Gradients in polymeric materials

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In this paper we consider the structure and properties of polymeric materials possessing spatial gradients as well as potential applications of such materials. These gradients may be generated by varying the chemical nature of the monomers, the molecular constitution of the polymers and the supramolecular structure or morphology of the polymers. Gradients in each of these categories are possible for single-phase as well as heterophase systems. Such gradients are associated with gradients in properties.

The properties considered are chemical, mechanical, biomedical and transport properties. Structural gradients in the polymeric system may lead to a desired gradient in a single property, or to a combination of more than one property which may assume optimum values in different regions of the material. In the latter case, one of the properties is frequently related to mechanical integrity.

Possible applications of gradient polymeric systems include platic gasoline tanks, biomedical implants, and damping materials for a wide frequency range.

1. Introduction

The structure and properties of polymeric materials can be varied over wide ranges. Most of the pertinent efforts in this regard have been devoted to homogeneous and in some measure to laminated polymeric systems. Little attention has been directed toward gradient systems, that is, systems in which structure and properties vary continuously in space.

Gradient materials in general are beginning to attract some attention. Bever and Duwez [1] have considered gradients in composite materials. Ferry [2] has analysed some aspects of gradients in the crosslinking and swelling of polymers.

In this paper we shall systematically discuss possible gradients in polymeric materials. We shall be concerned primarily with the structure and properties of these materials rather than the techniques for their preparation. We shall mention various illustrative examples but shall not attempt to explore exhaustively the entire range of possible applications.

2. Structure

We shall consider the structural features of polymers on three levels of resolution: (i) the chemical nature of the monomers; (ii) the molecular constitution of the polymers; and (iii) the supramolecular structure or morphology of the polymers. In each of these categories the possibility of gradients in space exists. We shall discuss these gradients first for single-phase systems and then for heterophase systems.

2.1. Single-phase systems

The nature of a polymer depends first of all on the constituent monomers. For instance, at room temperature the polymer of methyl methacrylate (commonly known as "Plexiglas") is a tough, hard plastic [3]. Its Young's modulus is about 10^{10} dyn/cm^2. By contrast, the polymer of methyl acrylate is a soft rubber with a modulus of approximately 10^7 dyn/cm^2, depending on the degree of crosslinking. These two monomers can be combined to form random copolymers of any composition ranging from pure poly(methyl methacrylate) to pure poly(methyl acrylate). A gradient polymer with a spatial variation in composition can therefore be prepared. Polymer chemistry offers many possibilities for creating

similar compositional gradients by copolymerization and other techniques [4, 5].

The degree of crosslinking is an important variable in many polymers. For example, natural rubber crosslinked with 1% sulphur is soft and highly extensible. Incorporation of 30% sulphur into natural rubber yields a hard plastic known as "Ebonite" [6]. Up to a moderately high degree of crosslinking, the statistical theory of rubber elasticity predicts [3]:

$$G = 2NRT \qquad (1)$$

where G is the shear modulus, N the number of tetrafunctional crosslinks in mol/cm³, R the ideal gas constant and T the absolute temperature. Various techniques are available for controlling the degree of crosslinking, such as irradiation [7] and the use of chemical crosslinking agents [8]. These techniques can be adapted to producing gradients in the degree of crosslinking. Some of these techniques have been considered by Ferry [2] for gradient structures in hydrophilic polymers.

Differences in the degree of crosslinking are also associated with differences in the degree of equilibrium swelling ϕ (i.e. the amount of solvent imbibed in the polymer network). The degree of equilibrium swelling can also be controlled by changing the chemical nature of the monomers. For example, pure poly-(hydroxyethyl methacrylate) can absorb an appreciable amount of water. The addition of a moderate amount of a nonhydrophilic monomer, such as methyl methacrylate, to form a copolymer with hydroxyethyl methacrylate substantially reduces the degree of swelling due to the absorption of water [9]. These two factors are governed by the following equation [6]:

$$Gv(\phi - \phi^{1/3}) = RT[\ln(1 - \phi) + \phi + x\phi^2] \\ \cdots \cdots (2)$$

where v is the molar volume of the solvent and x is the polymer-solvent interaction parameter. In general, the shear modulus of a polymer decreases with increasing degree of swelling.

The average molecular weight and the molecular weight distribution are other variables affecting single-phase polymers. Since these variables can in principle be manipulated (e.g. by high-shear flow) [10], corresponding gradient structures may be achieved.

Oriented polymers possess certain unique features which distinguish them from unoriented ones. For instance, biaxially stretched poly-

carbonates offer superior resistance to crazing and uniaxially stretched nylon has improved yield resistance [11]. Gradients in the degree and the direction of the orientation are of obvious interest.

Recent electron microscopic evidence suggests the possibility of the existence of supramolecular structures in single-phase, non-crystalline polymers [12, 13]. The morphology associated with such structures merits further investigation. Their effects would probably be similar to those of the supramolecular structures encountered in heterophase polymers.

2.2. Heterophase systems

The gradients discussed in Section 2.1 for single-phase systems can also occur in heterophase systems. Other gradients are uniquely characteristic of heterophase systems; they will be discussed in this section.

2.2.1. Crystallinity

Crystalline polymers are heterophase because total crystallinity can almost never be achieved, at least not in the bulk state. An amorphous fraction which is always present constitutes a second phase [6]. The ratio of crystalline to noncrystalline material, however, can be varied. The degree of crystallinity may be changed by several methods. For a given material, this is possible by changing the rate of cooling from the molten state or by annealing of the solid polymer.

The ability of a polymer to crystallize is also determined by the regularity of its chain structure. An isotactic polystyrene, for example, being more regular in structure is semicrystalline, whereas atactic polystyrene is always amorphous because of the greater randomness of its structure. The degree of crystallinity is therefore affected by the degree of tacticity. Similar effects can also be achieved by adjusting the relative ratio of cis and trans isomers of a block polymer. For instance, trans-polyisoprene is crystalline, while cis-polyisoprene, i.e. natural rubber, is amorphous.

A third method of affecting the crystallinity of a polymer is copolymerization. Polytetrafluoroethylene or "Teflon" is a highly crystalline polymer. The addition of an appropriate amount of perfluoropropylene as a random comonomer reduces the degree of crystallinity. In fact, a composition of 30% perfluoropropylene and 70% tetrafluoroethylene yields an excellent high-temperature-resistant rubber, known as Teflon

FEP, in contradistinction to Teflon, which is a hard plastic.

It is evident that each of the three methods of changing the degree of crystallinity described in the foregoing may be utilized in such a manner as to produce a gradient in the crystallinity of a polymer. Other aspects of crystallinity, such as the orientation [14] and size [15] of the spherulites, may also be varied. Their effects, however, are in general less marked than those of the degree of crystallinity.
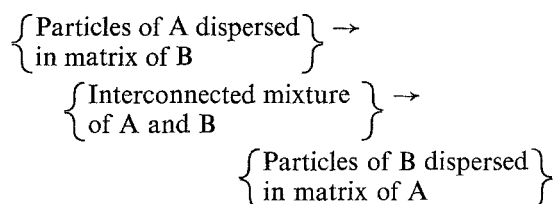
2.2.2. Polymer mixtures

Another important class of heterophase polymers can be prepared by mixing different polymers ("polyalloying"). Most polymers are insoluble in each other and thus show microphase separation. Most polymer mixtures, therefore, are heterophase. Three principal methods of mixing are available. The first consists of milling or solvent-casting of two or more polymers, which produces the so-called "polyblends", the second is the synthesis of block copolymers and the third the synthesis of graft copolymers. The preparation of polyblends by mixing is the simplest and most flexible method. The structures of block and graft copolymers are on a finer scale than those of the polyblends.

The morphology of heterophase mixtures results from the amount and configuration of the constituent phases [16, 17]. In one possible case, one phase is continuous, i.e. the matrix, and the particles of the other are dispersed in it. The variables are the amount of the dispersed phase and the sizes and shapes of the particles of this phase; for example, they may be spheres, rods or platelets. In another case, each of the two phases is interconnected with itself and the two phases are interpenetrating. In the third case, alternating layers of the two phases occur.

In polymers some of these different configurations can be generated by varying the relative amounts of the components or by the method of preparation. An example of the latter is the preparation of a polystyrene-continuous matrix of a styrene-butadiene-styrene block copolymer by casting from its solution in tetrahydrofuran/methyl ethyl ketone, whereas a poly-butadiene-continuous matrix of the same block copolymer results if it is cast from a solution of benzene/heptane [18].

Typical gradients of the morphological features of heterophase systems may involve the amount, the particle size and the particle shape of the dispersed phase. Examples of geometrical possibilities, applied on the scale of composite materials, have been discussed by Bever and Duwez [1]. In the case of heterophase polymers a gradient may be carried to the point where an inversion occurs according to the following scheme:

$$\left\{ \begin{array}{l} \text{Particles of A dispersed} \\ \text{in matrix of B} \end{array} \right\} \rightarrow$$

$$\left\{ \begin{array}{l} \text{Interconnected mixture} \\ \text{of A and B} \end{array} \right\} \rightarrow$$

$$\left\{ \begin{array}{l} \text{Particles of B dispersed} \\ \text{in matrix of A} \end{array} \right\}$$

2.3. Gradients involving nonpolymeric components

Reinforcing fillers, usually nonpolymeric in nature, cause marked changes in the properties of polymers, e.g. glass fibres in plastics ("fibre glass"). Another example is the use of carbon black in natural rubber. The good bonding between carbon black and rubber suggests that glassy carbon can perhaps also be combined with a polymeric phase [19, 20]. The use of a concentration gradient of such fillers in polymers is an obvious possibility. A porosity gradient can be introduced into a polymer. For example, a foaming agent may be suitably incorporated to bring about this effect [20].

Another possible development is the joining of a polymer with an inorganic material [21], such as a metal or a ceramic, through a gradient. One type of such a joint requires a porosity gradient at the surface of the inorganic material and the impregnation of the pores by the polymer.

The doping of a polymer, such as the doping of poly(vinyl carbazole) with iodine, changes the material from an insulator to a semiconductor [22]. The use of a concentration gradient of the doping agent constitutes a possible development.

3. Properties and applications

The properties which make gradient-polymers of interest are chemical, mechanical, biomedical and transport properties. In each of these categories, a variation in space of a given property can be achieved by a suitable gradient in the polymeric system. In addition, more than one property may be varied to satisfy multiple requirements of a potential application. Thus the coupling of several optimal properties is possible under certain conditions. In the follow-

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ing we shall consider the aforementioned classes of properties and suggest potential applications.

3.1 Chemical properties

Certain chemical properties of polymers are intimately related to the nature of the constituent monomers. For example, many polymers are hydrophobic. Hydrophilicity may be introduced by copolymerizing such hydrophobic monomers with hydrophilic monomers. One example is the copolymerization of the hydrophobic monomer of styrene with the hydrophilic monomer of styrene sulphonic acid. A gradient of hydrophilicity will result from continuously varying the ratio of these two monomers.

A possible application for materials of this type is the construction of gasoline tanks for aircraft or automobiles. A hydrophilic interior layer will prevent the gasoline from swelling the material, while a hydrophobic exterior layer will be inert to water in the environment. The strength may be increased by blending the material with polyacrylonitrile and polybutadiene, like ABS resins. The use of a gradient in this case would be advantageous for maintaining structural integrity.

Other chemical properties that may be imparted to one surface layer of a gradient polymer may be increased resistance to oxidation, weathering, high-temperature degradation and irradiation. Resistance to specific chemical attack, such as by strong acids, may similarly be achieved.

3.2. Mechanical properties

In general, rubbery polymers are characterized by a high elastic limit, low elastic moduli, low fracture stress, large fracture strain and high impact resistance. By contrast, glassy polymers have a low elastic limit, high elastic moduli, high fracture stress, small fracture strain and low impact resistance [3, 23]. The values of these properties of crystalline polymers approximate those of the glassy polymers. Most of the properties of one of these three classes can be modified by the addition of a material from another class. These modifications cn be achieved by methods such as solvent-swelling, degree of crosslinking, copolymerization, filler addition and blending. All of these methods have been shown in previous sections to be capable of producing gradients in composition and structure: corresponding gradients in mechanical properties can thus be achieved.

For the mechanical properties of some of the materials, geometrical configurations play an especially important role. A good illustration of this is the case of mixtures of polystyrene and polybutadiene in nearly equal proportions [18, 24]. If polystyrene is the continuous phase and polybutadiene the dispersed phase, the composite is relatively rigid. If the same volume of polystyrene is present as dispersed particles in a matrix of polybutadiene the material is rubbery. A transition between these two types of configuration requires the coexistence of domains of both types, thus leading to a gradient in structure and properties.

Applications requiring a gradient in strength properties of polymeric materials can readily be envisioned. For example, if a relatively weak material is to be fastened to a structure, the region in which the fastener is to be applied should have a higher strength. This can be achieved by a suitable gradient material. Another example is the provision of a surface layer that is resistant to indentation and abrasion. The case of a soft surface layer on a hard substrate, which is of special interest for biomedical applications, will be mentioned in Section 3.3.

The damping capacity of polymers, due to their viscoelastic nature, is highly frequency dependent at a given temperature [3, 25]. The usefulness of a polymer as a damping material, therefore, is confined to a limited frequency range. This range may be extended by using graded materials (prepared, for instance, by copolymerization) each of which has a damping maximum at a different frequency. The gradient in this application must not be steep in order to achieve maximum effectiveness.

3.3. Biomedical properties

Two essential requirements for biomaterials are compatibility with blood and tissues and inertness to body fluids. Both of these are surface properties, and hence can be achieved by the use of suitable gradient polymers. Silicone rubber, for instance, is a versatile biomaterial [26]. However, its lack of rigidity limits its range of applicability. By combining silicone rubber with a rigid base material in a continuous gradient, this limitation may be overcome. Ferry [2] has analysed mechanisms of achieving the same effect in hydrophilic polymers.

Glassy carbon is known to possess good biomedical properties [27]. The possibility of forming a gradient material consisting of such

polymers has been mentioned in Section 2.3. Such a material would be of obvious interest for some biomedical applications.

3.4. Transport properties

The transport properties to be considered are the electrical conductivity, heat conductivity, and mass diffusivity. Each type of these transport properties depends on the characteristics of the polymeric system.

Generally polymers are good electrical insulators. However, by special modification some of them may be made into semiconductors. The example of iodine-doped poly(vinyl carbazole) was mentioned in Section 2.3. On the other hand, as insulators polymers vary in their dielectric strength [28]. Polymeric systems with spatially varying conductivities or dielectric strengths can be obtained by suitable gradients.

Since polymers are poor heat conductors, they are used as thermal insulating materials. They are particularly effective in the form of foams [20], e.g. "Styrofoam". A problem encountered in the use of polymeric foam as a thermal insulator for cryogenic fuel tanks in rockets has been delamination due to thermal shock. This difficulty can probably be overcome by the use of a gradient material, which combines in a continuous manner across its thickness mechanical strength and the insulating capacity due to porosity.

Many polymers permit the diffusion of liquids and gases of low molecular weight. In applications in which permeability is undesirable, such a polymer may be made impermeable by the introduction of an impermeable surface layer. The layer may confer greater mechanical strength by a gradient structure with the bulk. On the other hand, selective permeability for some substances may be useful. Examples are polymeric membranes used for sea-water desalination or haemodialysis [29]. In such instances a gradient structure may impart superior mechanical strength and rigidity without risk of delamination.

3.5. Combination of properties

In Sections 3.1 to 3.4, we have been primarily concerned with the spatial variations of a single property. However, several applications considered involve the combination of more than one property. An example of this, which was mentioned in the preceding section, is the use of polymeric foam with variable porosity as a

thermal insulator in which effects of both a thermal and a mechanical property gradient are operative. Applications requiring combinations of mechanical properties with any of the other properties can certainly be envisioned.

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