	3/13/92	
CCE48	120	PET SODA BOTTLE	3/13/92	
CCE49		MCC5SIA 100-200	3/16/92	*
CCE50		MCC5SIA 0-100	3/16/92	
CCE51		MCC5SIA 300-400	3/16/92	
CCE52	120	PET FROM SODA BOTTL;E	3/20/92	
CCE53		TRASH		
CCE54		ALTERED VERSION OF CCE45	3/20/92	
CCE55		TRASH		
CCE56	130	MOBILE PS	3/23/92	*
CCE57		FLOATS LOW TEMP PROCESSED	3/23/92	*
CCE58	130	MOBILE PS	3/23/92	*
CCE59		FLOATS HIGH TEMP. W.E.T.	3/23/92	*
CCE60		PS PLASTICS AGAIN	3/23/92	*
CCE61	30	PET FROM COKE BOTTLE	3/23/92	*
CCE62	30	PET FROM COKE BOTTLE	3/23/92	*
CCE63	60-100	MCC5SIA 0-100	3/26/92	*
CCE64	100	MCC5SIA 100-200	3/26/92	*
CCE65		FLOATS SURFACE FILM LOW TEMP.	3/27/92	*
CCE66		FLOATS SURFACE FILM LOW TEMP.	3/27/92	*
CCE67		FLOATS FROM CENTER OF SAMPLE 1500	3/27/92	*
CCE68		MCC5SIA 100-200	3/27/92	*
CCE69		MCC5SIA 1500-1600	3/27/92	

CE70		MCC5SIA	200-300	3/27/92	
CE71		MCC5SIB	500-600	3/31/92	*
CCE72		TRASH			
CE73		MCC5SIB	750-850	3/31/92	*
CE74		TRASH			
CCE75		MCC5SIA	1000-1100	3/31/92	*
CE76		MCC5SIA	0-100	4/2/92	*
CE77		CCE76	ALTERED	4/2/92	*
E78A	25-35	PET FROM SODA BOTTLE	ALTERED	4/2/92	
CE79U		FLOAT, 2000 USED AS BASELINE		4/2/92	*
E80U		MCC5SIB	750-850 2000=BASELINE	4/2/92	*
E81U		MCC5SIA	750-850 2000=BASELINE	4/2/92	*
CE81A		MCC5SIA	750-850 MULTIPLIED	0.021739	*