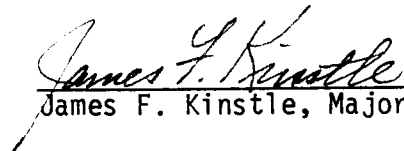
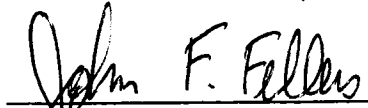
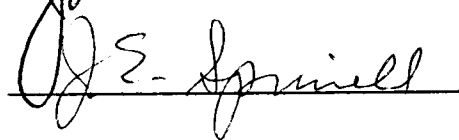


To the Graduate Council:

I am submitting herewith a thesis written by Edward Maury Bridge entitled "Synthesis, Structure, and Property Relationships in Gradient Polymers." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


James F. Kinstle, Major Professor

We have read this thesis and
recommend its acceptance:

Accepted for the Council:


The Graduate School

SYNTHESIS, STRUCTURE, AND PROPERTY RELATIONSHIPS
IN GRADIENT POLYMERS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Edward Maury Bridge

June 1984

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ABSTRACT

Initial experiments involved modification of thin poly(vinyl chloride) films with butyl methacrylate (BMA) and styrene. Synthesis involved the immersion of the substrate films into liquid monomer for predetermined diffusion times and subsequent exposure of the samples to ionizing radiation from an electron beam source. Doses of one and ten megarads were applied to each specific sample type. The synthesis method was designed to construct composite materials with compositional gradients in their structure. Infrared analysis of the modified films indicated that little polymerization had taken place in any of the PVC/styrene systems. The PVC/BMA systems, on the other hand, were seen to contain polymerized BMA in the samples which had been exposed to ten megarads.

In a subsequent set of experiments, high density polyethylene (HDPE) films and PVC films were modified with BMA liquid monomer in a manner similar to that described, using ten megarads radiation dose in all of these experiments. The major portion of the research involved the synthesis and characterization of this set of films.

Compositional variations in the films were investigated by determining the variations in mass, density, and thickness of the samples. Infrared spectroscopy was employed to semiquantitatively determine increases in new polymer content in the modified films. Attempts were made to observe morphological features of the composite films. Optical and electron microscopy were utilized for this

purpose. The important mechanical properties of the films were determined by tensile testing procedures.

The PVC/BMA systems studied showed systematic variations in composition as a function of allowed diffusion times. Mechanical property evaluations indicated that modification had produced a toughening effect in these films. The HDPE/BMA showed variations in composition as indicated by infrared analysis. Mechanical properties of these films showed little variation from sample to sample.

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CHAPTER I

INTRODUCTION

The construction of a polymer composite system involves a concept which is very simple and straightforward. The major objective in the mixing scheme is to combine different polymers in such a way that certain desirable properties of each component are manifested in the final product. One classic example of this type of combination is the well-known high-impact polystyrene composite, a system in which rubbery polybutadiene is dispersed in polystyrene, a glassy polymer. The composite shows increased impact resistance and toughening relative to typical mechanical property values for unmodified polystyrene (56). ABS (acrylonitrile-butadiene-styrene) resins are another prime example of two-phase systems formed by the dispersion of an elastomeric component into a glassy matrix. The composite material exhibits excellent resistance to chemicals and heat, while also showing good strength and toughness properties (56).

High-impact polystyrene and ABS materials are just two cases among the numerous examples of polymer composite systems which have been studied extensively. An incredible amount of research has been devoted to the study of synthesis-structure-property relationships in composite materials. This motivation, in part, derives its momentum from the boundless potential to create interesting and useful composite structures. It is in this spirit that research time and energy are directed toward the investigation of relatively

obscure systems, such as the gradient polymer composites (84). The synthesis-structure-property relationships of two separate gradient polymer systems are the subject of this research, which will attempt to more clearly define gradient systems in general.

For the purposes of this study, gradient polymers were defined by the method of synthesis employed in their production, rather than by any preconceived ideas about their projected physical structure. This approach was necessary due to the extremely investigative nature of the project and to the minimal amount of information in the literature regarding structural characteristics of gradient polymer films.

To define the gradient polymer in terms of its formation process, a few steps may be seen as fundamental to the overall synthetic scheme. The first step in the formation process involved the immersion of a pure polymer film into liquid monomer. The monomer was allowed to diffuse into the polymer substrate film for a predetermined length of time. After the planned diffusion time had elapsed, the sample was immediately exposed to high-energy radiation from an electron beam source.

The composite sample resulting from these formulation steps was expected to exhibit a gradient nature in its structure. This structure was expected to consist of pure polymerized material on the surface of the film, with a gradual decrease in new polymer concentration as a function of depth into the sample. Although systems similar to these have been investigated in the literature (1,43),

the systems studied here were unique in terms of component materials and polymerization methods.

The general objective of this research was to characterize several composite films which had been designed in accordance with the aforementioned experimental procedures. A secondary objective was to establish reproducible methods related to design procedures involved in the construction, or synthesis, of gradient polymer films.

In general, the methods of characterization included infrared analysis, optical microscopy of cross-sections of the films, and Instron tensile testing of the samples. An attempt was made to correlate conditions of synthesis with variations in structure and properties.

In addition to the "fingerprinting" techniques of simple infrared spectroscopy, a more complex analysis employing the FTIR/ATR system was performed on the samples. Fourier Transform Infrared (FTIR) analysis, when complemented with an ATR (Attenuated Total Reflection) attachment, provides information on the distribution of specific components in composite structures (36).

The outline of research activities may be broken down into several general categories for purposes of clarification. These categories include the experimental procedures which were employed in the construction, spectroscopic evaluation, morphological characterization, and mechanical property determination of the gradient polymer films. The ultimate goal was to utilize the

gathered information in an attempt to better understand the synthesis-structure-property relationships in these unique composite structures.

Several phenomenological factors which related to experimental design were taken into account in the analysis of the data. First and foremost among these factors was the chemical nature of the materials under study. Thin films of high density polyethylene (HDPE) and poly(vinyl chloride) (PVC) were used as the substrate materials in the research, while butyl methacrylate liquid monomer acted as the diffusing agent in all cases. Another factor of importance was consideration of the effect of diffusion phenomena on the form of the structure of the composite materials after completion of synthesis. The effects of high-energy radiation on the substrates and the diffusing monomers during the polymerization sequence was also considered in the interpretation of data.

The quantity of information in the literature which treated gradient polymers directly was found to be minimal. It was necessary, therefore, to utilize information on related materials, such as laminates and interpenetrating networks, in an attempt to better understand the interrelationship among experimental variables and phenomenological factors in this specific research area.

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

A. General Polymer Composite Systems

The first commercially important multicomponent polymeric materials included such composites as high-impact polystyrene (HiPS) and acrylonitrile-butadiene-styrene (ABS) resins (56). The establishment of many applications for such materials led researchers to recognize the importance of composites in the field of polymer science and engineering. In general, the prime motivation for research in this area was the potential to combine existing polymers in an effort to create a material with new and useful properties (56).

Methods which have been used to mix polymers include mechanical blending, block copolymerization, graft copolymerization, and interpenetrating polymer network formation. These methodology classifications have traditionally been employed to describe the composite form of the material resulting from their application. Sperling and Ferguson (88) have pointed out, however, that the inclusion of all polymer composites into one of these categories is an oversimplification of an accurate organizational scheme. They have reported that over two hundred permutations of multicomponent polymer organization are known to exist, and that additions to this list have been frequent in recent years.

B. Gradient Polymers

Polymer composites which have received the most extensive study have been typically characterized by uniform composition on a macroscopic scale in all dimensions. Recently, however, materials classified as gradient polymers have received some minimal attention (1,43). The systems which have been studied are reported to exhibit a structure in which the composition was not found to be homogeneous on a macroscopic scale. In these systems the composition was found to vary as a function of position in the sample.

Shen and Bever (84) outlined the basic motivation behind the development of gradient polymers and suggested specific applications for their use. They treated gradient systems in a general sense, including single-phase as well as heterophase organization of polymeric species. They suggested that generation of gradients in polymeric systems was possible by three routes:

1. variation of the chemical nature of monomers within a polymer chain;
2. variation of the molecular constitution of polymers in a composite;
3. variation of the morphology of polymers.

Most of the information in the literature dealing with gradient polymers has dealt with research directed at creating systems whose compositions varies as a function of position in the sample. Akovali, Biliyar, and Shen (1) prepared two separate gradient systems by following the general procedure of dipping a polymer substrate into a

liquid monomer and subsequently photopolymerizing the samples with an ultraviolet source. Crosslinked polystyrene and acrylonitrile monomer were the starting materials used to form one of the gradients in their work, while the other polymer-monomer pair consisted of a mixture of crosslinked poly(methyl methacrylate) and methyl acrylate. Jasso, Hong, and Shen (43) prepared gradient polymers by diffusing 2-chloroethyl acrylate into a crosslinked poly(methyl methacrylate) film for a specified interval of time. At the conclusion of the allowed time, photopolymerization was used to fix the diffusion gradient profile within the sample. A set of samples in their study were allowed to reach equilibrium swelling conditions and to form macroscopically homogeneous interpenetrating polymer networks (IPN's). The IPN's were used for comparison purposes in the evaluation of the mechanical properties of the samples.

Predecki (77) employed silicone rubber as a substrate material and hydroxyethyl methacrylate monomer as a swelling agent to form a gradient composite. The gradient was designed to exhibit a hydratable surface and to act as a possible alternative to surface coatings in arteriovenous shunts. Heat energy was used as the polymerizing source in this work. Research involving gradient polymers has also been reported by Berry and his coworkers (12,25). In this study, polyether-urethane-urea block copolymers were used as substrate materials and combined with a series of monomers, including acrylamide, 2-hydroxyethyl methacrylate, and N-vinyl-2-pyrrolidone, to form gradient systems. Cobalt-60 was used as the radiation source in

each of these polymerizations. These materials were also intended for biomedical applications, exhibiting hydrogel surfaces for water absorption and blood compatibility.

Although minor differences have been shown to exist in comparisons of the synthetic methods used by researchers in the field of gradient polymers, the basic formula of construction has been shown to involve a few basic steps. The model of synthesis was set forth in the work of Akovali, Biliyar, and Shen (1), in which a host polymer was immersed in a neat monomer for a length of time sufficient to establish a diffusion gradient profile. Important experimental variables included the rate of diffusion and the rate of polymerization. In all cases the rate of polymerization was very rapid in comparison with the diffusion rate. This experimental design was intended to create a system in which composition of the two-component polymer varied with the diffusion gradient in a direct correspondence.

As was stated previously, the amount of information in scientific literature concerning synthesis, structure, and properties of gradient polymers was found to be minimal. Numerous accounts, however, have discussed gradient related materials, such as IPN's, polymer grafts, and laminated structures. Akovali et al. (1) have envisioned laminated materials as extreme examples of gradient systems, in which the boundary layer between components represents a discontinuous step change. Sperling et al. (87) and Huelck et al. (39) have prepared interpenetrating polymer networks (IPN's) by

allowing a monomer to diffuse into a polymer substrate until an equilibrium state was reached. They considered the IPN's which they had formed to be a special case of a "flat" gradient profile.

The necessity for slow diffusion on a comparative basis with polymerization rates has been pointed out (1). Therefore, gradient polymer substrates which have been used in experimentation were generally restricted to semicrystalline or glassy polymers (1,43). These materials have been shown to exhibit fairly low diffusion coefficients for typical monomers (20).

Matsuo et al. (58) have performed electron microscope studies on various IPN's and concluded that a heterogeneous structure exists in these materials. Akovali et al. (1) have attempted to use structural information of this sort to define the organization of matter in the gradient samples. Gradient polymers are defined by these authors as layers of IPN's. The layers were seen on a compositional level as a dispersion of new polymer (from the diffusing monomer following polymerization) in the original substrate material. The relative concentrations of the components were thought to vary continuously from the surface of the specimen to the depth of penetration of the advancing front. Experimental evidence gathered in the research appeared to support this hypothesis. Successive layers of the polystyrene/acrylonitrile composite were shaven from the specimen and analyzed for nitrogen content by combustion methods. The quantities of nitrogen in the samples were found to diminish as the core of the films was approached from the surface. It was

therefore concluded that the concentration of polyacrylonitrile (PAN) decreased as a function of distance through the thickness of the PS/PAN composite, pointing toward the existence of the gradient structure which had been suspected.

The majority of the research involving the study of structural and property characteristics of gradient polymers has been devoted to amorphous systems. Typically, the substrate has been a noncrystalline material, such as poly(methyl methacrylate), which was paired with such monomers as methyl acrylate or halogenated acrylics (1,43,77). Kryszewski and Czeremuskin (49) prepared gradient polymers which used a partially crystalline polymer as the substrate material. Specifically, they diffused styrene monomer into low density polyethylene (LDPE) substrates for specific time intervals. The polymerization method employed was ultraviolet irradiation. The thicknesses of the original LDPE samples prior to diffusion and irradiation were on the order of 0.50 mm. Shavings of thicknesses on the order of 0.05 mm were taken from the composite materials and analyzed for polystyrene (PS) content by ultraviolet spectroscopy. They reported the data in terms of weight percentages of polystyrene as a function of L/L_0 , where L_0 was the initial thickness of the LDPE sample and L represented distance into the film. From the results they concluded that the concentration profile of PS in LDPE was dependent upon allowed diffusion time. Their findings are shown in Figure 1.

In addition to his findings concerning the relationship between diffusion times and weight percentage distributions in LDPE/PS

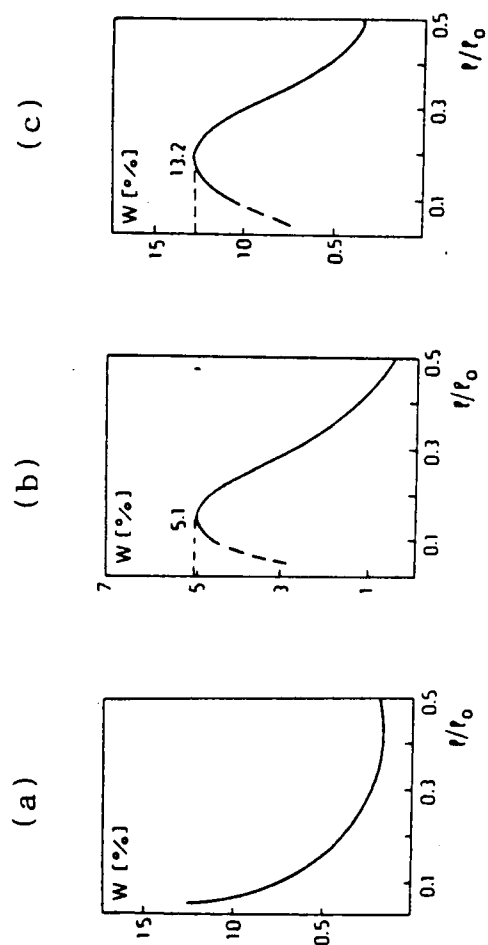


Figure 1. Weight percentages of polystyrene as a function of depth of diffusion into polyethylene films for time periods of (a) 2.5 hours; (b) 5 hours; and (c) 25 hours.

systems, Kryszewski (49) has also reported some important generalizations about systems of this type. From his work with semi-crystalline substrate materials, he concluded that:

1. the amount of monomer imbibed during diffusion was dependent upon the density and degree of crystallinity of the substrate;
2. the degree of crystallinity of substrates was found not to be a function of the various reaction conditions;
3. the rapid evaporation of monomer from the surface of the substrate affected the structure of the initially created gradient.

Although Kryszewski et al. (49) have worked with LDPE as a substrate in their studies, the material has received little attention from others in the field of gradient polymers. No apparent information has been reported on the use or potential applications of high-density polyethylene (HDPE) or poly(vinyl chloride) (PVC) as substrate materials in the gradient composite systems, though these materials have been treated heavily in the literature in terms of their wide acceptance as important engineering materials in both pure and composite formulations.

C. Poly(vinyl chloride) and Polyethylene Composites

Poly(vinyl chloride) homopolymer has been shown to be a rigid and somewhat brittle plastic with a glass transition temperature (T_g) of approximately 80°C (15). Numerous accounts in the literature have

reported attempts to combine PVC with elastomeric components for ductility improvement. Petrich (75) combined methacrylate-butadiene-styrene (MBS) impact modifiers with PVC and subsequently improved toughness properties in the material. Several other reports of PVC modification using acrylic materials have appeared in the patent literature (31,65,76).

Matsuo (58) has reported the use of random copolymers of butadiene and acrylonitrile as the elastomeric components in PVC composites. The incorporation of these copolymers into the substrate was seen to improve toughness characteristics.

O'Toole et al. (72) have studied PVC composites which were formed by the incorporation of chlorinated polyethylene into the substrate. Lee et al. (54) looked at PVC/nitrile rubber composites, paying special attention to variations in mechanical property characteristics as functions of the content of modifier.

Sionakidis et al. (85) have prepared IPN's which consisted of PVC as the substrate and butadiene/acrylonitrile copolymers as the modifying agents. The synthesis of this material was accomplished using a two-stage emulsion polymerization technique.

High density polyethylene (HDPE) has been shown to be a highly crystalline polymer with melting temperatures ranging between 110°C and 140°C (15). The glass transition temperatures for amorphous regions has been found to range between -110°C and -80°C. As with PVC, a fair amount of research has been devoted to the study of polyethylene composites of various types. On a comparative basis,

however, composites with crystalline components have received far less attention than their amorphous counterparts (79).

Martuscelli et al. (59) have combined HDPE and polypropylene for the purpose of forming composite structures. They have pointed out that the most interesting aspects of systems of this type involve the effects of compositional variation on such phenomena as mechanical behavior and morphology. Greco et al. (30) found that properties such as the modulus and tensile strength of HDPE were improved by the incorporation of isotactic polypropylene. This composite was formulated by mixing the two polymers in the melt. Composites of high-density polyethylene and low-density polyethylene have been prepared by Sato et al. (81).

In work by Yamakawa (96), various monomers were grafted onto the surfaces of polyethylene films, by means of a Co-60 irradiation technique. The monomers which were used included methyl acrylate, vinyl acetate, acrylic acid, acrylamide, and methylolacrylamide. The objective of this work was to determine the relationship between surface composition and adhesive bonding characteristics. The results of the study indicated that adhesive properties were dramatically improved in the highly grafted polyethylene films.

D. Structural Classification of Composites

In general, polymer composites can be divided into four major structural categories. These categories have been given general descriptive titles, including mechanical blends, graft copolymers,

block copolymers, and interpenetrating polymer networks (IPN's). Materials such as gradient polymers have been described structurally as a combination of grafts and IPN's. Typically, composites have contained only two distinguishable polymeric species, although these materials have not been restricted by definition to binary composition.

Much research has been directed toward the formulation and evaluation of mechanical blends. Mechanical blends have been defined as mixtures of polymers with co covalent bonds between them (56). The formulation of these composites has typically involved the blending of a thermoplastic and noncrosslinked elastomer through extrusion or on open rolls (79).

An important study by Schrenk and Alfrey (83) involved the co-extrusion of three-layered laminated films. The films were described as consisting of polyethylene skins and a polystyrene core. This type of laminated structure has been described as an extreme example of a gradient system (1).

Block copolymers have been described as composite systems which consist of chemically different polymer segments joined at their ends to form chains (56). The synthesis of these materials has typically been achieved by anionic polymerization (35).

Investigations concerned with the synthesis and characterization of graft copolymers have been frequently treated in the literature. Battaerd and Tragear (11) have described the graft copolymerization method in detail. The general synthetic sequence

has included a dissolution of the first polymer into the second monomer and subsequent polymerization of the mixture. The "grafted" structure of the resulting material has been visualized as consisting of covalent linkages between the original polymers and newly-formed polymeric molecules at various points along the initial chains.

Sperling and Friedman (87) have described the synthesis of interpenetrating polymer networks (IPN's) as consisting of several basic steps. These systems have generally been prepared by the equilibrium swelling of a crosslinked polymer network with a second monomer, followed by polymerization. In several accounts (1,21,40, 87) activators and crosslinking agents were added to the monomers prior to the diffusion and polymerization steps. The general structure of the IPN has been described as consisting of two cross-linked networks which interpenetrate but have no covalent linkages between the different species (40).

The synthesis and structure of gradient polymers has been described previously (1,43). Several similarities between gradient systems and IPN's have been seen to exist. The most notable of these has been the use of crosslinked polymers as substrate materials in each case of gradient synthesis.

Akovali et al. (1) have described the structural form of gradient polymers as layers of IPN's which vary in concentration ratios of components through the thickness of the sample. In the opinion of these authors, the fundamental difference between gradient

polymers and IPN's results from the macroscopic heterogeneity characteristic of the gradient samples.

E. Diffusion Phenomena

The diffusion characteristics of the polymer-monomer system prior to polymerization have been treated as an important aspect in the determination of synthesis-structure relationships in gradient polymers and related composites. Akovali et al. (1) have mentioned the importance of the choice of substrate materials, restricting themselves to the use of glassy or semicrystalline polymers in their experiments. These choices were made in order to create situations in which diffusion rates of monomers into the substrate would be slow in comparison to polymerization rates. In this manner they hoped to "fix" the gradient profile which existed at the moment of polymerization.

In the 1960's and early 1970's, a great deal of research was carried out which studied the diffusion of small molecules into glassy polymers. Work in this area was spearheaded by Turner Alfrey, Jr., whose initial studies led to many subsequent investigations.

Work of Alfrey (2) at Dow Chemical Company revealed that diffusion of solvents (or monomer molecules) into glassy polymers was possible if the solvent was cooled below the glass transition temperature of the polymer. Upon sorption of solvent molecules, it

was seen that glassy polymers sometimes underwent cracking as a result of the development of mechanical stresses.

Ideal Fickian diffusion (Case I diffusion) has been described mathematically as

$$F = -D \frac{\partial C}{\partial X} , \quad (\text{II-1})$$

where F is the rate of transfer of substance per unit area of section, C is the concentration of the diffusing species, X is the distance normal to the section, and D is the diffusion coefficient. This simple equation has been used to describe the diffusion of small molecules into isotropic substances (3). Alfrey (2) has pointed out that the kinetics of Case I diffusion can be reduced to essentially one numerical value, namely, the diffusion coefficient. The fundamental Case I diffusion equation (in Cartesian coordinates) has the form

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (\text{II-2})$$

Alfrey et al. (3) have pointed out that the diffusion kinetics of polymer systems seldom follow the classical Fickian law. Their studies have shown that small molecules diffuse into a polymer substrate in a manner more complicated than that of systems following Case I kinetics. They have found that the diffusion coefficient

in polymer systems is a variable which depends upon concentration.

The defining equation in this case has been given as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) . \quad (\text{II-3})$$

Crank et al. (20) have determined that Eq. (II-3) can be used to describe the diffusion kinetics in nonhomogeneous media, in which diffusion coefficient values vary from point to point in the sample.

Assumptions about the nature of the diffusion process have been used to simplify Eq. (II-2) and Eq. (II-3) (20). When diffusion is assumed to take place in only one direction, Eq. (II-2) reduces to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (\text{II-4})$$

and Eq. (II-3) to

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (\text{II-5})$$

Frisch et al. (28) have noted that the diffusion characteristics of polymer-solvent systems have typically shown large deviations from classical Fickian behavior. Systems that follow Fickian behavior have been shown to exhibit a linear relationship when the amount of absorbed substance is plotted versus the square root of time. Polymer systems have been characterized by curvature

in the standard absorption plot. This behavior has been classified as non-Fickian, or "anomalous" diffusion.

Another type of simple diffusion behavior, commonly known as Case II diffusion, has been shown to exist in systems in which the polymer substrate was subjected to solvent at temperatures well below its glass transition. This behavior was described in terms of three characteristics, including:

1. a sharp boundary which separated the inner core of the substrate from the swollen outer layer;
2. a swollen gel structure in the portions of the sample where the diffusion process had occurred;
3. a constant rate of advancement of the sharp diffusion boundary (2).

Alfrey et al. (3) have explained that the conditions associated with Case II diffusion define a behavior which is in many ways simpler than classical Fickian diffusion. Systems of this type, for instance, have shown diffusion behavior in which the solvent uptake varies in direct proportion with time. It has also been stated that the kinetics of systems undergoing Case II diffusion may be defined by a single experimental parameter, namely, the velocity of the advancing solvent front.

The nature of the advancing front in diffusion studies with glassy polymers has been analyzed by Kwei and Zupko (51). In their experiments, they diffused methylene chloride monomer into an epoxy resin, which had been prepared by mixing a diglycidyl ether of

bisphenol A and diethylenetriamine in a ten to one proportion. They had predicted that the form of the advancing front would approximate that of the model structure shown in Figure 2, with d representing the distance from original film surface to the solvent front, and l representing the thickness of swollen shell. Shadowgraph photos taken during diffusion confirmed their predictions, revealing a sharp, advancing boundary for the diffusion of monomer into the glassy polymer.

The understanding of diffusion phenomena in glassy polymers has been the basis for predictions of gradient structure. The determination of the existence of sharp advancing fronts (51) with constant velocities in these systems has helped to conceptually define the gradient. A hypothetical picture of the development of gradient structure in polymer substrate films is given in Figure 3.

Although the diffusion characteristics for glassy polymer systems (e.g. PVC) have been observed to follow simple Case II kinetics, diffusion of small molecules into heterogeneous media, such as HDPE, has been described as a more complicated event. In fact, the crystalline regions in polymers have been characterized by their impermeability to foreign molecules. Studies by Van Amerongen (93) with gutta percha demonstrated that increases in the crystalline content of a substrate had a reducing effect on average diffusion coefficient values. Michaels et al. (62) have studied the effects of crystalline morphology on permeability in polyethylene films. They hypothesized that the closely packed lamellar structures within

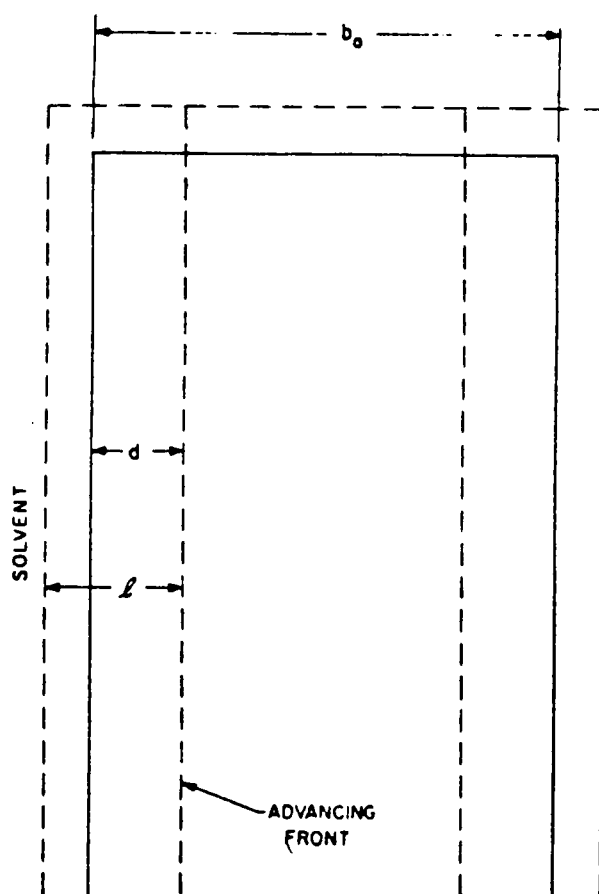


Figure 2. Schematic of the advancing front and swollen shell in Case II diffusion.

FORMATION OF GRADIENT STRUCTURE

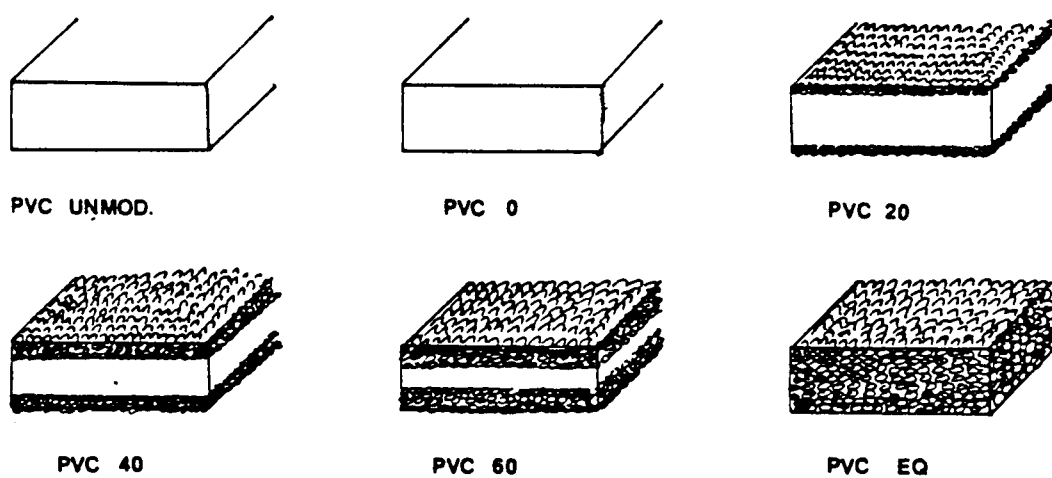


Figure 3. Development of gradient structure in a glassy polymer (numbers refer to diffusion times).

the spherulites may act as blockades to potential diffusion pathways. Yasuda et al (97) found that diffusion coefficient values of polyethylene films could be increased by applying a biaxial strain to the samples.

F. Irradiation Phenomena

The use of various types of radiation for polymerization purposes has received extensive attention in the literature. Interest in the effects of radiation on chemical systems has stemmed from an awareness of its potential to improve or enhance the properties of materials. In polymer systems, for example, radiation processing can be used to form crosslinked network structures known as thermosets (56).

It has been mentioned that the complex nature of the events associated with irradiation of polymer systems has made the study of such systems a formidable task (95). Difficulties have arisen from the inability to define the mechanisms or the transient structures which are associated with a specific radiation-initiated reaction.

Particular types of radiation have typically been classified in accordance with the levels of kinetic energy associated with each form. The term "ionizing radiation" generally refers to a class which consists of neutron, proton, electron, alpha, X-, and gamma radiation. These types of radiation have been characterized by the fact that their quantum or kinetic energies are much higher than typical bond dissociation energy values (82). Unlike ultraviolet

and visible light radiation, ionizing radiation has been found to react nonspecifically with molecular structures. The absorption of ionizing radiation by matter has been pictured as a series of interactions with the nuclei of atoms and their surrounding electron clouds (82).

Most of the work associated with the use of radiation in the formation of polymer composites has been centered on graft copolymerization. Several general accounts of grafting phenomena have proposed mechanisms for such reactions (5,29,78).

Restaino (78) has pointed out that grafting reactions in polymer systems are generally thought to occur by a free radical mechanism. Garnett (29) has attempted to classify free radical processes in polymer systems according to variations in experimental procedures. He has described systems in which graft copolymerization mechanisms are assumed to predominate. He has given titles to the various procedures, including

1. mutual, or simultaneous technique;
2. pre-irradiation technique;
3. peroxidation technique;
4. cross-linking technique;
5. prepolymer technique.

In the "simultaneous" technique, the free radical processes have been visualized as shown in Eq. (II-6)



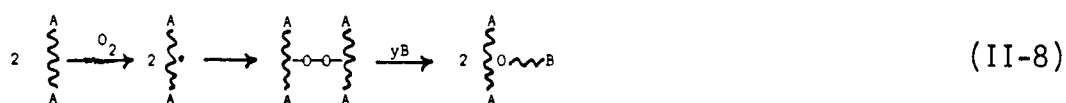
or as in Eq. (II-7).



Equations (II-6) and (II-7) have been used to illustrate the free radical processes which are thought to occur when polymer A is irradiated while in contact with monomer B.

The pre-irradiation technique has been used to describe a process in which the polymer is irradiated in the presence of an inert gas and then exposed to liquid or gaseous monomer. Graft formation is thought to occur by the same processes illustrated in Eqs. (II-6) and (II-7).

The peroxidation method has been used to describe a process in which polymer A is irradiated in the presence of oxygen. It has been shown that irradiation of polymers in air leads to the formation of diperoxides, as diagrammed in Eq. (II-8)



and hydroperoxides, as illustrated in Eq. (II-9).



The peroxide intermediates shown in Eqs. (II-8) and (II-9) have been found to be extremely stable species in some cases (29,78). Dilli et al. (22) have found, in fact, that peroxide forms of cellulose could

be used to initiate styrene copolymerization for several years following their synthesis.

Garnett (29) has described the fourth important free radical process as a crosslinking reaction. This process usually occurs as a result of the irradiation of an intimate mixture of polymer A and polymer B. Equation (II-10) has been used to illustrate this phenomena.



The prepolymer procedure has been described as a modification of typical crosslinking reactions (29). In this method, monomers are polymerized under controlled conditions to low-range molecular weights. These species, which contain points of unsaturation, have been found capable of copolymerization with another monomer/prepolymer combination. These rapid reactions have generally been initiated by high doses of radiation administered over short time periods (e.g. irradiation by an electron beam).

Although free radical mechanisms have been the most widely discussed phenomena in the area of graft copolymerization, ionic processes have also been utilized in grafting procedures. Garnett (29) has pointed out that ionic processes have been used to describe the radiation grafting of polyethylene. The general reaction events have been described as the process illustrated by Eq. (II-11)



in which the irradiated polymer exists as a cation that is capable of reacting with various monomers.

Restaino (78) has pointed out that the extent of a particular graft copolymerization is dependent upon the relative abilities of polymers and monomers to form free radicals upon irradiation. Quantities known as "G-values" have been assigned to many molecular structures in order to quantify this capability. The G-value of a substance has been defined to be equivalent to the number of free radicals formed per 100 electron volts of energy absorbed by that substance (82). Garnett (29) has stated that the efficiency of radiation grafting in a particular polymer/monomer system is largely dependent on the relative radical yields of the components. He reports that grafting is the predominant reaction when the G-value of the polymer is significantly greater than that of the monomer, but that homopolymerization predominates in the reverse case.

Quite a bit of research has been devoted to the study of the effects of ionizing radiation on poly(vinyl chloride) and polyethylene. The wide use of these materials has motivated various research interests toward gaining an understanding of the effects of processing conditions on their properties.

Salovey (80) has explained that the exposure of PVC to ionizing radiation generally triggers a free radical reaction which is

accompanied by discoloration and the evolution of hydrogen chloride gas. Chapiro (16) has contended that the discoloration results from the formation of polyene structures during dehydrochlorination. In early studies of radiation effects on PVC, Lawton et al. (53) suggested that degradation of the polymer was the predominant reaction. Alternatively, Charlesby (18) found that crosslinking prevailed as the dominant process in PVC irradiation. Later research revealed that the relative extent of degradation or crosslinking was dependent upon specific experimental conditions (16). Chapiro has reported that radiation experiments which were carried out in a vacuum at high dosages (e.g. 41 megarads) resulted in extensive crosslinking of PVC. On the other hand, degradation was reported as the predominate process in similar experiments carried out in the presence of air. Garnett (29) has suggested that dehydrochlorination of PVC may be minimized by administration of the lowest possible radiation dose necessary for efficient grafting.

G-values for PVC have been determined at various temperatures (80). These values were determined by measuring hydrogen chloride yields following irradiation. The G-values for PVC were found to vary in a temperature range from -145°C to 70°C . The room temperature G-value was found to be 12.8.

Many studies have investigated the effects of radiation on the properties and structure of linear polyethylene. The initial experiments in this area were carried out by Dole (23) and Charlesby (18). Mandelkern (55) has pointed out that the chemical and physical events

associated with the irradiation of polyethylene have been found to be extremely complex in nature.

Crosslinking has been found to be the predominate reaction resulting from the exposure of linear polyethylene to ionizing radiation (55). The mechanism of the crosslinking reactions has been found to be either a free radical process (55) or an ionic process (29), depending upon the conditions of the experiment. The evolution of hydrogen gas has been found to accompany the irradiation of polyethylene, along with the development of unsaturation in the chains (29). G-values for irradiated polyethylene systems have been calculated in terms of the hydrogen gas evolution which accompanies the free radical process. Dole et al. (24) have reported a G-value of 3.2 for linear polyethylene irradiation with a dose of 15 megarads at 25°C. In the same study, G-values were found to vary between 2.8 and 4.0 for samples of various molecular weight distributions.

Ballantine et al. (10) have performed experiments in which gamma radiation was used to initiate graft copolymerization of acrylonitrile monomer onto polyethylene. They found that the grafting that took place was predominantly the result of a surface reaction. They pointed out that the rate of diffusion of acrylonitrile was much smaller than the rate of grafting in all of the cases.

Ballentine et al. (10) have also studied the graft copolymerization of styrene onto polyethylene films. In one experiment, polyethylene films were preirradiated with a gamma source and immersed in styrene monomer. After a period of ten days, the films

were removed from the monomer and weighed. Residual styrene monomer was extracted prior to weighing. The weight increases which were observed in the films were thought to be the result of a post-polymerization process.

Restaino (78) reported a graft copolymerization of a system consisting of polyethylene film and methyl methacrylate monomer. The materials in this study were chosen on the basis of several considerations. The comparison of the G-values for the materials was one important factor in the experimental design. G-values for methyl methacrylate and polyethylene have been determined as 27.5 (82) and 3.2 (24), respectively. The large disparity in G-values was seen as a basis for expectation of a great deal of homopolymerization of methyl methacrylate monomer. Secondly, the equilibrium swelling of polyethylene films immersed in methyl methacrylate monomer was found to be less than 4 percent by weight. The limited swelling power of the monomer was expected to result in minimal diffusion of methyl methacrylate into the substrate. Their results, which were based on weight increase measurements at various dose rates, demonstrated that grafting in the system was largely restricted to the surface. Yamakawa (96) found similar results when he irradiated a polyethylene sample in the presence of methyl acrylate vapor. Interference microscopy was used in this experiment to determine the composition distribution of poly(methyl acrylate) which had been grafted to the polyethylene.

Restaino (78) has reported that the most widely used sources of radiation in graft polymerization experiments have been Van de Graff generators and Cobalt-60, which produce electrons and gamma-rays, respectively. Akovali et al. (1) and Jasso et al. (43) employed ultraviolet light as the radiation source in their work with gradient polymers.

Garnett (29) has pointed out that the polymerization time requirements of the more common radiation sources (e.g. Cobalt-60) often restricts their general applicability. These sources have been shown to require several minutes (and in some cases, hours) to complete typical polymerization processes. Electron beam processing has been offered as an alternative to conventional polymerization methods. Radiation cure times of one hundredth of a second have been reported in applications of electron beam processing. Electron beam processing has generally been used in connection with the polymerization of polymer/prepolymer mixtures and in other systems which require rapid development of a large pool of free radicals.

An excellent account of electron beam processing operations has been described in the literature (52). The most common types of electron accelerators in use include Van de Graaf generators, field emission machines, linear accelerators, Dynamitrons, betatrons, and synchrotrons. The industrial radiation processing of plastic materials has generally been conducted using the Dynamitron as the beam source. The energy of electrons accelerated by this instrument can range from 0.25 MeV (mega-electron-volts) to 9 MeV, depending

on the beam current. Instruments such as the Dynamitron have been distinguished from linear accelerators in terms of generating ability and dose rate. The lower energy levels associated with electrons from a Dynamitron source have been found to be well suited for uniform radiation processing of plastic films.

Williams (95) has given an excellent account of the interaction of high energy radiation with matter. The energy of an electron (generally given in MeV) has been shown to be the primary factor which governs the events which follow its interaction with the material. A fast electron moving through condensed matter transfers its energy to the molecules and subsequently decreases in velocity. Cleland et al. (19) have pointed out that energy transfer of the electrons occurs mainly through their interactions with orbital electrons of the atoms in the material. The interactions of the primary electrons with the target atoms may cause ionization or excitation. The energies of primary electrons are changed in collisions with target atoms. Collisions result in the ejection of secondary electrons from the target atoms. These secondary electrons interact with other atoms, and a subsequent chain of similar events occurs. The incident energy is gradually dissipated in the interaction process.

Linear energy transfer (LET) has been used as a measure of the incremental energy loss of an electron as it interacts with a medium. The LET values are given in terms of energy loss per distance traveled in a particular medium. The units which describe LET are

given in electron-volts per anstrom ($\text{eV}/\text{\AA}$). The relationships between energy loss and distance have been determined for several materials. Williams (95) has determined the relationships for polyethylene. This relationship is given by

$$\text{LET} = \left(\frac{980}{E}\right) \log 0.2 E, \quad (\text{II-12})$$

where E is the initial energy of the electrons in electron-volts. The use of these types of equations has enabled engineers to predict the uniformity of radiation dose throughout the thickness of the sample. For example, electrons of energy as low as 0.5 MeV (500,000 eV) would experience energy losses of approximately $0.01 \frac{\text{eV}}{\text{\AA}}$ as they travel through polyethylene film. In thin polyethylene films (e.g. 50 μm), energy losses would amount to 5000 eV as the electrons travel through the thickness. The 1 percent loss in the energy would be considered insignificant in typical radiation processing operations. The energy loss effect has been further minimized by application of radiation to both surfaces of the films (44).

G. Morphological Characterization

The morphological character of polymer composites has been shown to significantly affect the physical and chemical properties of these materials. Morphological characterization of the various forms of polymer mixtures has generally been applied in attempts to define the distribution of different chemical phases.

Manson and Sperling (56) have outlined several important factors which are generally taken into consideration in morphological studies. They have pointed out that the relative compatibilities of polymers have a significant effect on the phase distributions of systems in which they are combined.

Krause (47) defines compatibility as a state of miscibility between mixed polymers. Manson et al. (56) have mentioned that truly compatible systems exhibit a single, thermodynamically stable, phase. Incompatible systems have been characterized by the existence of distinct phases after the completion of mixing. The term "semi-compatible" has been used to describe systems in which partial mixing occurs at the molecular level (47).

Rosen (79) has pointed out that the optimum phase distribution requirements for useful two-phase systems lie somewhere in between that of the perfectly compatible and incompatible forms. He notes that the components of rubber-modified glassy polymers should be compatible enough to provide adhesion at the glass-rubber interface. On the other hand, the components of the mixture should not be compatible to the extent of destroying the two-phase character of the system.

Krause (47) has conducted a thorough study of compatibility in polymer systems. In this work, compatibilities were assigned to various polymer combinations on the basis of their behavior in solution. It has been shown that compatible polymers will form a single transparent phase when dissolved in a mutual solvent.

Incompatible polymers, on the other hand, exhibited phase separation under the same conditions. In this study, relative compatibilities were assigned to numerous polymer combinations. Poly(vinyl chloride) was found to be compatible with such polymers as poly(ethyl methacrylate) and poly(butyl methacrylate). Kern (46) also found compatibility to exist in the PVC/poly(butyl methacrylate) combination.

Krause (47) also reported the compatibilities of combinations of polyethylene and several other polymers. Polyethylene was found to be slightly compatible with polybutadiene, but incompatible with several other polymers in the study. In most of the experiments with polyethylene, the two components were combined by a milling operation and analyzed optically in an attempt to determine relative compatibility.

Compatibility phenomena have been shown to have a direct relationship to the amount of phase separation that takes place in a mixed polymer system (13). This phase separation has been observed to occur before, during, and after the polymerization sequence. In solution-type graft copolymerizations carried out by Battaerd et al. (11), assumptions were made that the polymer solutions were, at all times, homogeneous. High grafting rates were expected on the basis of this assumption. Later experimental evidence revealed that the graft polymerization products contained relatively few grafting points. The minimal grafting was assumed to be the result of phase separation during polymerization (13). Studies of this type have shown that the distribution of phases, or morphology, in composite

systems results in part from phase separation and compatibility phenomena.

Akovali et al. (1) were interested in the phase distributions in gradient polymer systems. Both of the systems which they studied [polystyrene/acrylonitrile and poly(methyl methacrylate)/methyl acrylate] consisted of incompatible polymer pairs (47). The substrate films were crosslinked prior to diffusion, thus minimizing the effect of phase separation. In the work by Jasso et al. (43) with gradient polymers, an incompatible pair of components [poly(methyl methacrylate) and 2-chloroethyl acrylate] were similarly used. It has been pointed out that phase separation effects are of less significance in reactions where rapid crosslinking or grafting occur, this due in most part to the relative immobility of the polymer network system (56).

Morphological characterization of polymer composite systems has generally been carried out using a variety of methods. The most prominent of these methods has been transmission electron microscopy (TEM). An extensive amount of research has been dedicated to the elucidation of phase distribution by TEM, which can provide resolution to a few hundredths of a micron. Although TEM studies were not performed in the work with gradient polymers (1,43), these methods have been applied to several related systems, such as interpenetrating polymer networks (21,39,58). Scanning electron microscopy (SEM) has been generally used to study surfaces of polymer films (37), but Hobbs (38) has pointed out that use of this method can sometimes

give structural information when applied to microtomed cross sections of composites.

Optical transmission microscopy has been used to define phase distributions in polymer composites, but its utility is limited to systems in which the components differ significantly in refractive index values (37). Optical microscopy with crossed polars has been shown to be of some use in composite systems where at least one component is crystalline (37).

Fourier Transform Infrared (FTIR), when complemented with an Attenuated Total Reflection (ATR) attachment, has provided a means to determine phase distribution in a composite sample (36). By altering the angle of incidence of infrared radiation with respect to the surface of the sample, compositional information may be acquired at various depths into the film (92).

H. Mechanical Properties

Mechanical properties have been defined as "those parameters or characteristics of a material which determine its response to applied stresses and strains" (79). The response of a material toward stresses and strains has been shown to be dependent on experimental variables, such as temperature, time scale of the experiment, and applied forces. From an engineering standpoint, however, the material parameters (e.g. morphological structure) have been studied most extensively in their relationships to mechanical properties.

Rubber-reinforced polystyrene materials and ABS plastics have received a great deal of study in terms of their morphological character and mechanical properties. Both composites have been characterized by a dispersion of rubbery polymer in a glassy matrix (56). This morphological arrangement has been shown to impart toughness and impact resistance to the material (79).

The toughness of an engineering material has been seen as a function of the number of deformation mechanisms available to the sample. It is thought that these mechanisms allow for strain energy dissipation during mechanical testing. This general theory assumes that energy which has been dissipated by toughening mechanisms is unavailable for the extension of existing cracks and flaws. Toughening mechanisms which have been considered include crazing, shear yielding, and diversion of crack growth (79).

Merz et al. (61) have theorized on the effects of phase distribution on mechanical behavior in glassy polymer/rubbery polymer systems. They suggested that the rubbery particles effectively hold the fracture surfaces of the glassy phase together during tensile strain, which prevents the propagation of crack growth in the material.

Important work on the deformation of two-phase systems has been carried out by Newman and Strella (67). They pointed out that the strain beyond the yielding point in two-phase materials was essentially recoverable upon heating the sample above the glass transition of the continuous phase (the glassy matrix). Thus, the

strain yielding was determined to exist as a consequence of molecular orientation of the glassy phase. Two possible mechanisms were proposed to explain the drawing behavior of the material at temperatures well below the glass transition. These included:

1. the possibility of localized heating of the glassy phase;
2. the possibility of an effective decrease in the T_g of the glassy phase.

Rosen (79) suggests that the rubbery phases in a composite system may act as points of stress concentration, thereby raising the local temperature in those areas. Newman and Strella (67) have related increases in free volume of the glassy phase to observed tensile behavior. Increases in free volume have been shown to effectively decrease glass transition temperatures. It has been shown that rubbery materials (Poisson's ratio equal to 0.5) exhibit little change in volume when placed under stress. Therefore, in composites, rubber phases will tend to prevent the expansion of glassy phases during deformation, provided a strong interface exists between the two. These considerations have led to the assumption that the drawing process occurs in glassy regions which are adjacent to rubber phases.

Figure 4 illustrates a typical stress-strain curve for a polymer composite system. The numbers refer to the weight percentage of rubber incorporated into the thermoplastic material. Important values which have been determined from evaluation of curves of this type include the

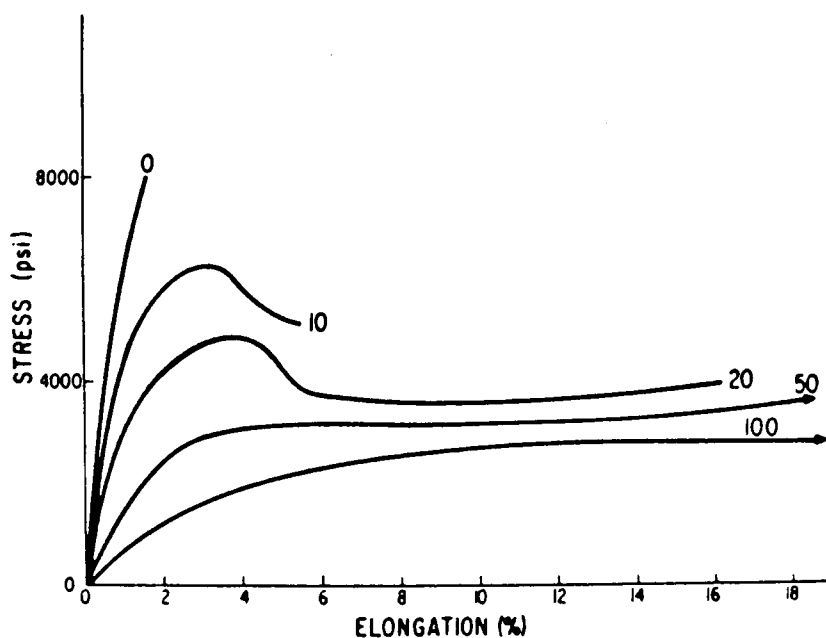


Figure 4. Typical stress/strain curve for a rubber modified glassy polymer (the numbers refer to weight percentages of rubber).

1. elongation to break;
2. elongation to yield;
3. tensile strength at break;
4. tensile strength at yield;
5. elastic modulus.

Tensile tests have generally been carried out with Instron-type instruments, which deform a clamped sample at a constant rate while variations in resisting force are recorded.

Numerous experiments have investigated the tensile properties of gradient polymers and related structures. Figure 5 shows the tensile behavior of the gradient polymers which were investigated by Akovali et al. (1). The curves essentially compare the tensile behavior of the gradients with unmodified poly(methyl methacrylate). The increased yielding of the gradients has been explained by a stress redistribution theory, which assumes that layers in the sample which require greater stresses to flow will receive the largest portion of the applied stress (26). The compositional gradient in the samples has been shown to vary through the thickness of the films, which were synthesized by polymerization of a poly(methyl methacrylate)/methyl acrylate mixture. Therefore, intimate mixtures of the components in the various layers will exhibit different effective moduli. Stresses are thought to be redistributed to the layers with the largest modulus values, resulting in improved yielding behavior.

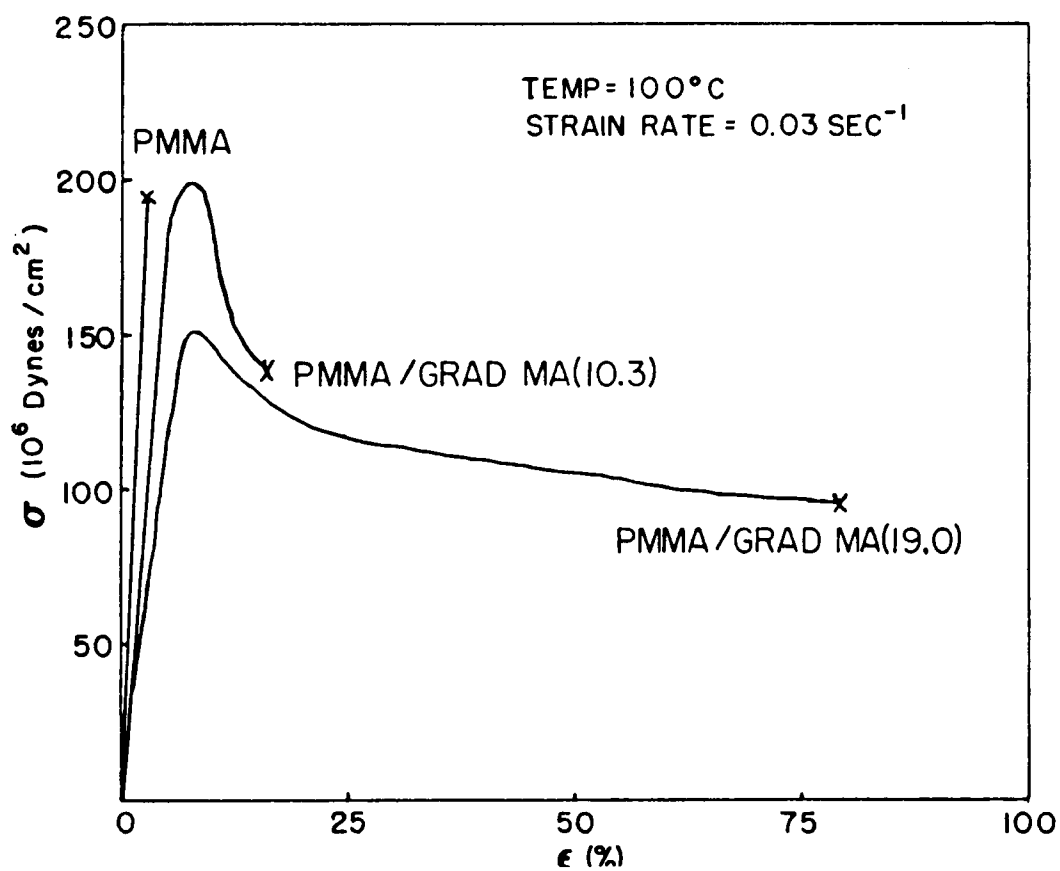


Figure 5. Comparative tensile behavior of pure poly(methyl methacrylate) and poly(methyl methacrylate)/methyl acrylate gradients.

Jasso et al. (43) found similar deformation properties in their studies with gradient polymers. They compared gradient materials with IPN's of identical chemical composition. IPN's have been characterized as molecularly intimate mixtures of components. The gradients in Jasso's et al. (43) study exhibited superior yielding behavior when compared with chemically similar IPN's. These results pointed to the fact that the gradients possessed mechanisms for the redistribution of stresses which were more effective than those of the IPN's. This phenomena was thought to be based on the layered-phase structure characteristic of gradient materials.

CHAPTER III

EXPERIMENTAL DETAILS

A. Materials

n-Butyl Methacrylate

This liquid monomer, produced by the Aldrich Company, was used as the diffusing agent in a majority of the experiments. The monomer was extracted three times with equal volumes of a 5 percent NaOH solution and then washed with pure water until the aqueous layer was neutral.

Polyethylene, High Density

HDPE films were used as substrate materials in one set of gradient unmodified and gradient samples. These films were prepared by the Phillips Petroleum Company from Marlex 6006 linear polyethylene. Attempts were made to extract any residual processing agents that may have existed in the films. 2-Butanone was used as the extraction solvent. After extraction, the films were dried in a vacuum oven at 80°C for 24 hours. A density of 0.9550 g/cm was previously determined for the films (86). The average thickness of the films was determined to be 0.038 mm.

Polyvinyl Chloride

PVC films were used as substrate materials in one set of unmodified and gradient samples. The PVC was Plivovic Type Bk75, and

was prepared by the Goodyear Company by a bulk polymerization process. A peroxycarbonate initiator was used in the polymerization.

The films which were used as substrates in this project were solvent cast from a solution of PVC in tetrahydrofuran. The concentration of the solution was 0.0339 g/ml. It was found 15.0 ml of this solution would form a film of desirable thickness when transferred by pipette to a glass plate. The dimensions of the glass plates were 10 cm x 10 cm. The glass plates were floated on mercury to assure a level surface. The whole solvent casting procedure was carried out in an argon atmosphere.

After the films were formed, they were peeled from the glass plates and placed in a vacuum oven for drying purposes. The films were dried for 90 hours at 47°C, 6 hours at 80°C, and then extracted with methanol for 18 hours. They were then placed back in the vacuum oven for 24 hours at 47°C and 6 hours at 80°C. Shrinkage of the films was observed after their removal from the drying oven. The dimensions of the films changed from 10 x 10 cm to approximately 8.2 x 8.2 cm upon drying. The density of the films was determined to have an average value of 1.4100 g/cm.

Styrene

This liquid monomer, produced by the Aldrich Company, was used as a diffusing agent in preliminary studies. An inhibitor, t-butyl catechol, was removed by the extraction procedure described for n-butyl methacrylate.

B. Synthesis of Gradient Films

General Comments

The synthesis of gradient films in this project involved two distinct but interrelated sets of experiments. The earlier set of experiments involved the formation of gradient films using one type of polymer (PVC) for the substrate films. The diffusion section of these experiments involved the immersion of the films in two different liquid monomers. The monomers which were chosen were n-butyl methacrylate and styrene. The predetermined diffusion times for styrene into PVC were 0.5, 1.0, and 2.0 hours, while those for n-BMA into PVC were 1.0, 2.0, and 4.0 hours. These time intervals were chosen on the basis of simple weight increase measurements which had been made with each pair of components.

The irradiation steps involved the exposure of the various films to an electron beam source. One of the variables chosen in these experiments was the total dosage of radiation to be delivered to the samples. Doses of one and ten megarads were administered, respectively, to samples of each possible compositional type. These doses were also administered to PVC films which had not been subjected to liquid monomers. A matrix of the general experimental scheme is given in Figure 6.

Analysis of the films following the diffusion and irradiation procedures led to several general observations. FTIR/ATR spectroscopy indicated that little, if any, polymerization had taken place in the films which had been immersed in styrene. Secondly, films which had

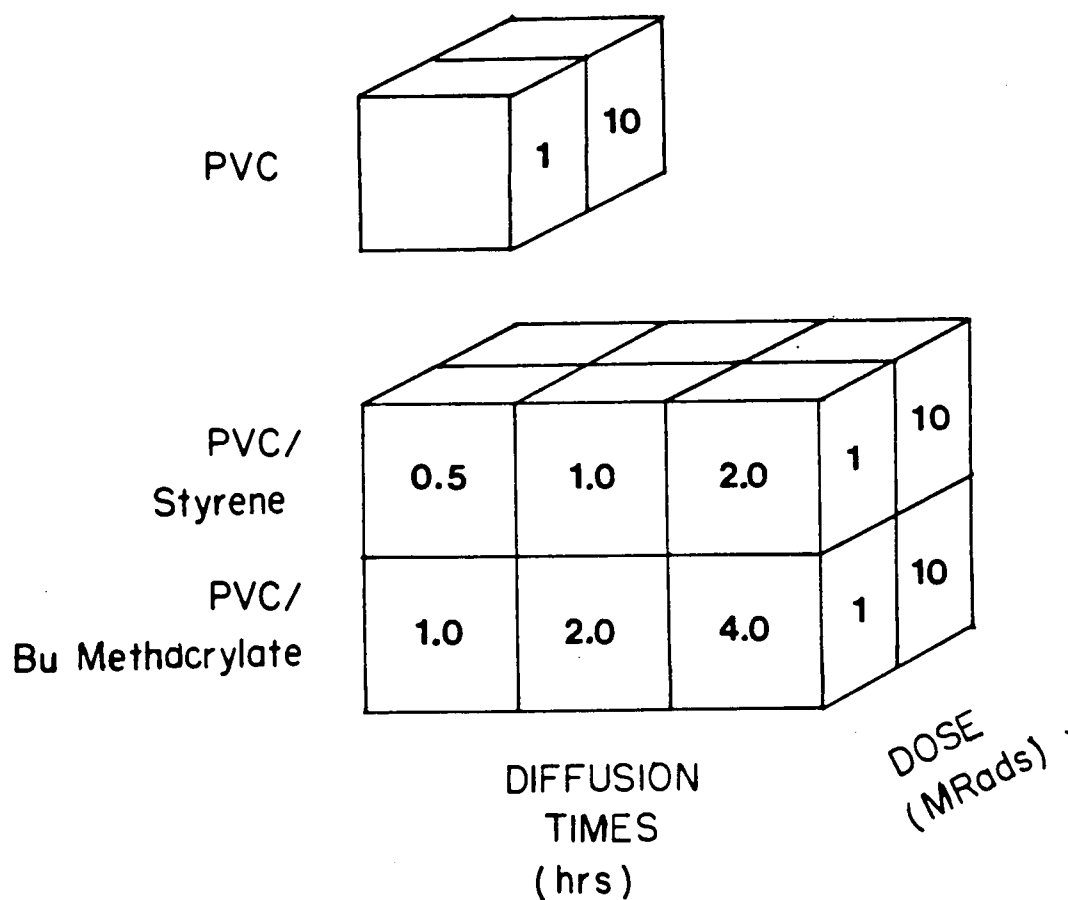


Figure 6. Original experimental design for the synthesis of PVC gradient polymers.

been exposed to one megarad did not show any substantial polymerization. A third observation was the negligible difference in the FTIR/ATR spectra of the PVC/BMA systems which had been exposed to 10 megarads.

Observations of phenomena which have been described above led to a readjustment of experimental design. Systems using styrene were eliminated from consideration for any further experiments. In similar fashion, 10 megarad doses were settled on as a constant quantity of exposure for all additional polymerizations. Allowed diffusion times were shortened for the PVC/BMA systems in subsequent experiments in order to avoid reaching an equilibrium state during immersion. One variable was added in the experiments which followed these initial studies. High density polyethylene films, in addition to the PVC samples, were used as substrates in the main set of experiments. This main set of experiments was carried out as described below.

Diffusion

The thickness of all PVC and HDPE films was determined prior to the diffusion sequence. These thickness values are listed in Table 1. The films were labeled according to substrate type and specified diffusion times. Three films of each possible combination were labeled, using the letters A, B, and C for designation purposes. Films which were exposed to neither monomer nor radiation were designated as "unmodified." PVC and HDPE films were stored in a vacuum desiccator prior to the reaction sequence.

TABLE 1
FILM THICKNESS VALUES PRIOR TO MODIFICATION

PVC Films		HDPE Films	
Designation	Thickness (μm)	Designation	Thickness (μm)
PVC-UN-A	39.6	HDPE-UN-A	39.9
B	40.4	B	40.1
C	39.9	C	39.6
PVC-O-A	41.1	HDPE-O-A	37.8
B	44.2	B	35.3
C	42.4	C	34.8
PVC-20-A	45.7	HDPE-20-A	40.4
B	42.7	B	37.3
C	40.1	C	40.3
PVC-40-A	39.8	HDPE-40-A	36.6
B	42.1	B	38.1
C	35.3	C	35.6
PVC-60-A	37.1	HDPE-60-A	37.3
B	40.9	B	35.6
C	40.6	C	36.1
PVC-EQ-A	43.1	HDPE-EQ-A	34.8
B	41.5	B	36.6
C	40.2	C	36.6

All of the diffusion processes were carried out at room temperature. Diffusion times for both PVC and HDPE substrates were 0, 20, 40, 60, and 1720 minutes (12 hours). The general procedure involved the removal of a particular film from the vacuum desiccator and immersion of the sample into a beaker containing BMA liquid monomer. The top of the beaker was then sealed off from the atmosphere and time of diffusion measured.

Irradiation

When the film had been immersed for the specified time, it was removed from the beaker and placed directly on one half of a wooden frame assembly. After placing the other half of the frame on top of the film, rubber bands were used to secure the assembly. The assembly was then placed in a Ziploc bag, which was subsequently flushed out with nitrogen. The bag was then clamped in a metal holder which was designed for use in the electron beam. The clamp was attached to a cable which carried the sample into the irradiation chamber. A photograph of the sample entering the irradiation chamber is given in Figure 7.

Ten megarads of radiation were delivered to each sample intended for modification. A photograph of the electron accelerator is given in Figure 8, while a larger view of the instrumentation appears in Figure 9. The general reaction sequence, from diffusion to irradiation, has been outlined in Figure 10. The voltage source for the electron accelerator was rated at 500 kilovolts. The amount of radiation delivered to the sample in the irradiation chamber was

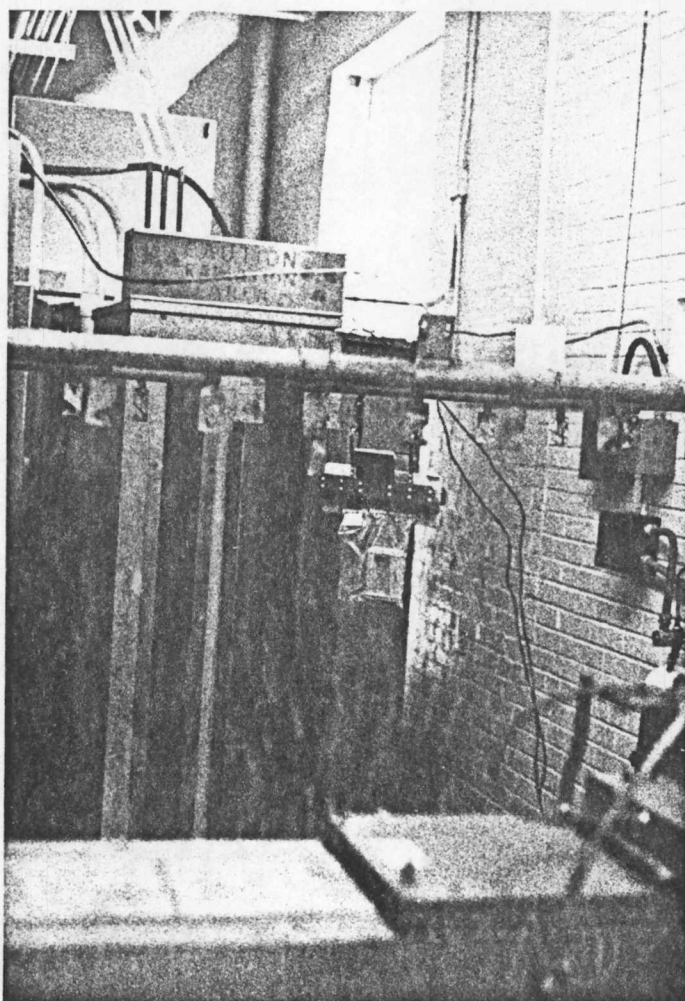


Figure 7. Film sample entering the electron beam irradiation chamber (following diffusion).

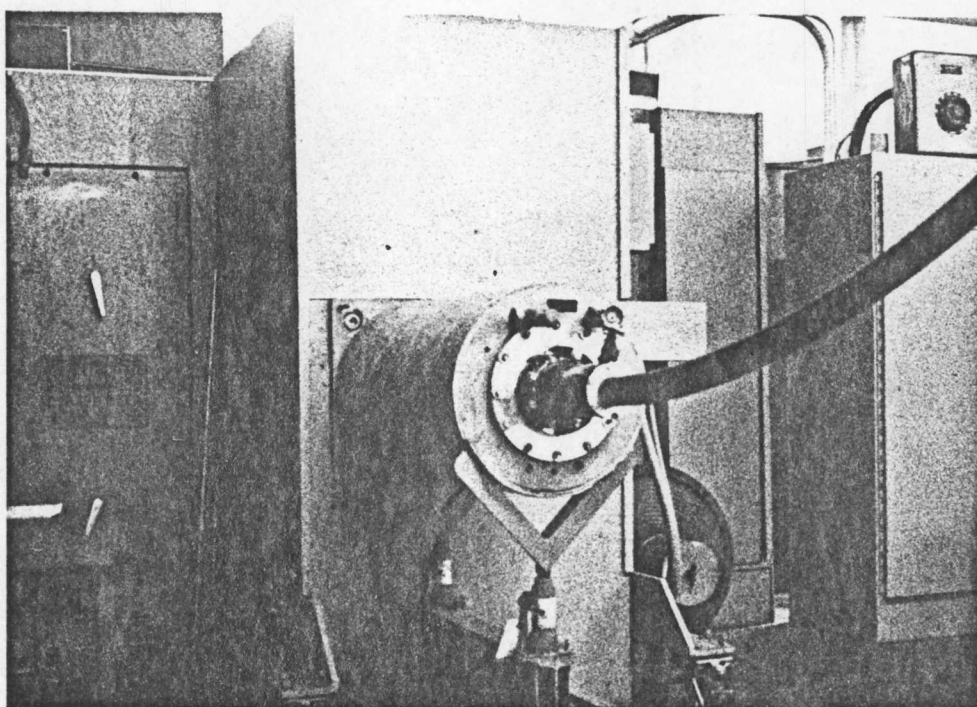


Figure 8. Electron accelerator.

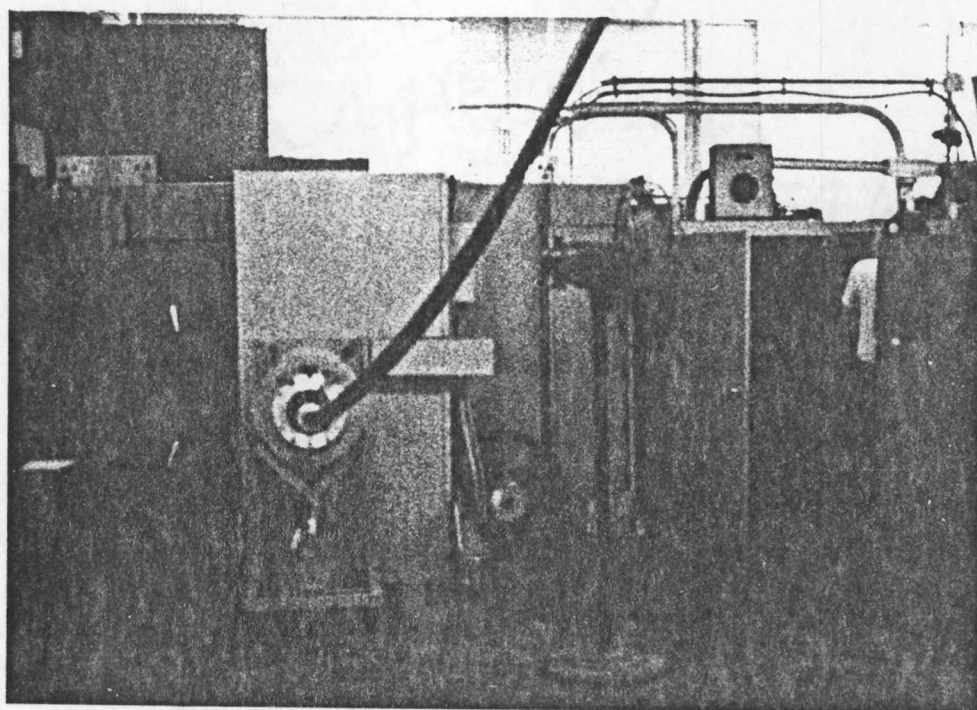


Figure 9. Electron beam laboratory.

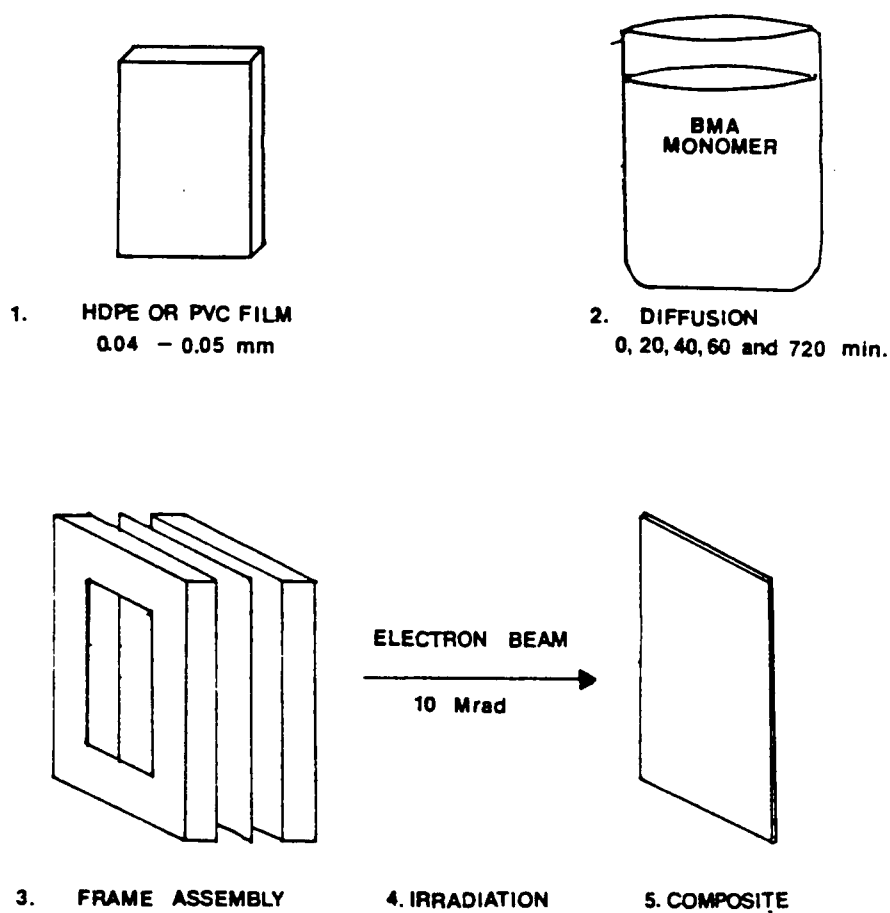


Figure 10. Design of experimental procedure for the synthesis of PVC and HDPE gradient films.

dependent upon the speed of the conveyor cable which carried the sample through. A speed of 10 feet per minute was used for the purpose of delivering 10 megarads of radiation. The radiation was delivered to the various samples in two doses of 5 megarads each. Half of the total dose was delivered to the samples on entering the irradiation chamber for the first time, while the other half was administered as the cable brought the samples back through the chamber on the return. The bags holding the irradiated samples were then removed from the clamps and returned to the vacuum desiccator.

The approximate energy values of the electrons which interacted with the samples were 0.5 MeV (94). The energy of electrons striking the surface of the samples was somewhat less than 0.5 MeV, due to the slight dissipation of kinetic energy as the negatively charged particles interacted with the polyethylene bags which contained the samples.

C. Characterization of Films

General Observations

The samples were examined macroscopically for any apparent changes in texture, color, clarity, etc. which might have distinguished them from the original films. Possible radiation damage effects were looked for in the samples.

Film Thickness

The thickness of each treated film was measured using a pressure sensitive thickness gauge. Thickness values were also measured from photographed cross sections of the films.

Mechanical Properties

Tensile tests were carried out on all samples, using the table model Instron Tensile Tester. All of the tests were carried out at room temperature in accordance with ASTM D-882, which is the testing method for "Tensile Properties of Thin Plastic Sheeting" (6).

Eleven samples were cut from each different type of PVC film by use of a razor blade. The dimensions of each sample were 45.0 mm x 5.0 mm. Five samples of 35.0 mm gauge length were tested on the Instron, along with three samples each of 25.0 mm and 15.0 mm gauge lengths. The gauge lengths were determined by the initial separation of the grips on the Instron. A crosshead speed of 20 mm/min was used in the deformation of all the PVC films. The full scale load was set at 10 pounds of force. The strain measurements were based on crosshead separation.

HDPE films were tested in a manner similar to the tensile measurements carried out on the PVC samples. Tensile strains were applied to these anisotropic films in the machine direction only. The crosshead speed was 500 mm/min for all samples, while the full scale load was set at 5 pounds of force.

Infrared Spectroscopy

Each sample type was analyzed by use of infrared spectroscopy. This analysis was carried out with the use of a Perkin-Elmer Infrared Spectrophotometer. Wave numbers which were scanned were in the range of 4000 cm^{-1} to 200 cm^{-1} . The scan mode and slit width were "normal," while the scan time was 12 minutes.

Density Measurements

Two separate density gradient columns were used for the determination of the density values for the samples. Three samples from each class of PVC films were placed in a column, which measured density in a range of 1.1250 g/cm^3 to 1.4250 g/cm^3 . Three samples from each class of HDPE films were placed in a column which measured density in a range of 0.9200 g/cm^3 to 0.9800 g/cm^3 . Density readings were made 24 hours after the samples had been immersed. The readings were taken again at 48 hours to assure that the positions of the samples had not changed.

Optical Microscopy

Cross sections of each class of PVC and HDPE films were viewed under optical microscopy at a magnification of 100X. The cross sections were obtained by microtoming sections of films which had been placed in LR White imbedding medium. Glass knives were used as cutting edges in the microtoming procedures. The sections were cut at a 5 micron setting and transferred to microscopic slides for observation. Light transmission microscopy was applied to all

samples, while the HDPE films were also viewed under crossed polars. Photographs were taken of each cross section and analyzed for thickness variation. Observations were also directed toward the characterization of optical phenomena which could indicate phase distributions in the composite films. Staining techniques which had been previously applied to composite polymer films (66) were attempted in these experiments.

Scanning Electron Microscopy (SEM)

SEM photomicrographs were taken of the various cross sections of the films. Films which had been imbedded in LR White were gold-coated and viewed at 1700X magnification.

FTIR/ATR Spectroscopy

In a related research project (86), spectra were obtained for the films using an FTIR/ATR system. The angle of incidence of infrared radiation was altered in respect to the surface planes of the films, and spectra were obtained at the various angles. Semi-quantitative information was gathered which was used to generally describe the distribution of poly(butyl methacrylate) with the various substrate films. The research project mentioned above has been designed to quantify the concentration profile within each of the modified films. This ongoing study will employ the variable angle FTIR/ATR system in an attempt to assign specific concentration values to the PBMA at various depths into the films. Variations

in the concentration of modifier will be detectable on the order of microns through the thickness of the films.

CHAPTER IV
COMPOSITIONAL AND MORPHOLOGICAL CHARACTERIZATION
OF THE FILMS

A. General Observations

Table 2 describes the nomenclature scheme for the PVC and HDPE films. The abbreviations designed in this labeling system will be used throughout the remaining text.

Table 3 provides information which was gathered through general observations of the films after their exposure to monomer and irradiation with the electron beam. The PVC films exhibited notable changes upon modification. The samples which were irradiated, but not exposed to monomer, exhibited definite color changes. A reddish tint could be observed in the PVC-0 films. This discoloration was also seen in the PVC-20 films, but diminished in the films of higher diffusion times.

The unmodified PVC films (HDPE-UN) were translucent materials which were homogeneous in their transmittance of light to the naked eye. All of the modified films were observed to exhibit similar translucency. Numerous small cracks were apparent in the modified PVC films, in contrast to the visual homogeneity displayed by the unmodified samples. The appearance of these small cracks was more pronounced in the PVC-60 and PVC-EQ samples than in the other modified films.

TABLE 2
NOMENCLATURE SCHEME FOR GRADIENT FILMS

Designation	Diffusion Time (min)	Radiation Dose (Mrad)
PVC-UN	0	0
PVC-0	0	10
PVC-20	20	10
PVC-40	40	10
PVC-60	60	10
PVC-EQ	720	10
HDPE-UN	0	0
HDPE-0	0	10
HDPE-20	20	10
HDPE-40	40	10
HDPE-60	60	10
HDPE-EQ	720	10

TABLE 3
GENERAL OBSERVATION OF THE VARIOUS FILMS

Sample	Description
PVC-UN	Clear, almost transparent film with smooth texture; slightly rigid.
PVC-0	Reddish-brown tint; slightly rigid.
PVC-20	Reddish tint; slightly rubbery.
PVC-40	Diminishing reddish tint; slightly rubbery; small cracks apparent.
PVC-60	Extremely faint reddish tint; slightly rubbery; small cracks apparent.
PVC-EQ	Clear film similar to PVC-UN; slightly rubbery; numerous small cracks.
HDPE-UN	Translucent film; smooth texture; extremely flexible.
HDPE-0	Translucent film; smooth texture; extremely flexible.
HDPE-20	Translucent film; large, smooth wrinkles; extremely flexible.
HDPE-40	Same as HDPE-20.
HDPE-60	Same as HDPE-20.
HDPE-EQ	Same as HDPE-20.

The general stiffness of the various PVC films was found to vary according to the degree of modification. While all of the films exhibited flexibility to a certain degree, the more highly modified samples showed a characteristically rubbery behavior.

Only minor differences were observed in the macroscopic investigation of the HDPE films. The highly modified HDPE films were wrinkled in appearance. These wrinkles were large and smooth, resembling waves with dimensions of one to two millimeters between the minima. The unmodified HDPE films, which could be considered translucent materials, were observed to be homogeneous in their transmittance of light. This same homogeneity was found in the modified HDPE samples. The modified HDPE films showed no discoloration. Finally, the differences in flexibility which were apparent among the PVC films were not found to exist in the HDPE samples. All of the HDPE samples were found to be extremely flexible.

Many of the observed changes in the PVC films were apparent effects of the exposure of the samples to high energy radiation. In many polymers, exposure to high energy radiation leads to chain scission or crosslinking. PVC is unique in the fact that its primary radiolytic process involves dehydrochlorination (80). Therefore, degradation in PVC is characterized by the elimination of hydrogen chloride gas and the absence of depolymerization (82).

As was mentioned, the PVC-0 films exhibited a reddish tint in their colors following irradiation. The monomer-modified films were also faintly colored. The appearance of red color in PVC has been

shown to be a result of the presence of polyene chains. These polyene chains consist of long sequences of conjugated double bonds (8).

The diminishing intensity of color in the PVC-20, PVC-40, PVC-60, and PVC-EQ films could have been the result of several factors. Chapiro (16) has pointed out that chain scission may be a predominant reaction when oxygen is present during or after irradiation. A predominance of chain scission over dehydrochlorination has been shown to reduce color intensity (80). Although every effort was made to provide an oxygen-free atmosphere, the transfer of the films from the monomer bath to the radiation chamber necessitated some exposure of the films to air. The PVC-0 films, which exhibited the most intense color formation, were exposed to the air for a shorter time period than the other samples. The samples which had been soaked in monomer were slightly more difficult to load into the wooden frames than the unsoaked PVC-0 samples. The differences in loading times between the two probably did not exceed thirty seconds, but the fact that disparities existed could account for color variations among the samples.

It has been shown that a predominance of crosslinking in PVC results in little color formation. This effect has been achieved by irradiating PVC in the presence of polyethylene glycol dimethacrylate (63). The crosslinking of PVC by this difunctional monomer limits polyene formation, thereby minimizing the formation of color. The inclusion of BMA monomer in our PVC films could have limited polyene

formation by forming PBMA chains from free radical sites on the parent chains. The diminishing color intensities of PVC-20, PVC-40, PVC-60, and PVC-EQ films, respectively, could have resulted from grafting reactions of this sort. In summary, PVC films with large quantities of monomer available during irradiation (e.g. PVC-EQ) may have exhibited higher levels of grafting, which led to minimal polyene formation and correspondingly weak color formation.

The appearance of minute cracks in the PVC films following irradiation could have occurred as a result of several phenomena. Meares (60) has pointed out that diffusion processes generally set up stresses in the polymer substrate. The cracks may, therefore, exist as a consequence of local stresses initiated during diffusion. Stresses may have also been set up during the polymerization of BMA. The new polymer chains which were formed may have acted to disrupt intermolecular forces between PVC chains. Radiation damage could be designated as a possible cause for the cracking phenomena, although the 10 megarad dose which was applied to the samples is not considered to be large (82).

The increasing rubbery behavior of the more highly modified PVC samples may be explained in a very general sense, as a consequence of the mixing of two polymers with distinctively different properties. The glass transitions of PVC and PBMA have been given as 85°C and 10°C, respectively (15). Therefore, PVC would be expected to exhibit a degree of stiffness, while PBMA would show rubber characteristics. A physical mixture of these materials (in the solid state) would be expected to exhibit properties intermediate to the extremes (56).

Macroscopic contrast was not apparent among the various HDPE films which were used in these experiments. The similarities in clarity, color, texture, and flexibility among the samples may indicate that little difference in composition or morphology exists. The diffusion of small molecules into a highly crystalline structure, such as HDPE, has been shown to be a relatively slow process (62). The incorporation of PBMA into the HDPE films may therefore be negligible. If this is the case, one would expect only slight differences in physical properties. The large, smooth wrinkles which appeared on the HDPE films that had been soaked with monomer were thought to be some type of solvent effect. The HDPE-0 films did not exhibit this wrinkling. Swelling at the surfaces of the films could have set up stresses, which in turn caused the wrinkling effect, although no documentation of this type of behavior was found in the literature.

B. Compositional Characterization

Table 4 gives the masses of rectangular sections which were cut from the PVC and HDPE films. The length and width dimensions of the sections were 45 mm and 5 mm, respectively. Table 4 also gives the measured thickness of each sample. The two thickness values which are given correspond to the average thickness before modification and the average thickness following modification. Figure 11 shows the relationship between thickness variations and diffusion times in the samples. Figure 12 shows the relationship between percentage mass increases and diffusion times.

TABLE 4

AVERAGE MASS INCREASE OF FILMS

	Thickness ^a (μm)	Thickness ^b (μm)	Mass ^a (g)	Mass ^b (g)	Mass increase (%)
PVC-UN	44.0	44.0	0.0138	0.0138	0.00
0	44.0	44.0	0.0138	0.0141	2.17
20	44.0	54.0	0.0138	0.0162	17.30
40	44.0	56.0	0.0138	0.0174	26.10
60	44.0	60.0	0.0138	0.0188	36.20
EQ	44.0	64.0	0.0138	0.0197	42.80
HDPE-UN	40.0	40.0	0.0087	0.0087	0.00
0	40.0	40.0	0.0087	0.0087	0.00
20	40.0	41.0	0.0087	0.0089	2.30
40	40.0	41.0	0.0087	0.0089	2.30
60	40.0	42.0	0.0087	0.0094	8.05
EQ	40.0	52.0	0.0087	0.0099	13.80
^a Before modification			^b After modification		

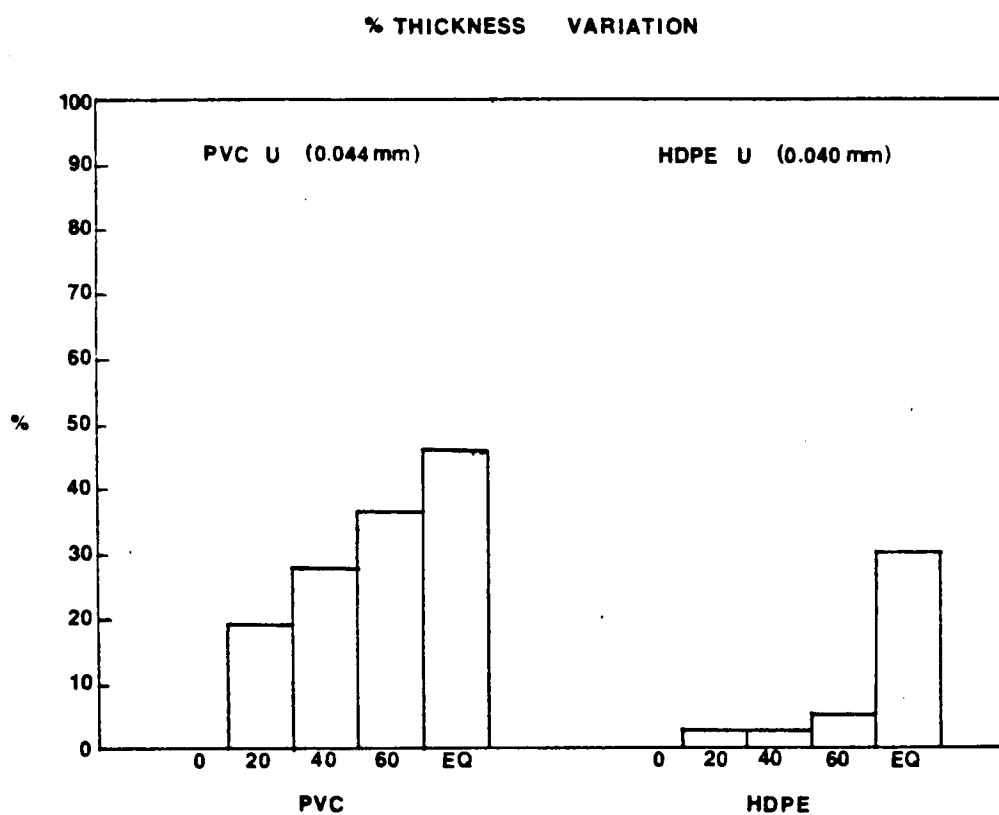


Figure 11. Percentage thickness variation vs. diffusion time for PVC and HDPE films.

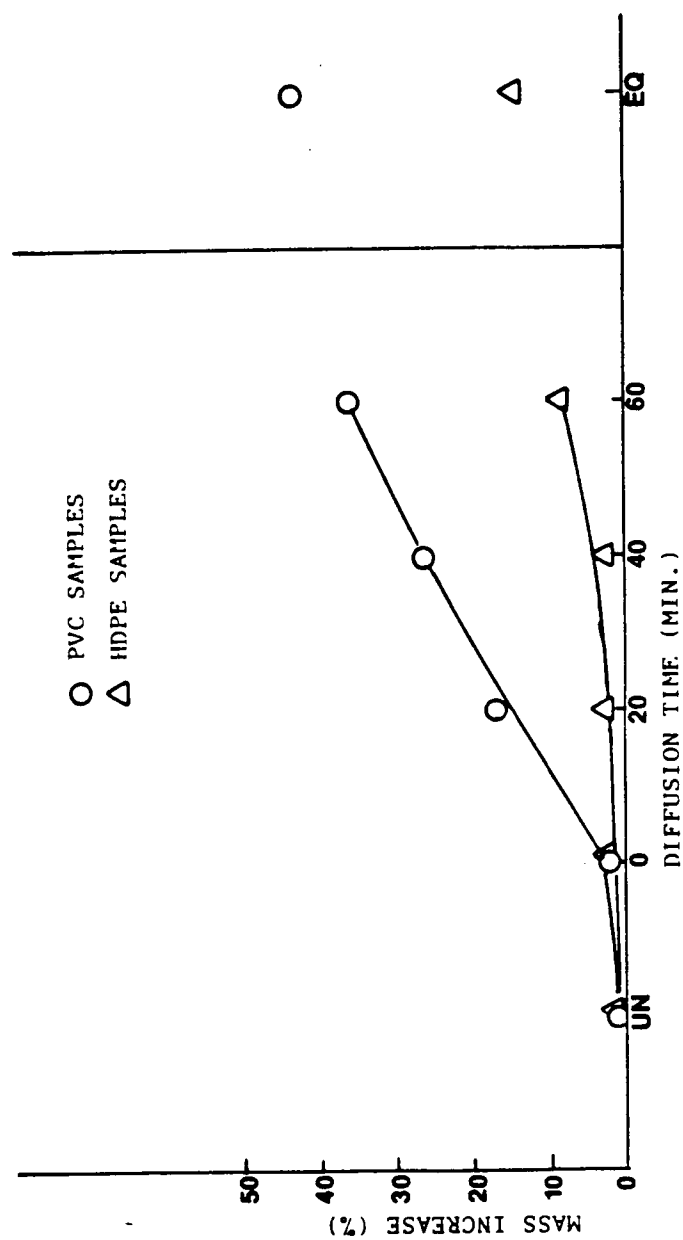


Figure 12. Percentage mass increases vs. diffusion time for PVC and HDPE samples.

The results indicate that the percentage mass increases in the PVC films are linearly related to diffusion times. This linearity does not extend to the point represented by a diffusion time of 720 minutes (12 hours). The percentage mass increases in the HDPE films do not seem to follow any sort of linear relationship. Mass increases among these samples are seen to be negligible with the exception of the HDPE-EQ films (12 hour diffusion).

Percentage thickness increases with diffusion time in the PVC samples seem to follow a somewhat linear relationship. The thickness variations among the HDPE samples, on the other hand, are minimal, with the exception of HDPE-EQ, which had a percentage thickness increase of 30 percent.

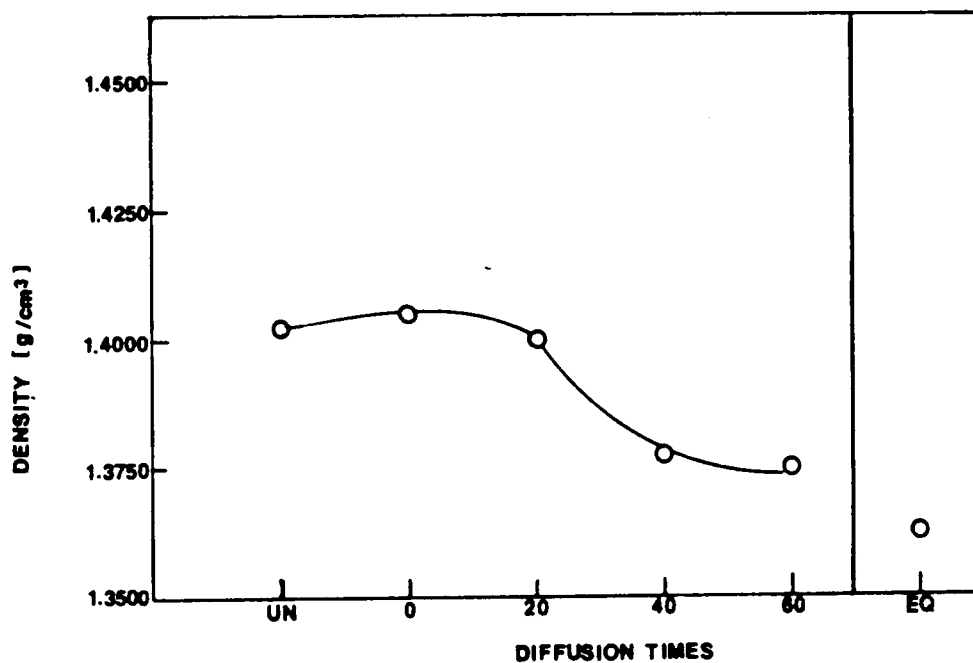
Table 5 lists the measured densities of modified and unmodified films. The density of a solvent cast film of poly(n-butyl methacrylate) was found to be approximately 1.1810 g/cm^3 . The density values of the PVC films were found to exhibit a linearly decreasing relationship with diffusion times. The density values of the HDPE films increased slightly with increasing diffusion times, with the maximum percentage gains reaching values of less than 1 percent. Figure 13 gives the variation of densities with diffusion times for the PVC and HDPE samples.

Comparisons of specific absorption bands from infrared spectra have been made in an attempt to draw a semiquantitative relationship between diffusion times and incorporation of PBMA into the PVC and HDPE substrates. Percentage absorption increases of the carbonyl

TABLE 5
DENSITY VALUES FOR PVC AND HDPE FILMS

Sample	Density (g/cm ³)
PVC-UN	1.4025
0	1.4050
20	1.4000
40	1.3800
60	1.3775
EQ	1.3625
HDPE-UN	0.9640
0	0.9625
20	0.9653
40	0.9680
60	0.9690
EQ	0.9720

PVC FILMS



HDPE FILMS

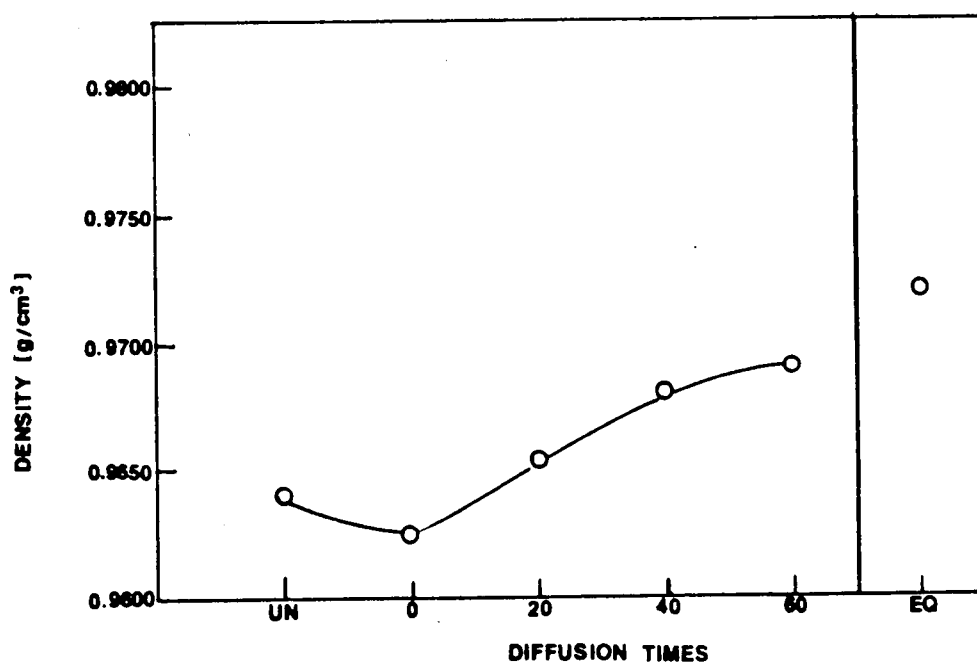


Figure 13. Density variation as a function of diffusion time for PVC and HDPE films.

group in PBMA (at 1720 cm^{-1}) as a function of diffusion time are given in Table 6. These increases in absorption are listed in relation to the absorption values for a $-\text{CH}_2-$ bending mode (at 1424 cm^{-1}) which is characteristic of PVC. In HDPE, an absorption band at 1463 cm^{-1} was chosen for comparison with the PBMA carbonyl band at 1720 cm^{-1} . A ratio of the absorbances of the two peaks is given in both the PVC and HDPE samples in order to minimize the effects of sample thickness variation on absorption. The ratios of carbonyl absorption (from PBMA) to $-\text{CH}_2-$ bending (from PVC) tend to increase linearly with respect to diffusion time. The ratios of carbonyl absorption to specific absorptions at 1463 cm^{-1} in HDPE (also $-\text{CH}_2-$ bending) are shown to be fairly constant with respect to diffusion times. The graphical representation of these relationships are given in Figure 14. Infrared spectra for the PVC samples are given in Figures 15-17, while Figures 18-20 show the spectra for the HDPE films.

The experimental methods used to arrive at mass increases of the various samples could only give a rough estimate of actual values. Although the samples were cut with a sharp razor blade along the edges of a solid metal plate, many variables could have affected the accuracy of weight measurements. For instance, although the original PVC samples were of very uniform thickness, some variation was found in these measurements. A section cut from one of these films following modification could have been taken from an area where the thickness was several microns greater than or less than the original

TABLE 6
RATIOS OF ABSORBANCE FOR CHARACTERISTIC PEAKS
IN PVC/PBMA AND HDPE/PBMA

	C=O at 1720 cm^{-1}	-CH ₂ - Bending ^a	Absorbance Ratio
PVC-UN	0.0123	1.2760	0.0097
0	0.0521	0.9508	0.0548
20	0.2147	0.9318	0.2304
40	0.5850	0.8539	0.6851
60	0.6021	0.5575	1.0800
EQ	0.9830	0.8097	1.2140
HDPE-UN	0.0000	0.8239	0.0000
0	0.6882	0.8386	0.8207
20	0.7905	0.8041	0.9831
40	0.7747	0.8239	0.9403
60	0.7800	0.8297	0.9401
EQ	0.7520	0.7959	0.9448

^a1424 cm^{-1} in PVC; 1463 cm^{-1} in HDPE.

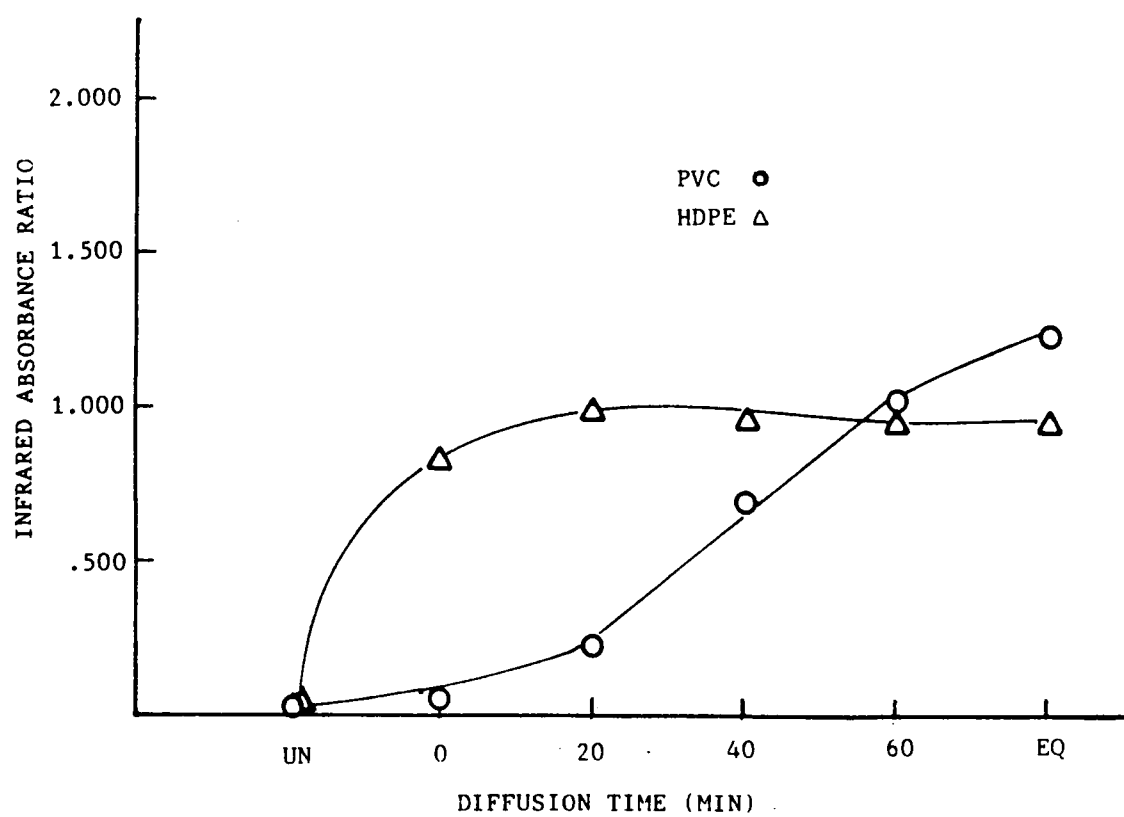


Figure 14. Infrared absorbance ratios vs. diffusion time for PVC and HDPE films.

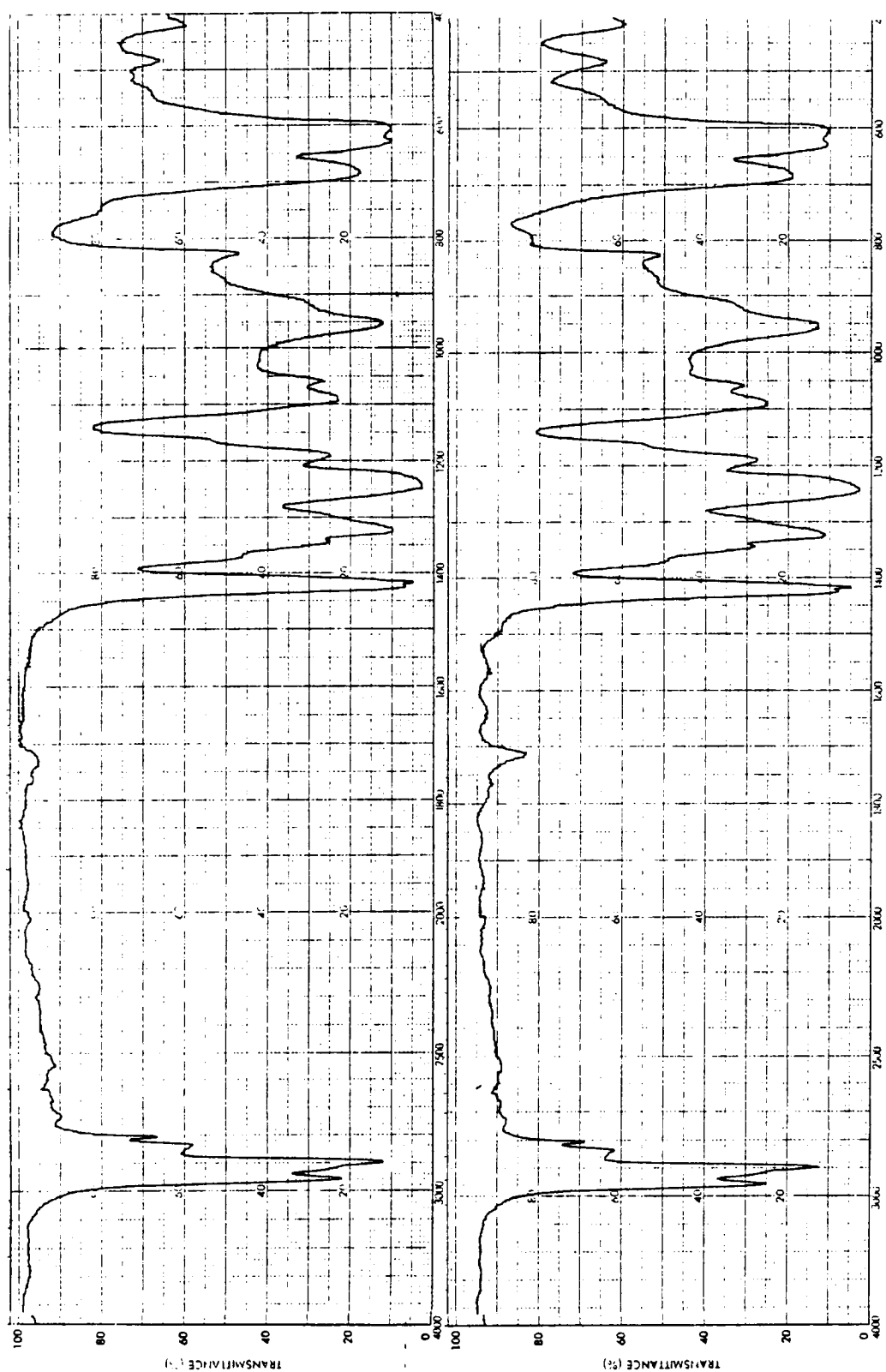


Figure 15. Infrared spectra of PVC-UN (top) and PVC-0 (bottom)

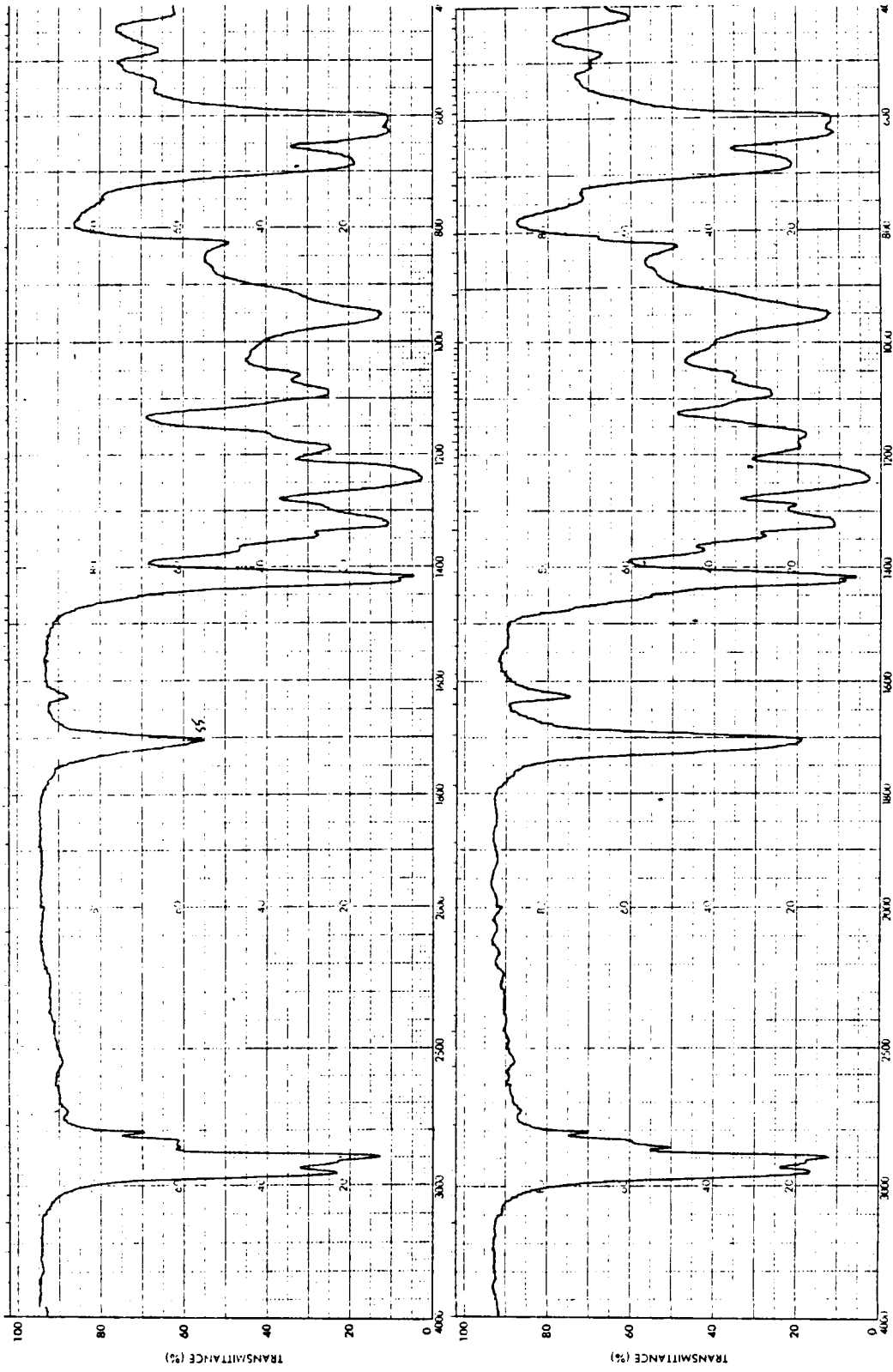


Figure 16. Infrared spectra of PVC-20 (top) and PVC-40 (bottom).

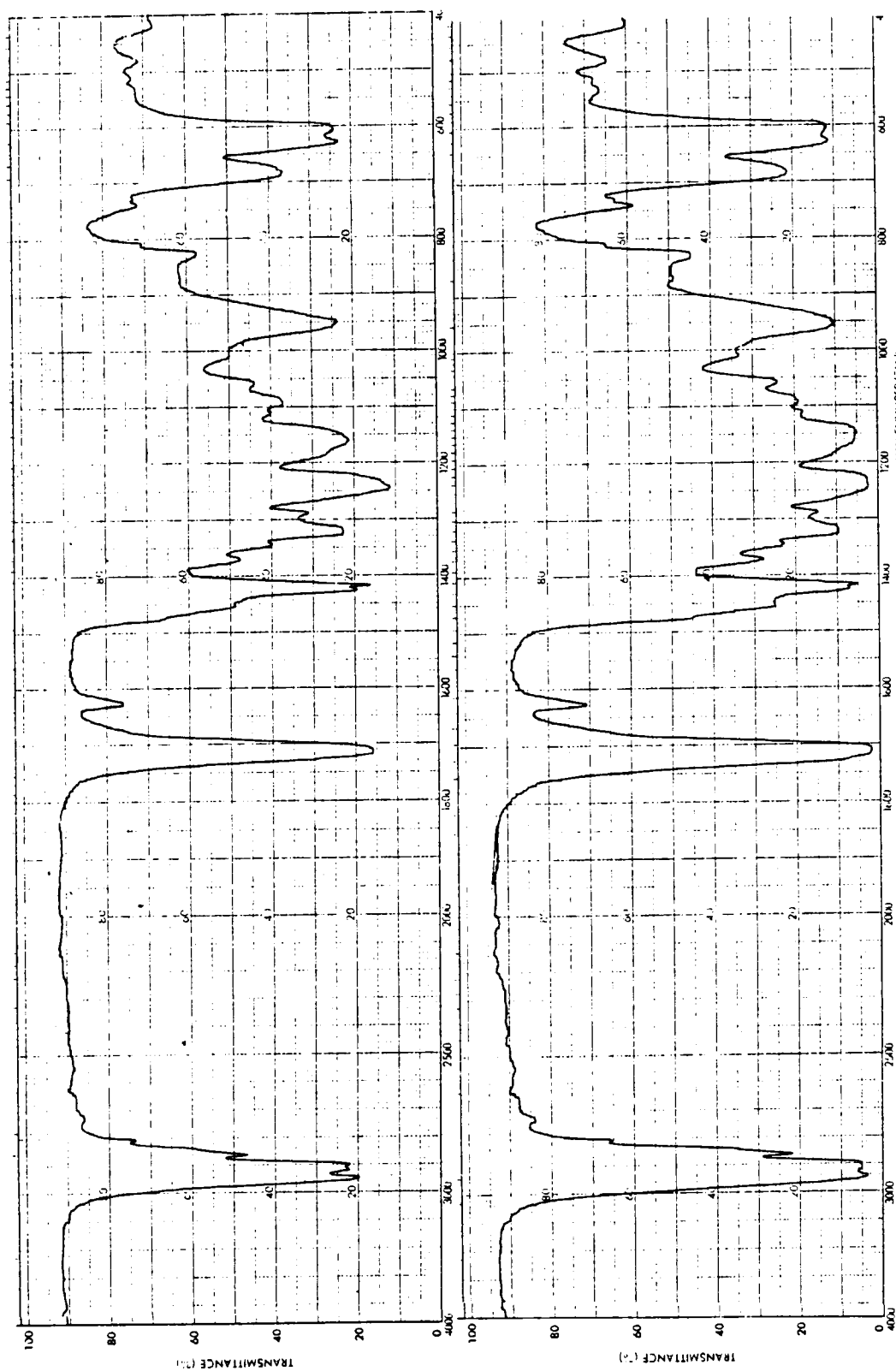


Figure 17. Infrared spectra of PVC-60 (top) and PVC-EQ (bottom).

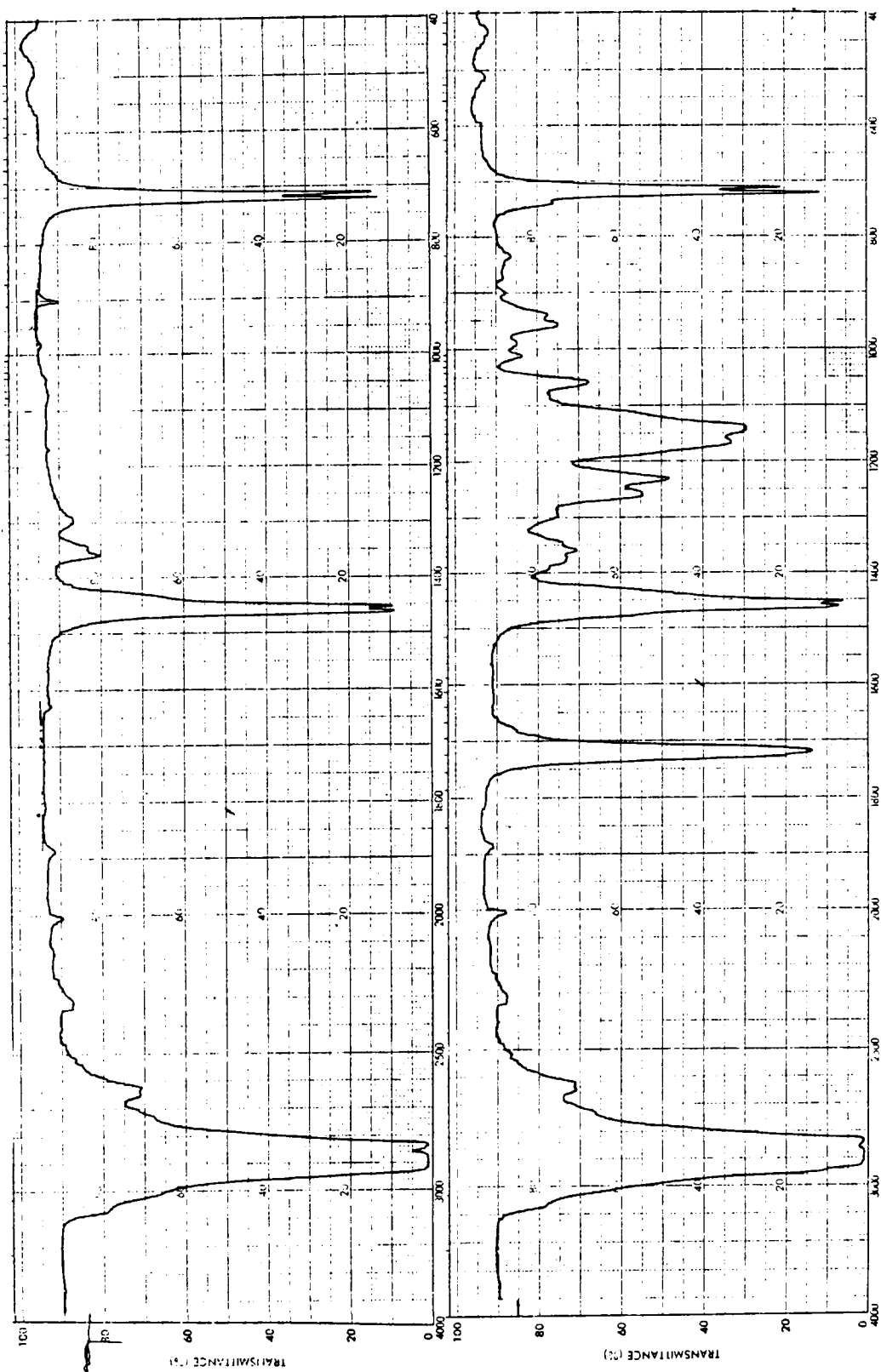


Figure 18. Infrared spectra of HDPE-UN (top) and HDPE-0 (bottom).

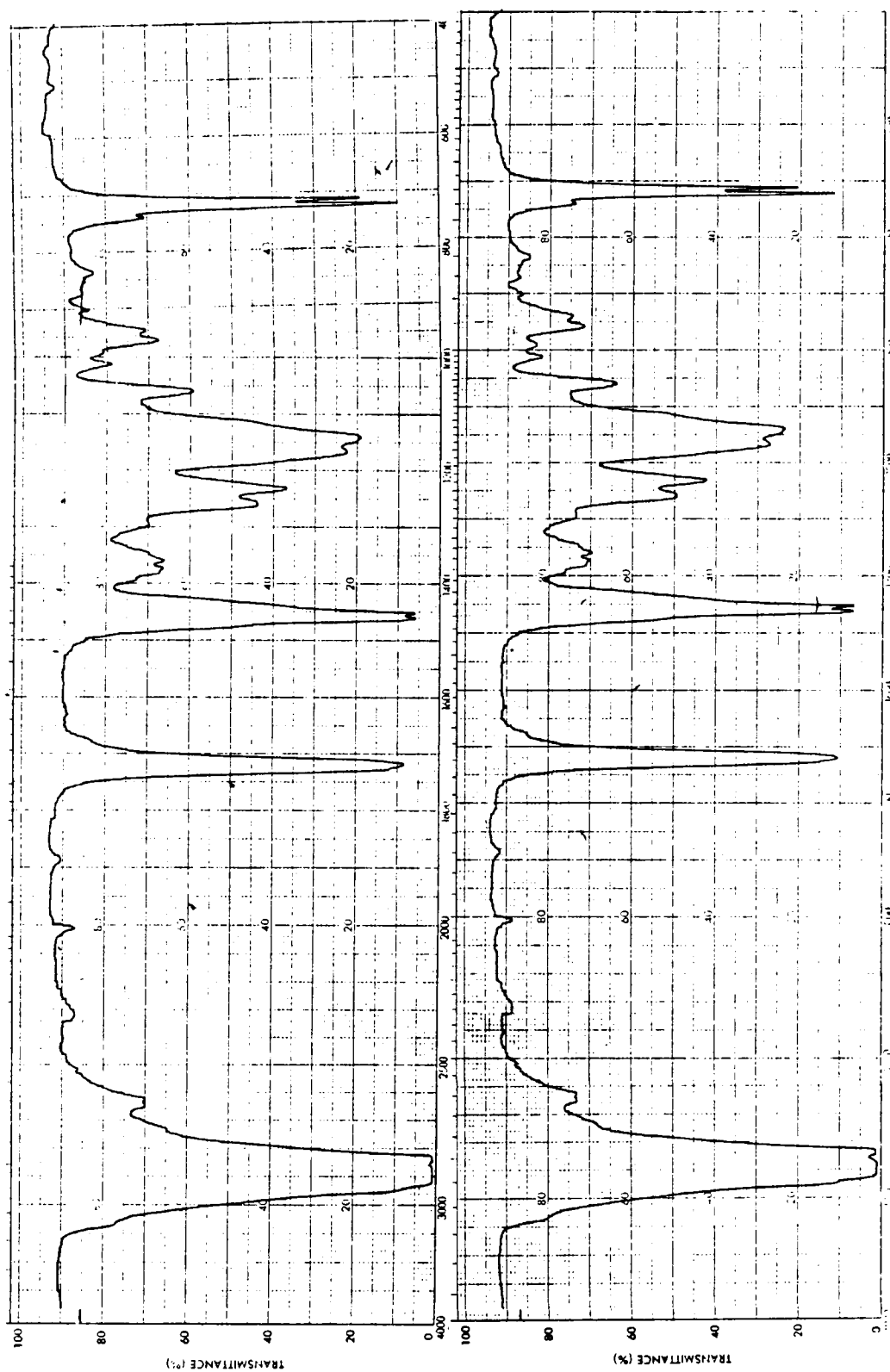


Figure 19. Infrared spectra of HDPE-20 (top) and HDPE-40 (bottom).

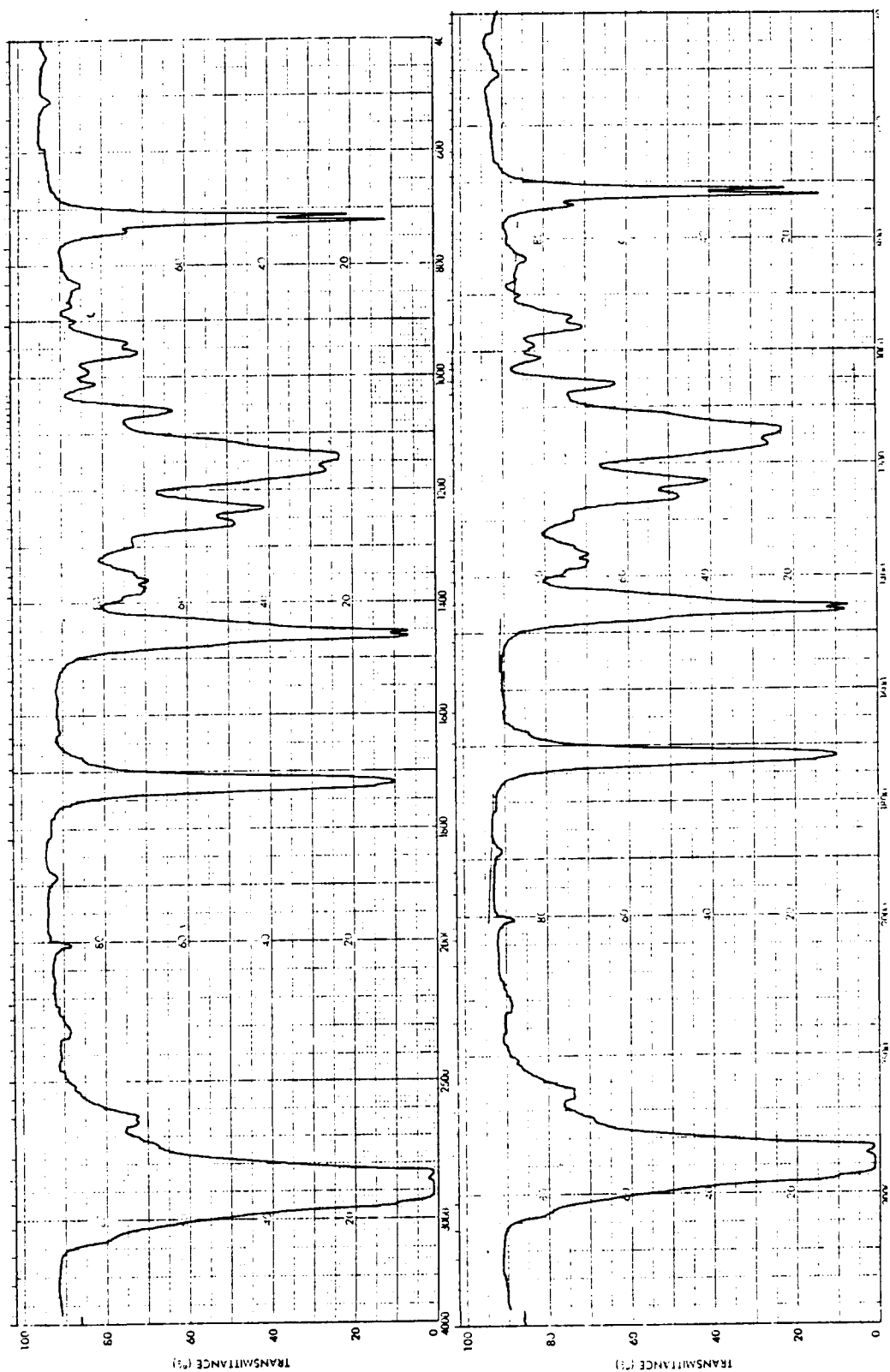


Figure 20. Infrared spectra of HDPE-60 (top) and HDPE-EQ (bottom).

average measurement. Also, polymer films tend to expand in all directions upon introduction of monomer. Therefore, the original mass of substrate material contained within a certain volume would not necessarily be included in that same volume following modification. The most efficient method by which mass changes could be measured would be to weigh the entire film (rather than sections) before and after modification. This method was not used in light of the fact that the frame assembly blocked portions of the films from electron beam radiation.

Although the percentage mass increase values must be considered as rough estimates, several trends in the data may be seen. The relationship between BMA diffusion times and percentage mass increases was shown to be essentially linear in the PVC substrates, while no particular pattern was seen in the HDPE samples. The behavior of the PVC films under diffusion conditions was found to be similar to the behavior of the glassy polymers studied by Kwei et al. (51). Several articles (3,20,28) cited in Chapter II discussed diffusion studies in which percentage weight increases were directly proportional to time. Linear weight increases with respect to time have been attributed to systems in which Case II diffusion is taking place. As mentioned previously, Alfrey et al. (3) characterized Case II diffusion by describing sharp advancing solvent fronts which traveled at a constant velocity. Kwei et al. (50) found that linear weight increases with time and constant velocities were analogous phenomena. They found this behavior to occur at temperatures well below the glass transition of the unswollen polymer.

The PVC films which underwent diffusion in this study seem to follow the general trends of systems characterized by Case II diffusion. The experiments were carried out at room temperature, which at 25°C is well below the glass transition of PVC (85°C). The percentage mass increase measurements, although rough, were indicative of Case II diffusion.

The percentage mass variations in the HDPE samples indicated that BMA uptake by the substrate films was very low in the 20, 40, and 60 minute diffusion times. The PVC-EQ films showed slightly greater mass increases. The diffusion of BMA into HDPE was probably a very slow process. Polyethylene's crystalline structure has been shown to obstruct diffusion of solvents in general. The small increases in weight percentage gains found in the most highly modified HDPE samples indicate that any formation of new polymer was most likely restricted to surface regions. These data find agreement with the work of Restaino (78) and Yamakawa (96), who found surface grafting to be the predominant reaction in their studies with HDPE.

Although the weight increase measurements of the various samples do not specifically characterize depth of penetration or phase distribution in the films, these data indicate that the behavior of the PVC and HDPE substrates are very different under identical experimental conditions. PVC substrates appear to imbibe BMA monomer at a constant rate up to swelling equilibrium. HDPE substrates appear to impair the diffusion of BMA monomer.

The thickness variation behavior exhibited by the PVC films was found to be very similar to the behavior of the glassy polymers studied by Kwei et al. (51). Linear increases in thickness were expected in the PVC films on the assumption of Case II diffusion behavior. In Case II behavior, the variation in distance from the advancing front to the swollen polymer surface during diffusion has been found to be proportional to time. As the monomer moves deeper into the film, similar swelling behavior would theoretically occur at each imaginary layer. Therefore, the film would expand in a linear manner.

The limited thickness variation which was witnessed in the HDPE samples was most likely a reflection of the limited swelling power of BMA for the substrate. It is impossible to interpret the data in this case, in light of the fact that the original, unmodified HDPE samples exhibited fairly significant thickness variations.

The density measurements which were made are obviously very closely related to both mass increases and volume increases in the samples. The addition of PBMA (1.180 g/cm^3) to PVC (1.4025 g/cm^3) would be expected to cause fluctuations in density. The swelling of PVC which was encountered would have to be taken into account to interpret density variations. Interpretation was considered on the basis of a number of experimental variables. Nevertheless, the density variation trend which was seen in PVC would be expected. The PVC films, which apparently were consuming monomer and swelling at constant rates, would be expected to exhibit decreasing density

values in their various composite forms. The minimal density variation values found in the HDPE films were apparently the result of limited uptake of monomer.

The infrared spectra provide a semiquantitative picture of compositional variation among the samples. The important absorption band in these spectra was the 1720 cm^{-1} carbonyl from a stretching mode in PBMA. An important point which was considered was the thickness variation of the samples. Infrared absorption has been found to increase with the pathlength of the medium being analyzed (7). The film thickness values studied here were variable, with fluctuations on the order of several microns. Reference peaks characteristic of the substrate polymer were studied along with the carbonyl band (at 1720 cm^{-1}). This type of analysis revealed that specific absorption values varied insignificantly with sample thickness. The absorption at 1720 cm^{-1} was, therefore, used directly for comparative composition studies. Theoretically, an increase in absorption at 1720 cm^{-1} may be directly related to an increasing quantity of PBMA. One problem in this type of analysis involves the potential presence of residual monomer that may not have reacted during the synthesis of the composite materials. The quantity of unreacted monomer, however, was probably quite small in comparison to the amount of PBMA. The reference bands which were chosen for the analysis of the PVC substrates ($-\text{CH}-$ bending); amorphous phase; 1424 cm^{-1}) and the HDPE substrates ($-\text{CH}_2-$ bending); amorphous phase; 1463 cm^{-1}) were identified previously by Krimm (48).

The results indicate that PBMA has been incorporated into the PVC films in linearly increasing amounts with respect to time. This information coincides well with the compositional characteristics which were expected in these films. The fact that the absorption peaks show essentially linear behavior lends credibility to the assumptions that diffusion occurred at a constant rate and that the 10 megarad dose polymerized the existing monomer instantaneously. If these events did occur as expected, the formation of a gradient structure would seem a strong possibility.

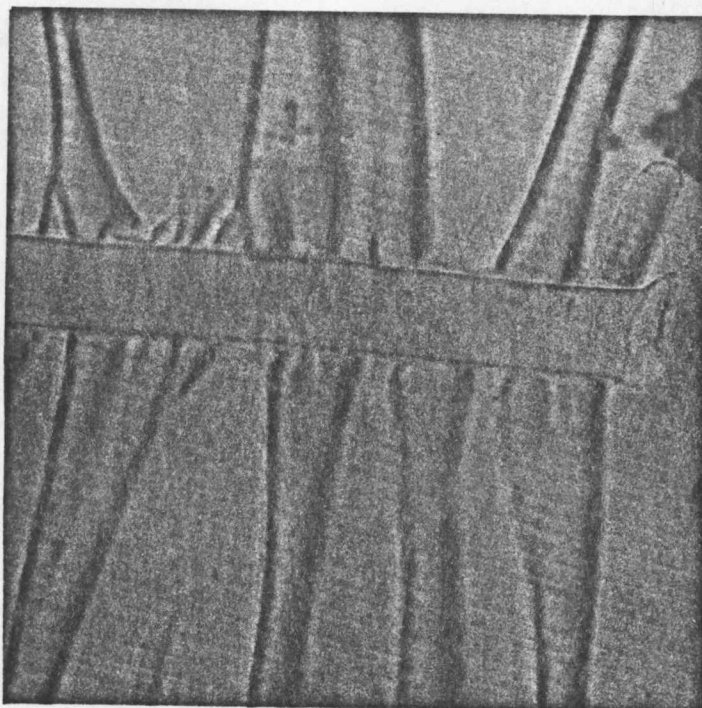
Analysis of the infrared spectra of the HDPE samples led to some unusual observations. The 1720 cm^{-1} absorption band was found to be equivalent in all of the samples which had been exposed to radiation. This observation would seem to indicate that equal amounts of PBMA existed in all samples (excluding HDPE-UN). The interpretation of the data was difficult in light of the fact that the HDPE-0 samples had not been exposed to BMA monomer. A flaw in experimental design was thought to account for this phenomena. After irradiation, the HDPE films were placed in the same desiccator in their individual sample bags. The presence of BMA vapor was obvious following irradiation. BMA vapor may have diffused into the films following irradiation and attacked the stable free radicals of the polyethylene chains. The stability of HDPE free radicals was discussed earlier (29). It is very possible that all of the irradiated films may have incorporated equivalent amounts of PBMA from the vapor source. Minimal diffusion of BMA liquid monomer into HDPE prior to

irradiation may have resulted in insignificant polymer formation during irradiation. It follows that the major portion of polymer formation may have occurred in the desiccator via attack of free radical sites by BMA vapor.

C. Morphological Characterization

Figure 21 presents a set of optical micrographs of cross sections of the unmodified and modified PVC films. Figure 22 shows optical micrographs of cross sections of the HDPE films, while Figure 23 presents the same cross sections viewed under crossed polars.

The use of "normal" optical microscopy revealed little about the morphological nature of the PVC or HDPE samples. Thickness values were determined microscopically and compared with the values which were obtained by use of a pressure sensitive micrometer (Table 1, p. 50). The appearance of dark and light regions was observed while viewing the HDPE cross sections under crossed polars. Measurements of the distances from film surfaces to the boundary lines of light and dark regions are given in Table 7. Microscopic observations through the edges of the HDPE films under crossed polars revealed the existence of several interesting phenomena. First, the photographs indicate the presence of some sort of phase distribution in the irradiated samples. Secondly, it appears that the phase distributions in the irradiated films are all very similar in nature. Last of all, the HDPE-UN films show no sort of phase distribution whatsoever.

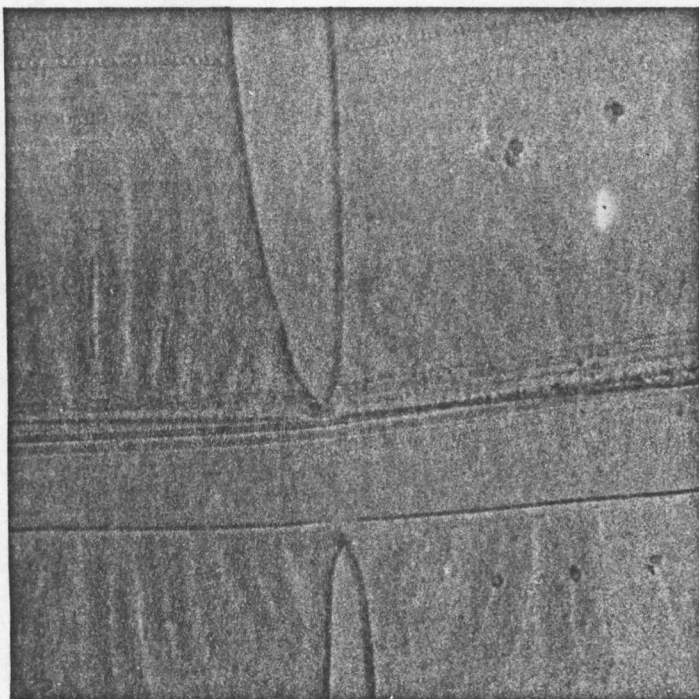


(a)

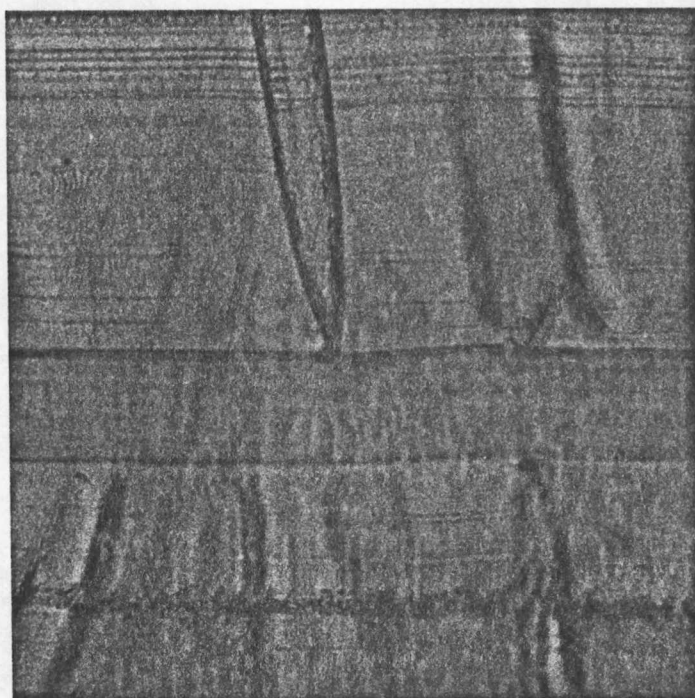


(b)

Figure 21. Optical micrographs of PVC cross sections: (a) PVC-UN; (b) PVC-0; (c) PVC-20; (d) PVC-40; (e) PVC-60; and (f) PVC-EQ. (250X).

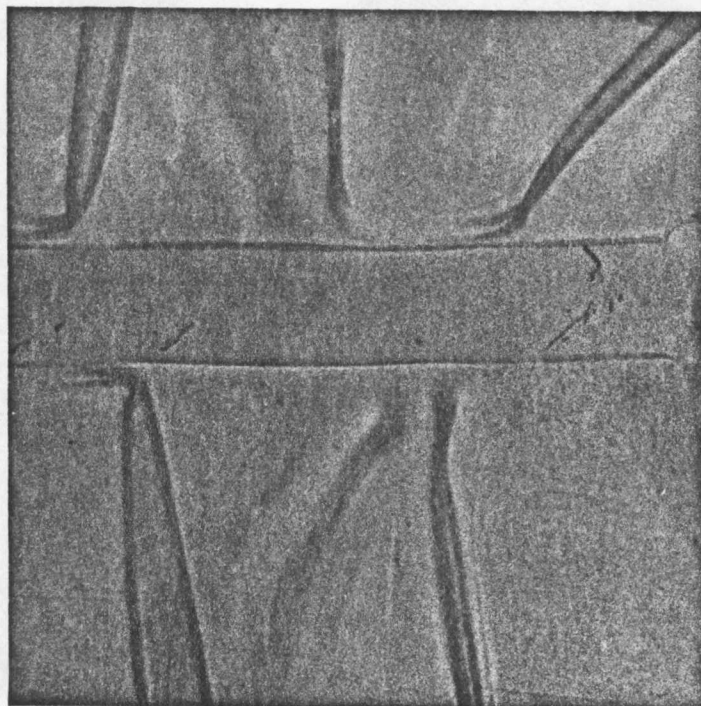


(c)

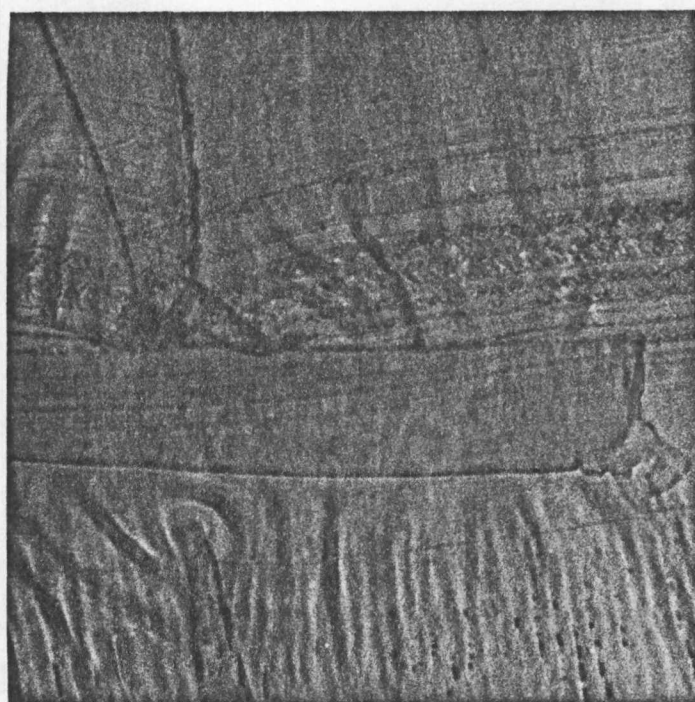


(d)

Figure 21 (continued)

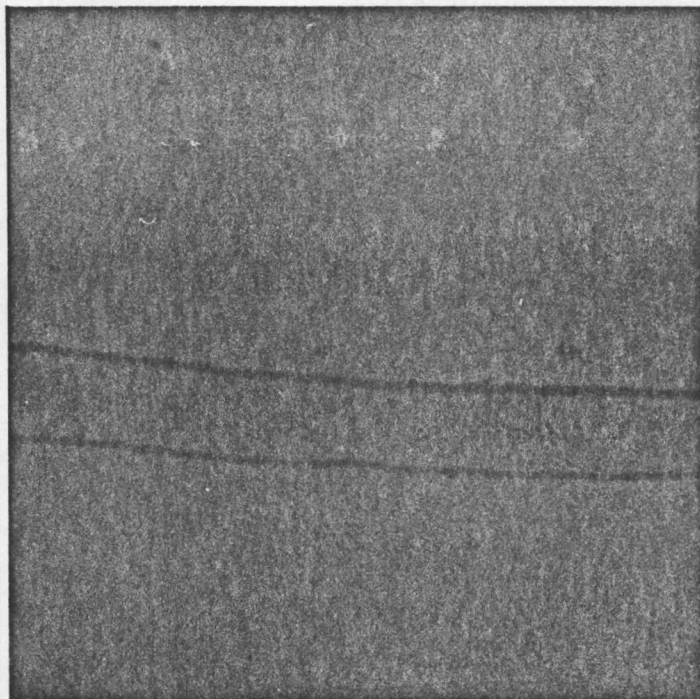


(e)

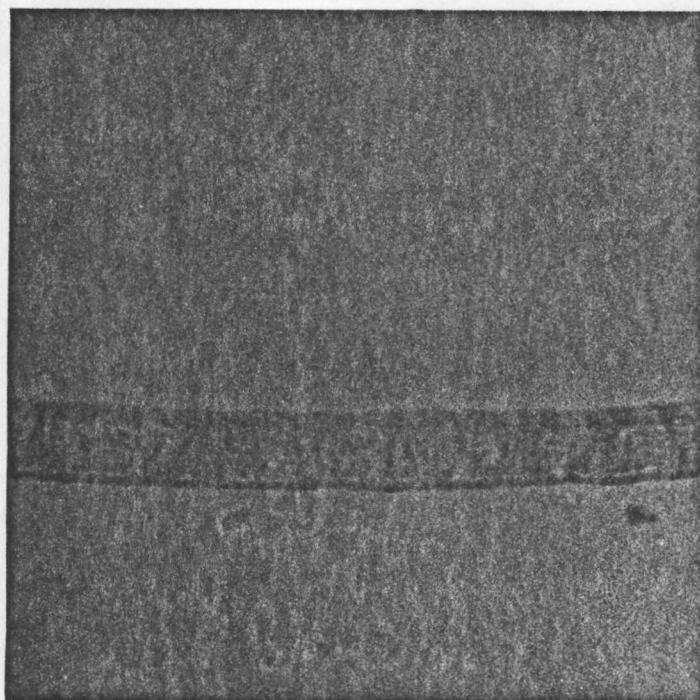


(f)

Figure 21 (continued)

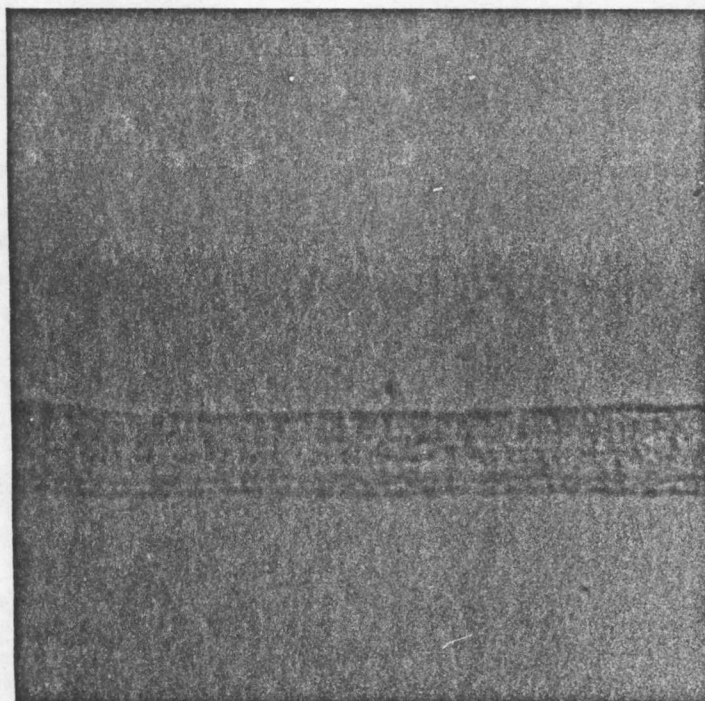


(a)

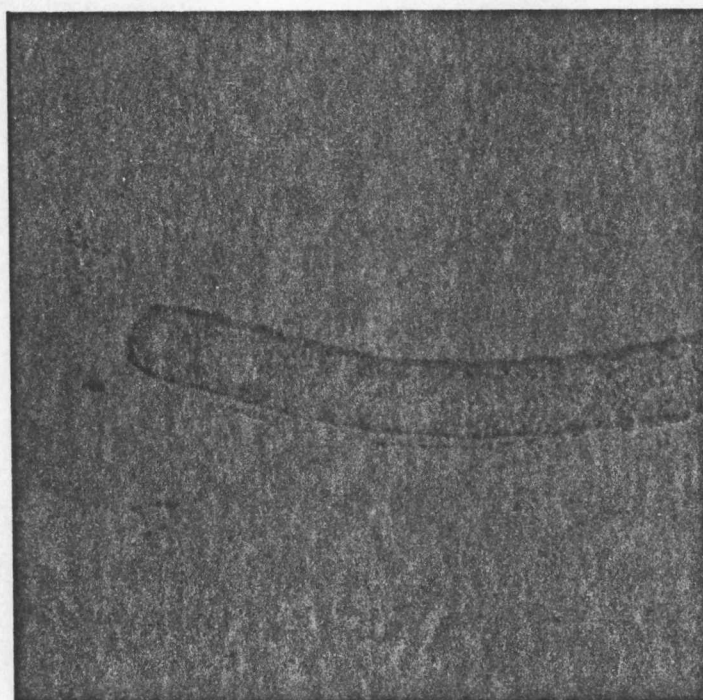


(b)

Figure 22. Optical micrographs of HDPE cross sections: (a) HDPE-UN; (b) HDPE-0; (c) HDPE-20; (d) HDPE-40; (e) HDPE-60; and (f) HDPE-EQ. (250X).

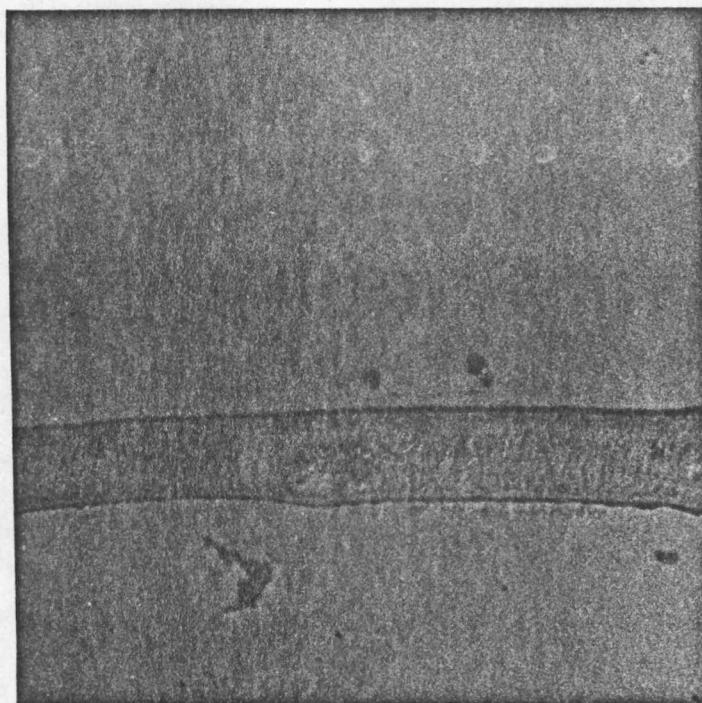


(c)

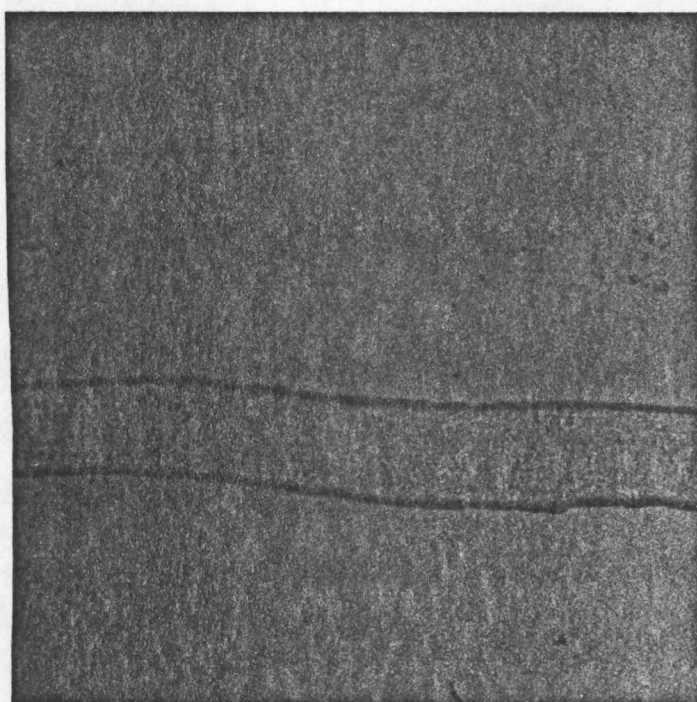


(d)

Figure 22 (continued)

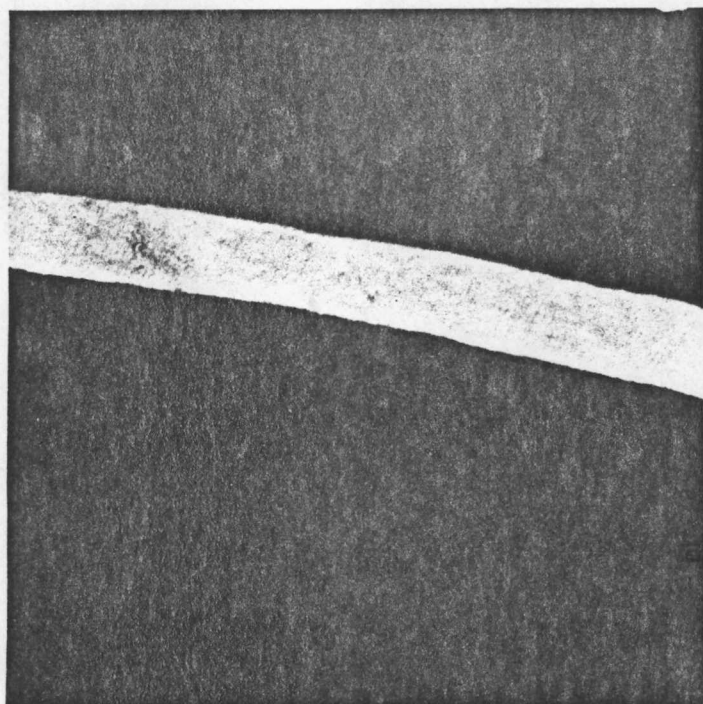


(e)

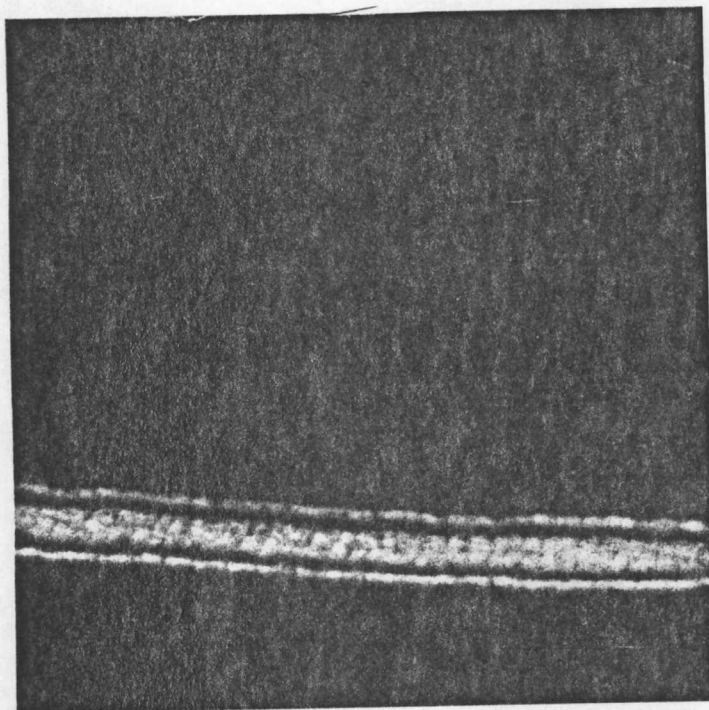


(f)

Figure 22 (continued)

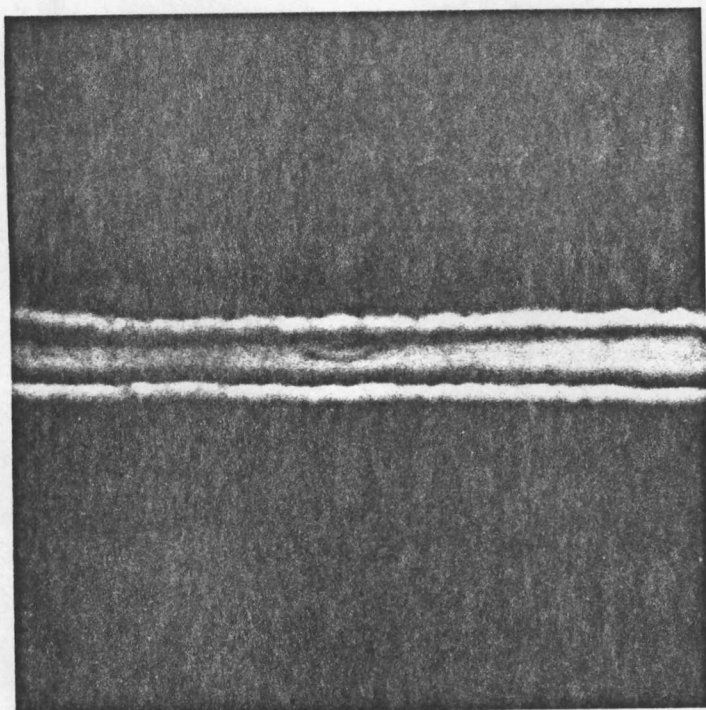


(a)

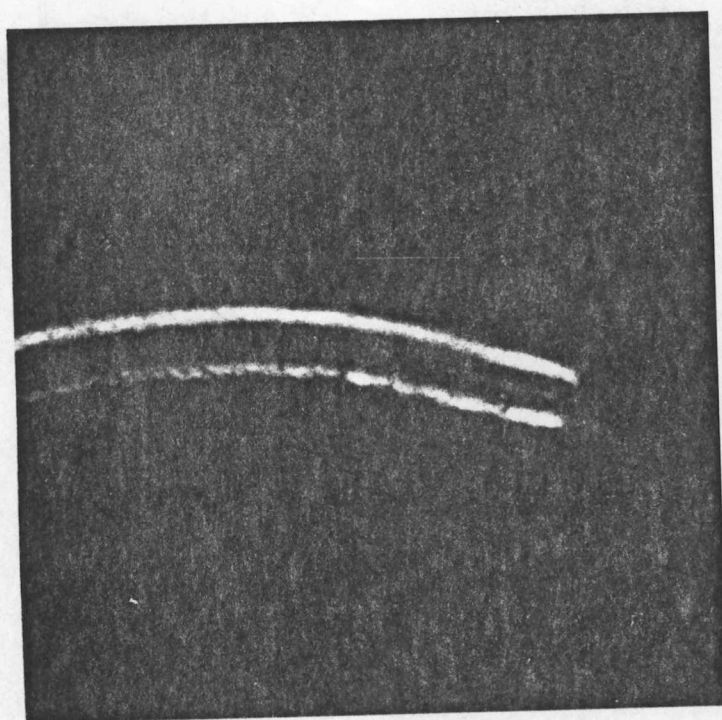


(b)

Figure 23. Crossed polar view of HDPE cross sections: (a) HDPE-UN; (b) HDPE-0; (c) HDPE-20; (d) HDPE-40; (e) HDPE-60; and (f) HDPE-EQ. (250X).

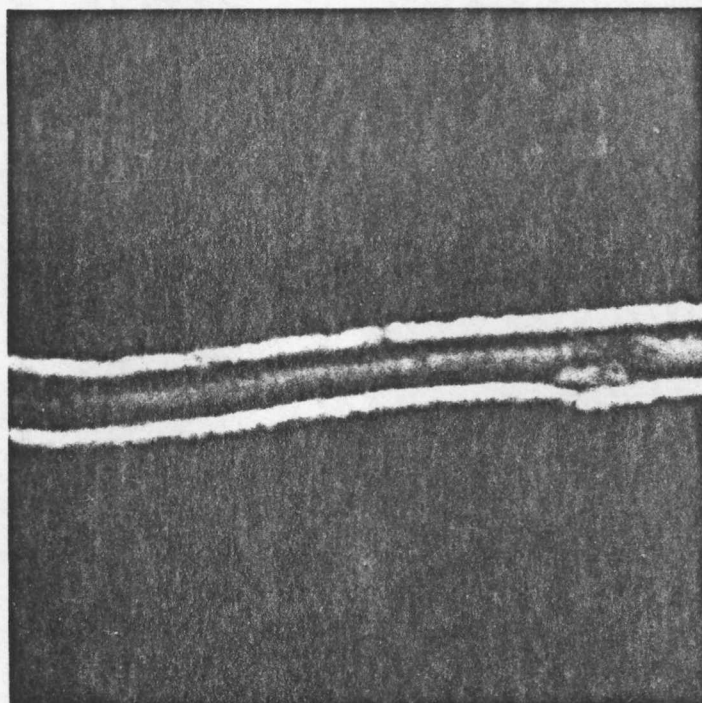


(c)

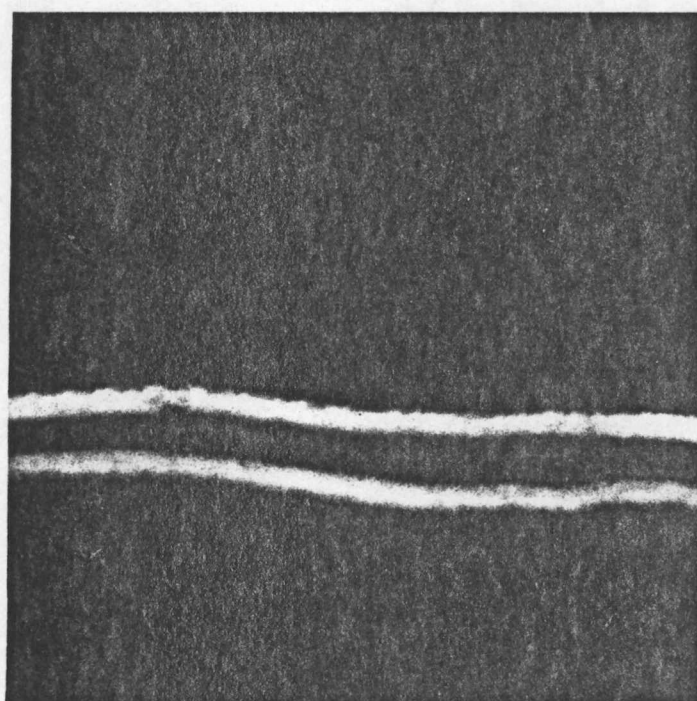


(d)

Figure 23 (continued)



(e)



(f)

Figure 23 (continued)

TABLE 7
BOUNDARY MEASUREMENTS FOR LIGHT/DARK
REGIONS IN HDPE CROSS SECTIONS

	Film Thickness (μm)	Depths of Surface (μm)	Core Width (μm)
HDPE-UN	40	--	--
0	40	8	24
20	41	12	17
40	41	12	17
60	42	12	18
EQ	52	16	20

In a related research project (86), the PVC and HDPE composite films were analyzed using FTIR/ATR analysis. The data which has been collected provides some important information about the concentration profiles which exist in the various films. A summary of these data appears in Table 8. Although this phase of the research project has not been completed, several trends have been observed in the analysis of the films by FTIR/ATR. First of all, the presence of PBMA chains has been detected in the surface regions of the PVC films which were exposed to monomer. Secondly, all of the evidence indicates that polymerization of the monomer occurred in deeper layers of the PVC films in the more heavily modified substrates.

Analysis of the HDPE films by FTIR/ATR yielded some rather unusual results. The spectra which were gathered suggest that little, if any, polymerization of BMA occurred in the surface regions. The cores of the films, however, apparently contain polymerized material.

Several other experimental techniques were attempted in hopes of characterizing the distribution of phases in these composites. Photographs obtained by use of Transmission Electron Microscopy (TEM) did not serve to distinguish phases in the PVC or HDPE materials. The results of Scanning Electron Microscopy (SEM), a technique which was applied to cross sections of the films, were not helpful in structure elucidation. Small Angle Light Scattering (SALS) photographs of the HDPE films did not contain any evidence of structural differences among the modified and unmodified films.

TABLE 8
GENERAL OBSERVATIONS FROM FTIR/ATR

PVC-UN	PBMA not detected in samples.
0	PBMA not detected in samples.
20	PBMA detected in surface regions of the samples.
40	PBMA detected on surfaces and in regions several microns into the films.
60	PBMA detected on surfaces and in region approaching the cores of the films.
EQ	PBMA detected throughout the thickness of the films.
HDPE-UN	PBMA not detected in samples.
0	PBMA detected in the core regions of the films but not on the surfaces.
20	Same as HDPE-0
40	Same as HDPE-0
60	Same as HDPE-0
EQ	Same as HDPE-0

Transmitted light microscopy has been used extensively in studies which attempt to determine phase distributions in composite polymer systems. The lack of contrast which was observed in the PVC and HDPE samples was not surprising. Generally, several criteria must be met before the distribution features of a composite may be distinguished by use of optical microscopy. First of all, the specimens which one viewed must be thin enough to allow the transmission of an appreciable fraction of light. This was not a problem with the PVC and HDPE films, which were cut in cross section to a thickness of 5 microns. The inability to distinguish structural features was a consequence of the similarities in refractive indices among the components. Average refractive indices of PVC, HDPE, and PBMA have been given as 1.540, 1.526, and 1.483, respectively. The differences in refractive index (0.057 for PVC/PBMA and 0.043 for HDPE/PBMA) were not great enough to cause distinguishable scattering of light from the phases. Attempts were made to differentially stain the components, but these procedures proved unsuccessful. The optical studies did prove useful in the characterization of film thickness. The thickness values which were found by viewing the cross sections were probably more accurate than those determined by use of the pressure-sensitive micrometer.

The phase distributions which were seen in the HDPE films through crossed polars were thought to be significant the cores of the HDPE films was discussed previously. The HDPE substrates did not allow appreciable amounts of BMA monomer to penetrate their surfaces

during the diffusion phase. After irradiation, the samples were placed in a common desiccator. It was necessary to remove the samples from their frames before they could be placed in the desiccator. At this point of the experimentation the films were momentarily exposed to oxygen. It is possible that oxygen may have diffused into the HDPE films and reacted at the stable free radical sites which were available. After the films were removed from their frames, they were placed back in their Ziploc storage bags and returned to the desiccator. They were still exposed to some oxygen at this point, but the atmosphere surrounding the film consisted mainly of BMA vapor.

One explanation of the occurrence of exclusive polymerization in the core of the HDPE films involves the interaction of the samples with oxygen. In this explanation, oxygen molecules are thought to have destroyed free radical sites to the depth of their penetration. This penetration depth was limited by the exposure times of the films to the air. Free radical sites in HDPE have been shown to be very stable (78). It is reasonable to assume that the cores of our HDPE films were populated by many active sites after oxygen diffusion had ceased. These active sites were subsequently available for attack by BMA vapor. The BMA vapor was in contact with the films for several hours without a constant vacuum source. It follows that BMA may have diffused into the films and polymerized in the core regions. The layered structures which are seen in the cross sections help support this hypothesis.

CHAPTER V

CHARACTERIZATION OF THE MECHANICAL PROPERTIES OF THE FILMS

Tensile properties of all modified and unmodified films were determined from data which was obtained from force versus elongation curves. The curves were experimentally obtained by stretching the samples at a constant rate with the Instron Tensile Tester. Strength properties were reported in terms of engineering stresses, which were obtained by dividing force values by the initial cross sections of the samples being tested. Strain values were reported in terms of percentage strains.

Table 9 gives the tensile property data for the films in which PVC was the substrate material. The values were obtained from films of 35 mm, 25 mm, and 15 mm gauge lengths. Typical stress-strain curves for a set of 35 mm gauge length samples are shown in Figure 24.

In general, it may be seen that the PVC films that were exposed to monomer for longer periods of time (prior to irradiation) tended to exhibit increased elongation properties. Yield strength showed a tendency to decrease in the more heavily modified samples (e.g. PVC-EQ). Tensile strength values also decreased for samples with higher diffusion times. Little change was seen in elastic moduli among the various PVC samples, although values did show a

TABLE 9
MECHANICAL PROPERTIES OF THE PVC FILMS

	Thickness (μm)	A ($\text{cm}^2 \times 10^3$)	Yield Strength (MPa)	Tensile Strength (MPa)	Modulus (MPa)	% Elong.
PVC-UN (35 mm.)	39.6	1.98	66.7	51.4	2100	29.94
0	42.7	2.14	57.7	46.7	1890	27.48
20	42.9	2.15	54.9	44.1	1830	32.51
40	42.4	2.12	51.2	42.5	1770	46.06
60	42.7	2.14	49.8	42.1	1740	50.11
EQ	50.8	2.54	38.8	31.5	1520	58.80
PVC-UN (25 mm.)	40.4	2.02	66.5	51.1	2030	31.20
0	42.4	2.12	57.8	46.3	1940	29.04
20	42.7	2.14	55.0	45.4	1880	30.96
40	42.9	2.15	51.0	42.5	1870	44.72
60	44.5	2.23	49.6	40.7	1810	50.96
EQ	52.1	2.61	38.4	31.2	1480	56.08
PVC-UN (15 mm.)	39.9	2.00	66.5	51.1	2190	28.80
0	42.7	2.14	58.5	47.2	1920	26.13
20	43.2	2.16	54.7	43.0	1880	34.00
40	43.4	2.17	49.9	42.3	1860	47.47
60	43.2	2.16	49.6	42.8	1830	49.73
EQ	51.3	2.57	38.6	31.7	1510	61.20

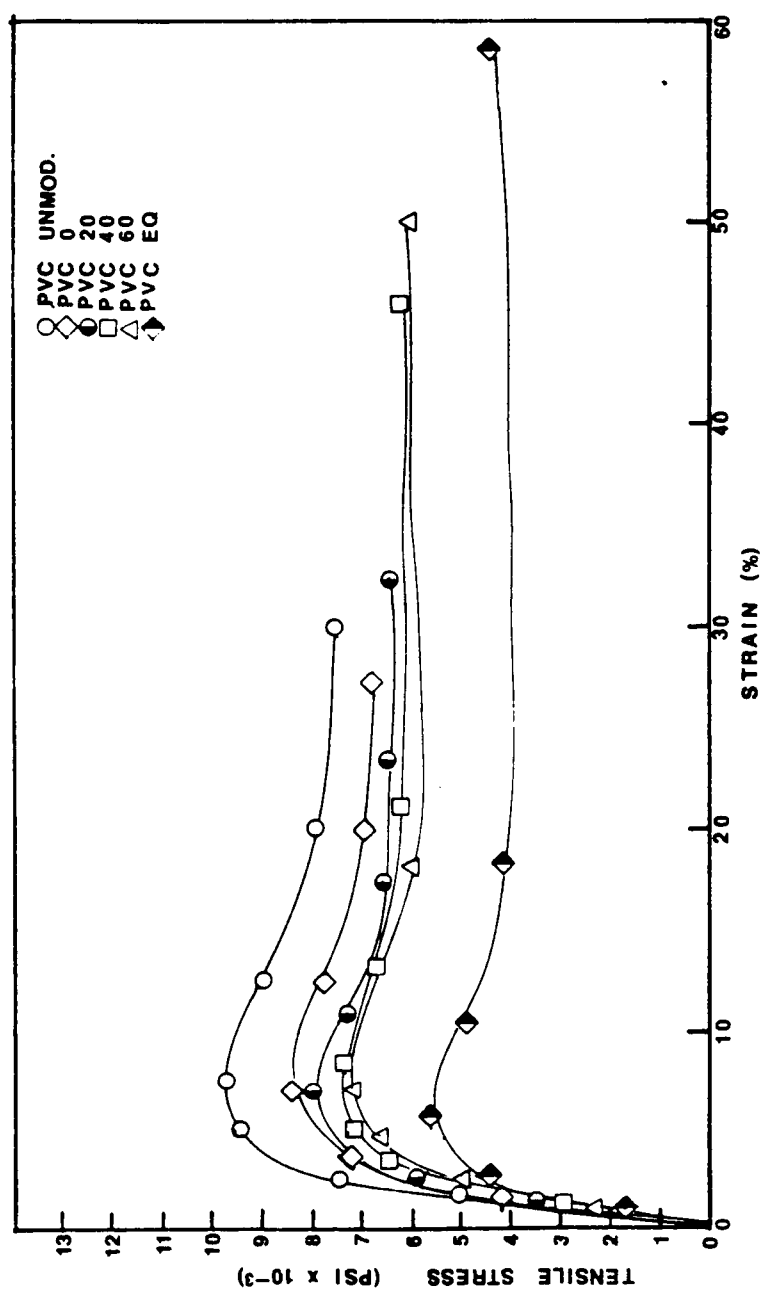


Figure 24. Stress/strain curves for PVC films (crosshead speed = 20 mm/min).

slight decreasing tendency in the more heavily modified systems. The graphical relationships between tensile properties (moduli, elongation to break, tensile strength, and yield strength) and prior diffusion are given in Figure 25.

Table 10 gives the tensile property data for the films in which HDPE was the substrate material. The values were obtained, as with the PVC films, from films of 35 mm, 25 mm, and 15 mm gauge lengths. Typical stress strain curves for a set of 35 mm gauge length samples are shown in Figure 26.

In general, it may be seen that tensile property values for the various HDPE films were fairly constant in all of the major categories (moduli, elongation to break, tensile strength, and yield strength). Modulus values showed a slight tendency to decrease in the increasingly modified films. Mechanical property values are plotted as a function of diffusion time in Figure 27.

The tensile properties of materials with high glass transitions (e.g. PVC at 85°C) are typically very different from those with values lower than room temperature (e.g. PBMA at 10°C). Glassy materials, such as PVC, generally exhibit low elongation to break values, high moduli, and brittle behavior. Rubbery materials, such as PBMA, exhibit high elongation to break values, low moduli, and ductile behavior. The incorporation of a rubbery material into a glassy substance yields a product with modulus values intermediate between the original components. Composite materials such as these also tend to show improvement over elongation properties of the original substrates.

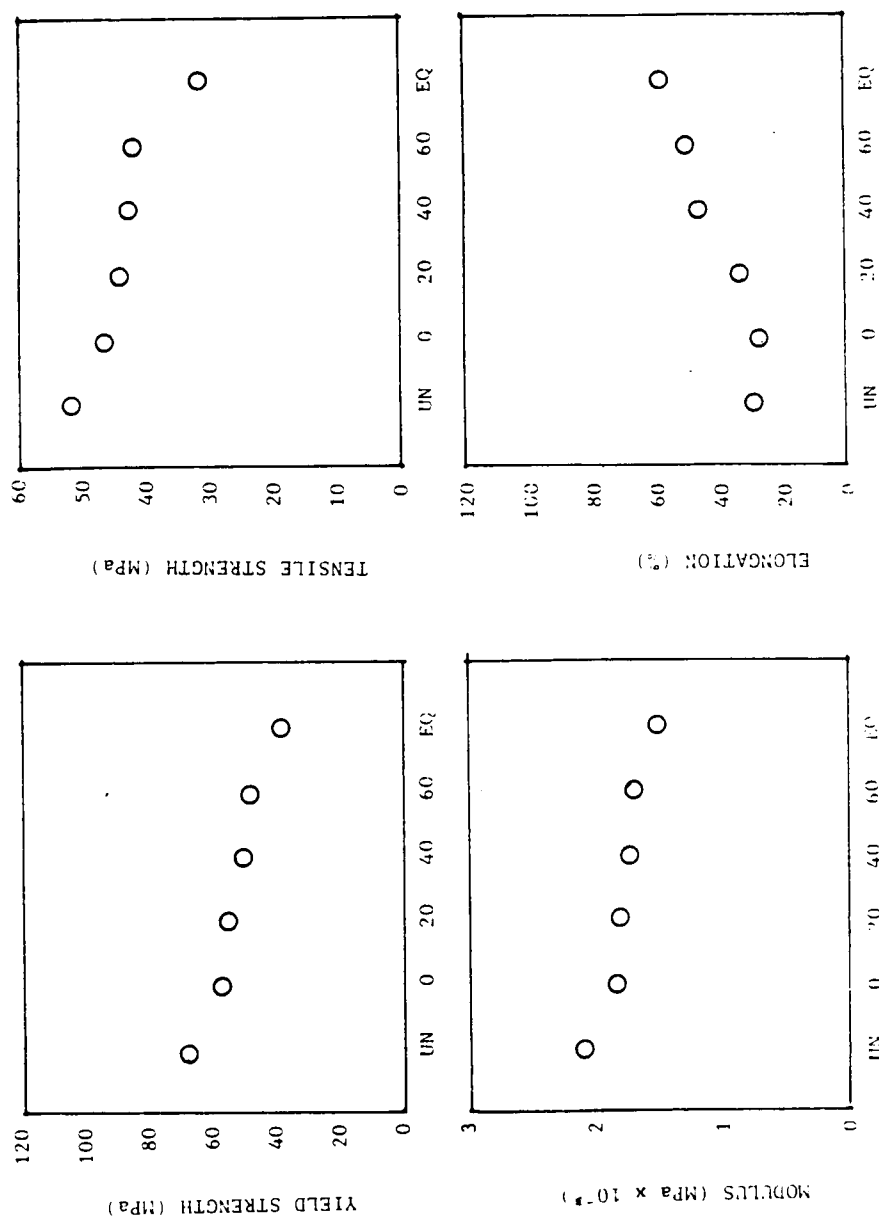


Figure 25. Mechanical properties of PVC films as a function of diffusion time.

TABLE 10
MECHANICAL PROPERTIES OF THE HDPE FILMS

	Thickness (μm)	A ($\text{cm}^2 \times 10^3$)	Yield Strength (MPa)	Tensile Strength (MPa)	Modulus (MPa)	% Elong.
HDPE-UN (35 mm.)	39.9	2.00	26.8	26.5	197	273.1
0	39.6	1.98	26.5	26.5	190	201.7
20	40.9	2.05	26.1	25.4	186	185.7
40	40.6	2.03	26.1	25.9	188	259.1
60	41.1	2.06	25.9	25.5	186	275.4
EQ	41.6	2.08	25.6	25.4	145	321.4
HDPE-UN (25 mm.)	40.1	2.01	27.0	26.8	199	250.0
0	40.1	2.01	26.6	26.4	188	193.6
20	40.4	2.02	25.8	25.3	194	215.6
40	41.4	2.06	25.7	25.5	181	218.0
60	41.4	2.07	25.6	25.4	188	280.4
EQ	41.4	2.07	25.8	25.6	139	275.6
HDPE-UN (15 mm.)	39.6	1.98	26.8	26.3	195	295.3
0	39.4	1.97	26.2	26.0	186	213.3
20	41.4	2.07	26.1	25.7	190	245.3
40	40.4	2.02	26.7	26.2	185	178.0
60	40.9	2.05	26.3	26.1	184	292.0
EQ	42.2	2.11	25.3	25.1	134	302.0

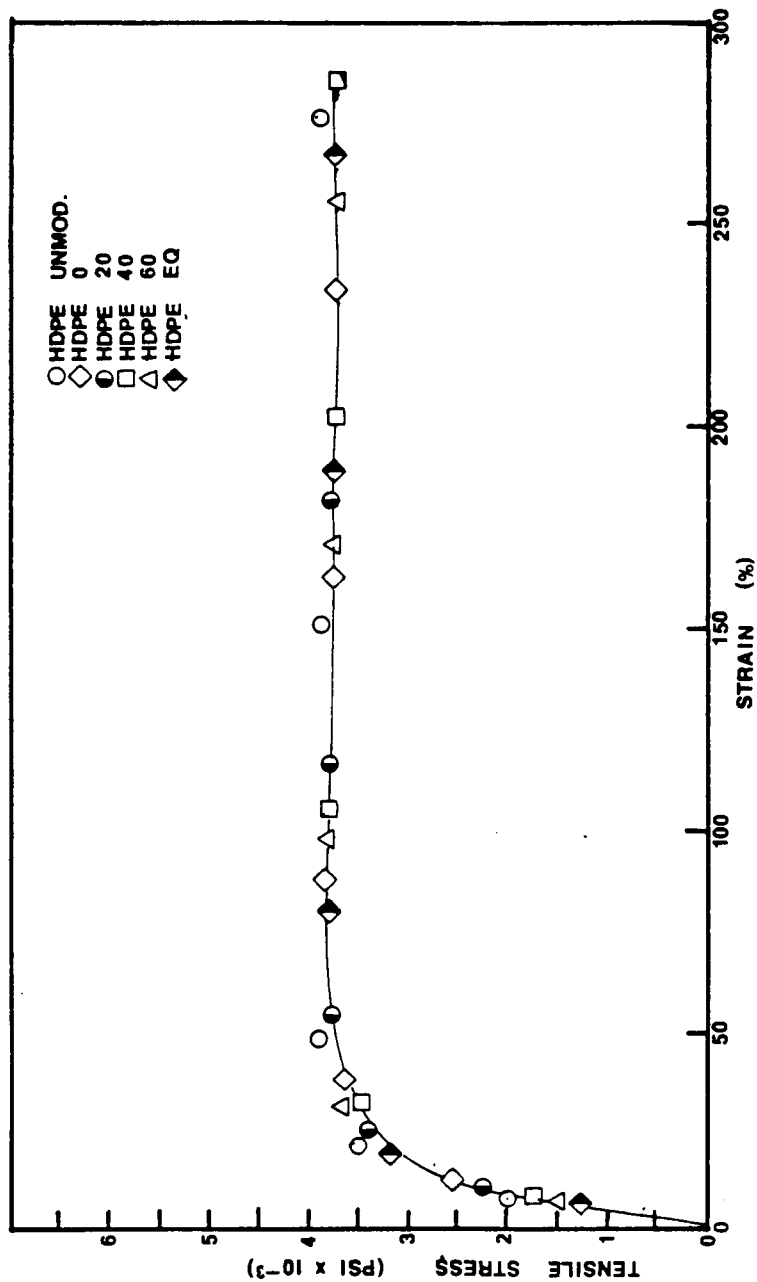


Figure 26. Stress/strain curves for HDPE films (crosshead speed = 500 mm/min).

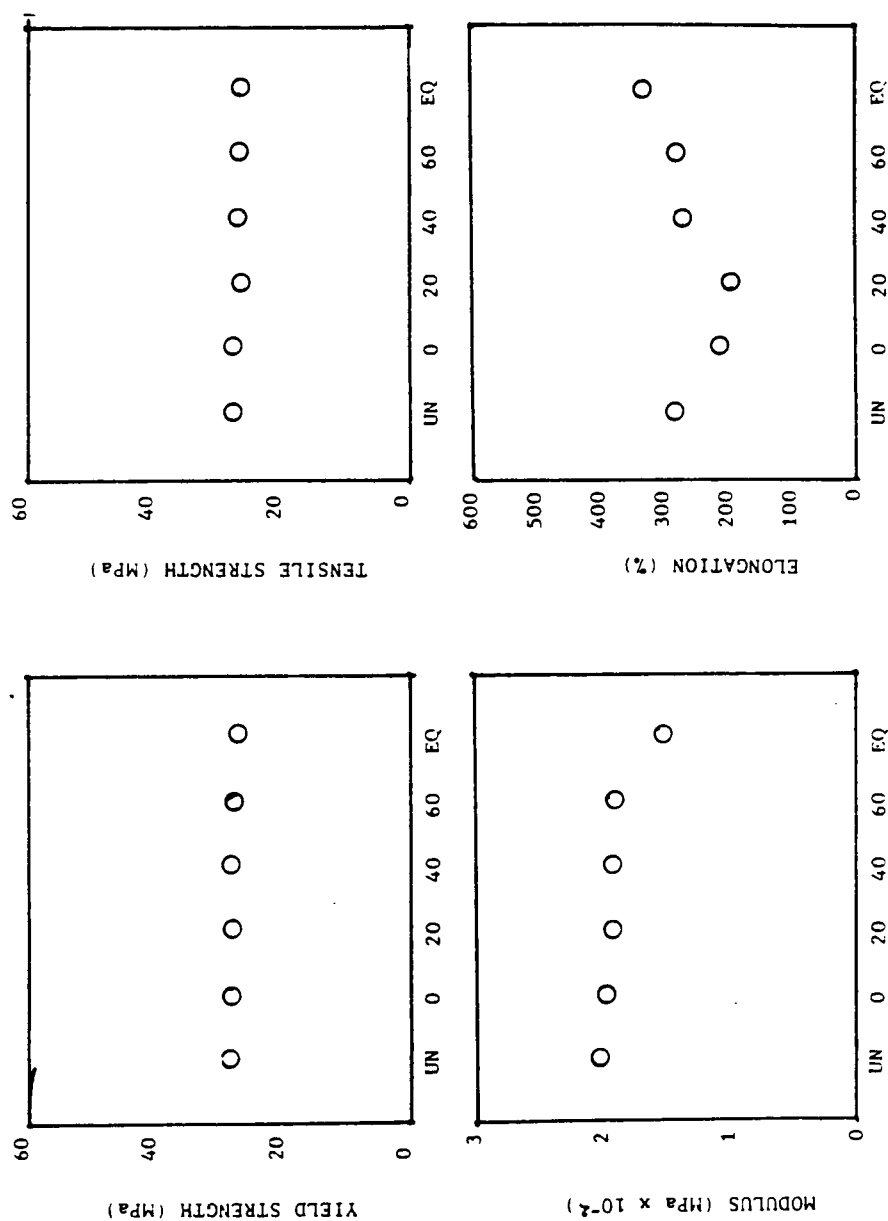


Figure 27. Mechanical properties of HDPE films as a function of diffusion time.

Although PVC may be considered a glassy material, its intrinsic ductility is much greater than most other amorphous polymers with T_g values above room temperature. The elongation properties of PVC have been improved by the incorporation of rubber modifiers, as was shown in the work of Petrich (75). Lower moduli and yield strength values accompanied the higher elongations in the modified PVC samples.

The PVC composite films in our research showed similar mechanical behavior to those previously studied (54,63,72,75). The results suggest that localized yielding has been improved in our samples in the regions of interfacial adhesion between PVC and PBMA. The PVC/PBMA system has been classified as a compatible mixture, and it is therefore impossible to hypothesize about the exact nature of the adhesion between phases. Grafting or homopolymerization could have occurred in our systems with similar mechanical property improvements in either case. Most likely, a combination of the two occurred.

The variations in mechanical properties which were brought about in our PVC/PBMA composite systems were very similar to the changes which were found to exist in the gradient polymers studied by Akovali et al. (1) and Jasso et al. (43). Their studies suggested a stress redistribution among layers of the gradient polymer systems, which was thought to account for the improved toughening mechanisms. Many variables must be considered before drawing a direct connection between previously studied gradient polymers and our composite systems. The substrate materials in our research were not

crosslinked prior to diffusion, as was the case in the previously mentioned studies. Our radiation source was applied at a fairly high dose rate, in contrast to the ultraviolet sources used in previous gradient polymer research. In spite of these differences, it appears that the PVC/PBMA composites which were synthesized in our research have mechanical properties typical of gradient structures. The increasing elongation values suggest that a direct relationship exists between the extent of modification and the ultimate mechanical properties. The PVC/PBMA composite materials which were formed show similar mechanical properties to the laminated structures studied by Alfrey et al. (3). One obvious advantage of gradient systems over layered structures, however, is their low potential for delamination.

It was difficult to interpret the mechanical property results in the case of the various HDPE films. The lack of contrast in mechanical properties might seem to suggest that incorporation of PBMA into the HDPE substrate was limited. Many other factors must be considered before making such an assumption. For example, the high elongation values for the unmodified HDPE films would tend to dwarf any contribution of PBMA to the values of extensibility in the modified films. Infrared spectra of the HDPE films showed that they contained approximately equal quantities of PBMA (or residual BMA monomer) in all of their modified forms. These quantities of PBMA could have affected the mechanical properties of the HDPE films, but the results indicate otherwise. The effects of high energy radiation on polyethylene have been well documented (24,78). Crosslinking

reactions generally result from the exposure of HDPE to high energy radiation. The crosslinked films typically have shown increased elongation properties. These effects were not seen in our studies, indicating that crosslinking may not have been extensive as expected. Cleland et al. (19) have pointed out that radiation doses of 10 to 20 megarads are required for most crosslinking reactions. The fact that our samples were irradiated at levels on the lower fringe of this range could account for this phenomena. Although the number of operating variables make the interpretation of mechanical properties a difficult procedure, the evidence suggests that the formation of a gradient structure in the HDPE samples was not likely.

CHAPTER VI

GENERAL CONCLUSIONS AND RECOMMENDATIONS

The experiments which were performed were designed for the purpose of creating polymeric composites which contained compositional gradients in their structures. Research interests have paid minimal attention to these types of materials relative to the more common forms of composites (blends, solution grafts, etc.). Our study was primarily motivated by a desire to better define the gradient structure.

The experiments which were conducted here would have to be classified as "basic" research. An important fact which was considered involved the number of variables which were in operation during the process of synthesis. Diffusion rates, irradiation effects, and relative compatibilities of components were all important variables in the experimentation. It follows that the interpretation of synthesis-structure-property relationships in these samples was a complex problem. The motivation behind the research, however, was based on the gathering of general information about the relatively obscure gradient polymer systems. It is in this nature that the observations were interpreted.

The PVC/BMA systems exhibited systematic differences in their properties which indicated the potential existence of a gradient structure. The following conclusions can be drawn from the experimental evidence which was gathered;

1. PVC/BMA systems which were studied showed diffusion behavior which was characteristic of Case II diffusion. Case II diffusion behavior has been defined in terms of a sharp, advancing solvent front which permeates a glassy polymer at a constant velocity. The observed linear compositional changes among the PVC composites led to this conclusion.
2. PVC/BMA systems were indistinguishable in terms of their respective phase distributions when viewed through various forms of microscopy.
3. Structural changes which resulted from modification of the PVC substrates significantly affected the mechanical properties of the films. The behavior was found to be similar to the expected behavior of gradient polymer systems.
4. Polymerization of BMA monomer within the PVC substrate was possible by means of electron beam processing. Infrared spectra indicated that PBMA was contained in the irradiated films which had been immersed in monomer.
5. PVC composite films which were formed consisted of component phases characterized by close adhesion. Increased elongation properties pointed toward the possibility of effective redistribution of stress in the samples.

6. Systematically variable concentration gradients were not set up in the HDPE/BMA systems.
7. Polymerization occurred in the HDPE/BMA films, but the extent of their process was not determinable.

Several observations made in this study could be applied to future research in the area of gradient polymers. First of all, it would be more beneficial to study gradient systems in which variables were changed individually and results were compared. Secondly, methods which could establish the exact nature of the phase distribution in gradient materials are needed. Microscopic methods depend upon the contrast of phases in composite systems. It would therefore be beneficial to choose components on the basis of their relative abilities to transmit light.

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LIST OF REFERENCES

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VITA

Edward Maury Bridge was born in DeSoto, Missouri, on January 23, 1955. His parents are Matthew M. Bridge and Elizabeth B. Bridge. He attended public schools in DeSoto and graduated from high school in May, 1973. He attended Maryville College and graduated with a Bachelor of Arts degree in Chemistry in June, 1977.

He taught Chemistry at Bearden High School in Knoxville, Tennessee, from January, 1978, to June, 1981. In September, 1981, he entered the Master's degree program in Polymer Engineering at The University of Tennessee in Knoxville.

In July of 1977 he married Carol Anne Paris of Owensboro, Kentucky.