อินเทอร์เพนิเทรทิง พอลิเมอร์ เนตเวิร์ค

Interpenetrating polymer networks

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บทคัดย่อ

อินเทอร์เพนิเทรทิง พอลิเมอร์ เนตเวิร์ค เป็นพอลิเมอร์ผสมลักษณะพิเศษ โดยที่อย่างน้อยหนึ่งในพอลิเมอร์ที่นำมาผสมกันต้องถูกสังเคราะห์ และ/หรือ ถูกทำให้เกิดโครงสร้างแบบร่างแหในขณะที่มีพอลิเมอร์อีกชนิดหนึ่งอยู่ร่วมในระบบ เทคนิคการเตรียมพอลิเมอร์ผสมนี้เป็นแนวทางหนึ่ง ที่สามารถแก้ปัญหาเกี่ยวกับลักษณะการไม่ผสมเข้ากันของพอลิเมอร์ โดยที่การเกิดโครงสร้างแบบร่างแห และการเกี่ยวพันกันของสายโซ่โมเลกุลสามารถลดระดับของการแยกวัฏภาคระหว่างคู่พอลิเมอร์ที่นำมาผสมกันได้ พอลิเมอร์ผสมที่เตรียมโดยเทคนิคนี้แสดงสมบัติการผสมเข้ากันได้ดี และการแยกวัฏภาคเกิดขึ้นในระดับสเกลเล็กซึ่งสามารถควบคุมได้ โดยวิธีการและสภาวะของการเกิดพอลิเมอร์ อินเทอร์เพนิเทรทิง พอลิเมอร์ เนตเวิร์คได้รับความสนใจเป็นอย่างมากในช่วง 20 ปีที่ผ่านมา เนื่องจากคู่พอลิเมอร์ที่ถูกนำมาศึกษามีสมบัติทางกายภาพและทางเคมีต่างๆ กัน การปรับเปลี่ยนอัตราส่วนของคู่พอลิเมอร์ และปัจจัยอื่นๆ ทำให้สามารถเตรียมอินเทอร์เพนิเทรทิง พอลิเมอร์ เนตเวิร์คที่มีสมบัติหลากหลายตั้งแต่อิลาสโตเมอร์ที่มีความแข็งแรงเป็นพิเศษ จนกระทั่งถึงพลาสติกที่ทนต่อแรงกระแทกได้

Abstract

Interpenetrating polymer networks (IPNs) are a unique type of polymer blend. They are defined as a combination of polymers in network form, at least one of which is synthesized and/or crosslinked in the presence of each other. IPN represents an innovative approach to solving the problem of polymer incompatibility. The crosslinked network and entanglement of the chains mean that gross phase separation is unlikely to occur. The polymer components remain intimately mixed, and the extent of micro-phase separation can be controlled by the method and condition of polymerization. IPNs have been among the fastest growing areas in the filed of blends during the past twenty years. The physical and chemical nature of the constituent networks, their relative proportion in the IPNs, and so on, control the ultimate performance of the resulting IPNs. The combination of two constituent polymers in an interpenetrating network results in a broad range of properties, from toughened elastomers to high-impact plastics.

Keywords : Interpenetrating, Polymer Networks

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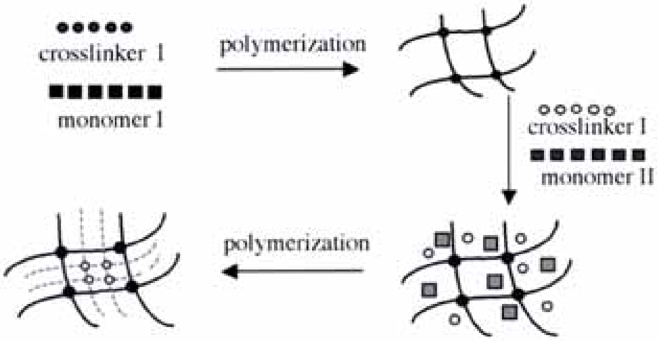
1. Introduction

An interpenetrating polymer network (IPN) is a special type of polymer blend containing networks of two or more polymers, at least one polymer being polymerized and/or crosslinked in the presence of the other (Sperling, 1994). The original concept of interpenetrating polymer networks was adopted because, in the limiting case of high miscibility between crosslinked polymers I and II, the networks can be visualized as containing extensive molecular interpenetration on a molecular scale and throughout the entire macroscopic sample (Manson and Sperling, 1976). In practice, most IPNs consist of chemically distinct polymers. As a result, incompatibility and some degree of phase separation usually occurs. On the other hand, the crosslinked network and entanglement of the chains mean that gross phase separation is unlikely to occur. The two components remain intimately mixed, and the extent of microphase separation can be controlled by the method of polymerization which leads to different types of IPNs (Paul and Newman, 1981).

(a) Sequential Interpenetrating Polymer Network



(b) Simultaneous Interpenetrating Network

Figure 1 A schematic of two basic polymerization methods of IPNs : (a) Sequential IPN, (b) Simultaneous interpenetrating polymer network (SIN) (Sperling, 1981).

2. Types of IPNs and Syntheses.

Several different types of IPNs have been synthesized and investigated. A classification of the important IPNs are as follows (Sperling, 1994; Satgurunathan, 1987; Sperling, 1981):

- ***Sequential IPNs.*** In this case, polymer network I is made first. Monomer II, plus cross-linking agent and initiator, are swollen into network I and polymerized in situ, see Figure 1(a).
- ***Simultaneous IPNs.*** *(SIN).* Monomer I and II, and/or prepolymers plus their cross-linking agents, and initiators are introduced simultaneously and polymerized by non-interfering reactions. Interference is minimized if monomer I reacts by radical chain polymerization, while the other reacts by step polymerization reaction, see Figure 1(b).
- ***Latex IPNs.*** In this system, two networks are made in the form of latexes by a two-stage emulsion polymerization. An emulsion of a crosslinked polymer I is first formed. Then, monomer II, initiator, and cross-linking agent are added and polymerized.
- ***Gradient IPNs.*** This IPN type is deliberately made so that the overall composition varies from location to location on the macroscopic level. For example, a film can be made with network I predominantly on one surface, network II on the other surface, and a gradient in composition throughout the interior. This can be achieved by swelling polymer network I in monomer mix II and polymerizing before homogeneity is achieved by diffusion.

- ***Thermoplastic IPNs.*** An IPN of two linear polymers in which the chemical crosslinks have been replaced by physical crosslinks. Because of this, this material softens and flows at elevated temperature, but behaves as a thermoset at temperature of use.
- ***Semi-IPNs.*** IPNs in which one or more polymers are crosslinked and one or more polymers are linear or branched.

3. Morphology of IPNs

3.1 Morphology and Phase Separation.

Most IPNs and other multicomponent polymer systems investigated to date exhibit phase separation. As monomers polymerize, miscibility decreases, resulting in phase separation. However, since crosslink reduces phase separation, and in particular reduces domain size, it often results in finely dispersed phase *domains of 10-100 nm* (Sangermano *et al.*, 2006). The phases vary in domain size and shape, interfacial bonding and degree of continuity. These features constitute the morphology, and the morphological detail strongly influences, in turn, the physical and mechanical behavior. For instance, an incompatible polymer pair exhibits two glass transitions, one for each polymer. When micro-heterogeneous phase domains are between 10-20 nm, the whole material is essentially interphase. Consequently, the glass transition tends to be very broad, covering the range between those of the two component polymers. After a certain degree of miscibility is reached, only one transition is observed (Song, 2001).

3.2 Factors Influencing IPN Morphology

The morphology of an IPN is its predominant feature. Because of their dual crosslinked nature, both constituent networks influence the morphology. There are many factors that control the morphology of IPNs. The major ones include immiscibility and miscibility of the polymers, crosslink densities of the two networks, polymerization method and condition, and also the IPN composition ratio (Sperling, 1994; Manson and Sperling, 1976; Sperling, 1981). While these factors may be interrelated, they can often be varied independently.

3.2.1 Immiscible and Miscible of Polymers.

Mixing of polymers is not as straightforward or predictable as the mixing of low molecular liquids. Nearly all two-polymer compositions when blended do not mix, but form separate phases or domains within the mixture. Such blends are defined as immiscible. In the vast majority of cases cited in literature (Yu *et al.*, 2006; Hernandez *et al.*, 2005; Culin *et al.*, 2005; Sperling, 1997; Kaplan, 1976) miscibility is defined in terms of the behaviour of a macroscopic property, usually single glass transition temperature. Miscibility, therefore, implies a level of homogeneity within the mixture, such that any separate domains present are smaller than the segmental size responsible for the glass transition. In a pragmatic sense, miscibility occurs when the system appears to be homogeneous in the type of test applied in the study [Utracki, 1990]. In thermodynamic terms, the basic criterion for the miscibility of two polymers is that the Gibbs free energy of mixing, ΔG_m, is negative, as determined by the following equation.

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔG_m is the enthalpy of mixing, T is the absolute temperature in K, and ΔS_m is the entropy of mixing. Since the entropy change on mixing two polymers is small or negligible, miscibility is usually only presented if the enthalpy of mixing is negative, which can be achieved in some cases involving specific intermolecular interactions, such as hydrogen bonding.

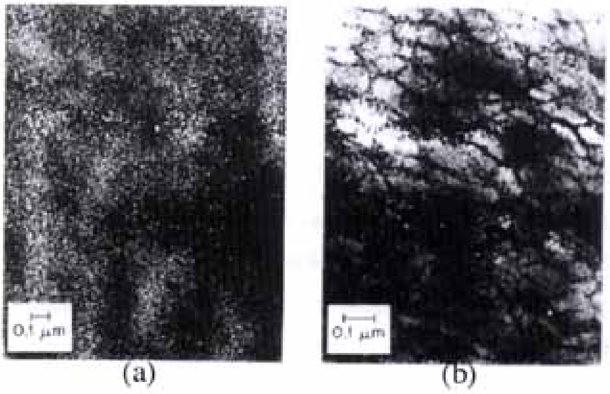
The morphology of IPNs can vary from a microphasic separation to a macrophase morphology. The more miscible the polymer system, the smaller the phase domains it exhibits (Tang, 2003; Lu and Zhang, 2002; Rosu *et al.*, 2001). Degree of miscibility is an important factor that controls the morphology, because solution of monomers, or swelling of networks during polymerization is needed. Phase separation generally proceeds in the course of polymerization, but the resulting phase domain size is smaller for higher miscibility systems. Many polymer pairs are classified as being either immiscible or miscible. To be considered miscible, a polymer pair usually must exhibit a range of compositions and temperatures where total miscibility occurs. Otherwise, the polymer pair is considered immiscible.

Two systems of poly(ethyl acrylate) (PEA)-based sequential IPNs differing in miscibility have been investigated (Huelck *et al.*, 1972). The effect of monomer miscibility on IPN morphology was examined by scanning electron microscopy (SEM). First, the system of PEA/PS IPN was prepared. The resulting IPN exhibited clearly incompatible morphology. When styrene monomers in the IPN were replaced by methyl methacrylate monomer (MMA), the coarse cellular structure became progressively smaller in size and less distinct, Figure 2. As MMA completely replaced styrene monomer, fine and more interpenetrating structures were found containing dispersed phase domains less than 10 nm in size. This can be considered as a result of high miscibility, since PEA and PMMA are chemically isomeric, having structures shown as follow. As miscibility is increased, initial phase separation will take place later during the polymerization of the second component. As a result greater mixing of the two networks occurs, and, so more interpenetrating on a molecular scale exists in final product.

Anzlovar and Zigon (2005) investigated a study on the morphology and mechanical properties of polyurethane/polymethacrylate (PUR/PM) semi-IPNs with and without complementary functional groups based on ester-urethane prepolymers with carboxylic groups and methacrylic prepolymers with tertiary amine functional groups. SEM micrographs and shifts in Tg showed the enhancement of miscibility in IPNs with high concentration of functional groups. The 50PUR/50PM IPNs having 0.45 mmol of functional groups/g of polymer showed exceptional enhancement of miscibility due to an intense interaction between complementary functional groups. Interaction between functional groups also stabilized the PUR and PM prepolymer mixture at elevated temperature and thus prevented the separation of components.

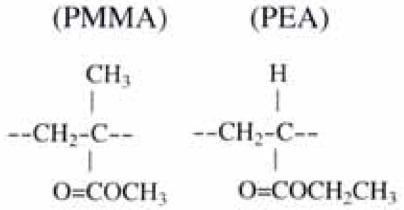
3.2.2 Level of Crosslink Density

This factor is also important in determining the network morphology, since it is the presence of crosslink that limits the degree of phase separation in IPNs compared to other multicomponent polymer systems.



(a) (b)

Figure 2 Electron micrographs of IPNs of (a) 75PEA/25PMMA, and (b) 50PEA/50PS (Huelck *et al.*, 1972).



(PMMA) (PEA)

$$--CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O{=}COCH_3}{\overset{|}{\underset{|}{C}}}}-- \qquad --CH_2-\overset{\displaystyle H}{\underset{\displaystyle O{=}COCH_2CH_3}{\overset{|}{\underset{|}{C}}}}--$$

The effect of polystyrene (PS) crosslink density in polyisobutene/PS IPNs was investigated by Vancaeyzeele and his co-workers (2006). They reported that the IPNs showed phase separation. However the extent of phase separation might be reduced if the crosslink density of at least one of both networks was increased. The miscibility of poly(methyl acrylate)/ poly(methyl methacrylate), (PMA/PMMA), sequential IPNs as a function of the crosslink density was studied by Sanchez *et al.* (2001). The PMA/PMMA system was immiscible and so, for low crosslink densities, phase separation appeared. If crosslink density was high enough, a homogeneous IPN could be obtained, achieving forced compatibilization of both networks. Distinct phase separation with a cellular domain structure was found in the study of styrene-butadiene rubber/polystyrene (SBR/PS) IPNs (Donatelli *et al.*, 1977). The crosslink level of both networks was altered in order to study the influence of the degree of crosslink density on the morphology. Electron micrographs of IPNs showed smaller network II (PS) domain sizes, as the crosslink density in polymer network I (SBR) was increased. On the other hand, the variation of crosslink density in the PS network had little effect on the IPN morphology, indicating that the first network exerted the major control of morphology.

3.2.3 Polymerization Method and Condition

In sequential IPNs, the network formed first appears to have the greater degree of continuity, even though it may be the minor component by weight. When the polymers are reversed in sequence, the new morphology is again controlled principally by the first network (Manson and Sperling, 1976). For simultaneous IPNs, the networks form during the same time period, although not necessarily at the same rate, and more complex morphology results (Paul and Newman, 1987).

A number of studies have been conducted in order to compare IPN morphologies prepared from the simultaneous with the sequential techniques. Fox *et al.* (1985) used PUR and poly(n-butyl acrylate-co-n-butyl methacrylate) as the constituent polymers in the study of the influence of sequential and simultaneous polymerization on IPN morphology. They found some evidence that indicated greater phase separation in the simultaneous IPNs. However, a contrasting result has been reported. Akay *et al.* (1993) prepared a variety of simultaneous and sequential IPNs based on PUR and PMMA. SEM micrographs confirmed that IPNs synthesized by the simultaneous process appeared to be more homogeneous than the ones prepared by sequential process. Synthesis conditions were also reported to have a significant effect on morphology and properties of IPNs. Hourston *et al.* (1992) investigated the PUR/poly(methyl acrylate) (PMA) IPNs system of a fixed composition (50/50 weight ratio) prepared at 200 MPa under a range of temperatures. All the dynamic mechanical analysis results indicated improved mixing as the synthesis temperature decreased. The IPN synthesized at 120 °C showed the most phase-separated structure, with very poor tensile strength. This was probably a consequence of thermal damage to the PUR network. At high temperature, the exothermic heat of polymerization of methyl acrylate could lead to excessive temperature rise, capable of degrading the already formed PUR network.

3.2.4 IPN Composition Ratio.

The composition ratio of each polymer exerts significant effects on IPN properties. Any given property of an IPN is the function of the properties of the constituent polymers and of the interactions between them. The combination of a glassy polymer with another which is rubbery can produce IPNs possessing a range of properties depending upon the composition ratio and which component forms the continuous matrix. IPNs, therefore, may be produced to exhibit a range of properties.

The morphologies of polyisobutylene/polystyrene (PIB/PS) IPNs were studied for different weight proportions (Vacaeyzeele *et al.*, 2006). AFM

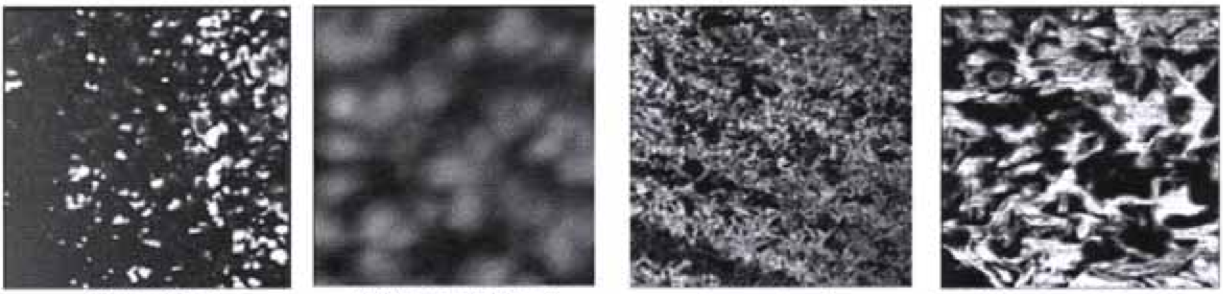
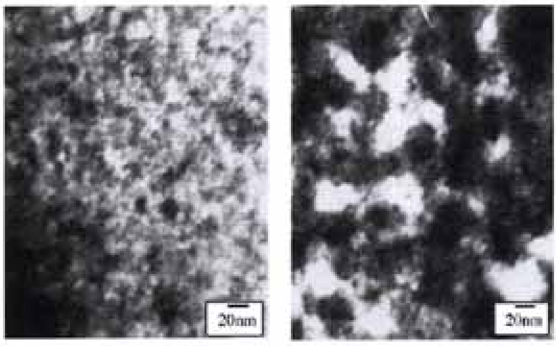

(2µm x 2µm) (500 nm x 500 nm) (2µm x 2µm) (500 nm x 500 nm)

Figure 3 AFM images of (a) 60PIB/40PS IPN and (b) 20PIB/80PS IPN - enriched PS phase in white and enriched PIB phase in dark (Vancaeyzeele *et al.*, 2006).

microscopy showed that the material morphology mainly depended on the weight proportion of each component (Figure 3). When the PIB network was the main component, it formed the matrix in which were dispersed PS rich domains. The resulting material had reinforced elastomeric properties. PIB and PS phase co-continuity was observed when the IPN was mainly composed of PS. The material was rigid. The mechanical properties and the UV aging resistance of the IPNs were tremendously improved by the introduction of a PS network in the IPN architecture.

Qin *et al.* (2004) examined a series of PUR/vinyl ester resin (VER) simultaneous IPNs synthesized with butyl methacrylate (BMA) as VER's comonomer. The effect of IPN component ratio on the morphology was investigated by TEM (Figure 4). They reported that the IPNs were heterogeneous with phase domain sizes ranging from less than 20 nm to 500 nm. The images provided direct evidence that the compatibility of IPNs was improved by introducing BMA into the VER component and the 60PUR/40VER(BMA) IPN showed greatest degree of interpenetration.



(a) (b)

Figure 4 TEM images of (a) 60PUR/40VER(BMA) IPN and (b) 70PUR/30VER(BMA) IPN.

Semi-IPNs of PUR/PMMA, in different weight ratio were prepared by Kumar and his research team [2006]. Surface morphology measured using SEM showed the two-phase morphologies with uniform distribution of second phase for all the IPNs. The 60PUR/40PMMA sample showed bi-continuous phase structure and hence better entanglement. As the percentage of PMMA further increased, the bi-continuous phase morphology led to the beginning of phase inversion. Similar results were found in the studies of IPNs based on the same polymer components (Cascaval *et al.*, 2002; Athawale and Kolekar, 2000).

4. Behavior of IPNs

4.1 General Properties

Three main parameters that are crucial in determining the properties of IPNs are generally considered as follow: i) the properties of the constituent polymers, ii) the phase morphology, and iii) interaction between the phases. As for other multi-component polymer systems, some properties, such as density of IPNs, in particular cases, can be accounted for approximately by the simple averaging of properties of the constituent polymers. On the contrary, optical transparency, one simple way of confirming miscibility, is more complex. Miscible amorphous IPNs are transparent whilst IPNs exhibiting phase separation are usually observed as white, opaque materials due to increased scattering as the size of the phase domains approaches the wavelength of light. IPNs of two amorphous, transparent, and incompatible polymers, such as PEA and PS, are hazy and translucent in thin sheet form, because the phase domains have different refractive indices and scattering light. However, if the IPN consists of two polymers whose the refractive indices nearly match, the resulting IPN can be clear (Paul and Newman, 1981). Optical clarity is a necessary, but not sufficient, criterion for blend miscibility of amorphous constituents. So, any conclusions drawn from such observation must be confirmed by another technique.

4.2 Glass Transition Behavior.

The study of glass transitions is essential with morphological studies of polymers. While homopolymers and random copolymers exhibit single, sharp glass transitions, polymer blends, in general, and IPNs in particular, show two transitions, one for each phase. The intensity of each transition is related to the overall composition and phase continuity while shift and broadening of the transition indicate the extent of molecular mixing [Manson and Sperling, 1976]. If the polymer pair are miscible, forming one phase, then one sharp glass transition will be observed at a temperature governed by the Fox equation,

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where T_{g1} and T_{g2} represents the glass transitions of the component polymer and W_1 and W_2 are weight fractions. For the simple binary case, $W_1 + W_2 = 1$. If the two polymers are totally immiscible, two glass transitions will be observed at the glass transitions of the homopolymers. Usually, at least some mixing is observed at the polymer-polymer interface, resulting in a broadening of the transitions. Slight actual solubility of the components within the phases results in an inward shifting of the two glass transitions, see Figure 5 (Sperling, 1997).

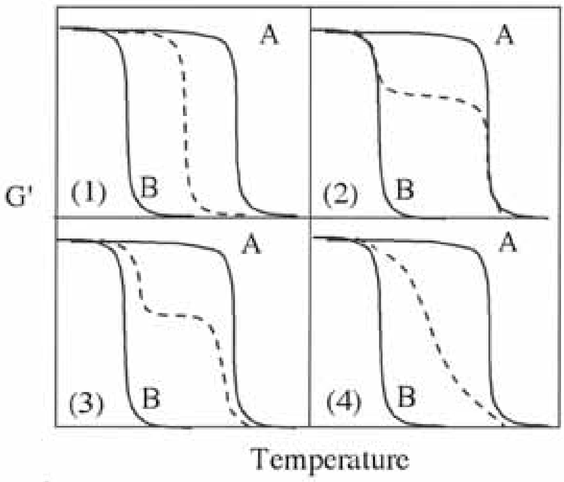


Figure 5 Schematic representation of the temperature dependence of storage modulus for polymer A and B (solid lines), and their 50/50 blends (broken lines). (1) miscible blend, (2) immiscible blend, (3) limited miscibility, (4) semi-miscible blend [Utracki, 1990].

A series of PUR/ epoxy maleate of bisphenol A semi-IPNs was synthesized by Cascaval and coworkers (2002). Differential scanning calorimetry (DSC) showed that the IPNs presented a single composition-dependent T_g. This behavior was evidence for good miscibility within the IPNs system and proved that the high degree of the intermolecular interactions, hydrogen bonding and van der Waals forces, existed between the components. Athawale and Kolekar (2000) examined the typical behavior of IPNs based on an incompatible polymer pair, uralkyd/poly(butyl methacrylate), (UA/PBMA), IPNs. Two separate transitions were observed from DSC investigation for all IPN compositions. However, they were shifted inwards, which indicated that some extent of interpenetration occurred between UA and PBMA. The IPNs were examined by SEM and found to exhibit phase separation.

5. Characterization

Various techniques employed in studying IPNs can be distinguished as: chemical characterization, morphological characterization, glass transition behavior and mechanical properties.

5.1 Chemical characterization

Due to their insoluble nature, most IPNs are difficult to be characterized by methods requiring a solution state of samples. Convenient analytical methods that can be used with solid samples include:

- **Elemental analysis**

This technique can be used to measure mass percen-tage of carbon, hydrogen, nitrogen, chlorine, etc. within samples. When this technique is applied, the elemental composition information obtained can be used to calculate the ratio of constituent polymers in IPN.

- **Fourier-transform infra-red spectroscopy (FTIR)**

This technique is capable of qualitative identification of the structure of polymer samples as well as the quantitative measurement of the components. The former is frequently used to elucidate polymer structure. This often entails the identification of the functional groups and groups of attachment to the polymer backbone. Samples can be mixed with potassium bromide and then pressed into pellets. Film can be prepared form melt or cast from solution and can be studied easily.

- **Nuclear magnetic resonance (NMR)**

NMR spectroscopy is a most effective and significant method for observing the structure of polymer chains. The widest application of NMR spectroscopy is in the field of structure determination. The identification of certain atoms or groups in an IPN as well as their positions relative to each other can be obtained by one-, two- and three-dimensional NMR.

5.2 Morphological characterization

Optical microscopy, scanning and transmission electron microscopy have been widely used to obtain evidence of the two phase nature in IPNs. In general, the microscopy techniques, to a large extent, rely on staining the IPNs, in order to gain better phase contrast in the micrograph. For examples, IPNs containing unsaturated groups such as polybutadiene can be stained using osmium tetraoxide. Thus the darker areas in the micrographs indicate polybutadiene phase or contain high polybutadiene content.

5.3 Glass transition behavior

The most common and perhaps the most unambiguous technique used for establishing the extent of mixing in IPNs, is through the determination of the glass transition temperature (T_g) of the IPN versus those of the constituent homopolymers. As the T_g value is inherent in the characteristics of a material, the existence of a single sharp, single broad, shifted or individual transition, reveals the macroscopic characteristics and the level of mixing in IPNs. The common techniques employed to determine T_g include differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dynamic mechanical thermal analysis (DMTA).

5.4 Mechanical properties.

The mechanical behavior of IPNs is described by their mechanical properties, e.g. tensile strength, impact strength and hardness, which are the results of idealized, simple tests. These tests are designed to represent different types of loading conditions. Tensile strength has been studied most extensively. The test describes the resistance of a material to a slowly applied stress. Important properties include yield strength, tensile strength, modulus of elasticity and %elongation.

6. Applications of IPN Technology

Many IPNs are combinations of an elastomer and a plastic. Consequently, the resulting IPNs exhibit properties of either reinforced rubbers or impact-resistant plastics, depending upon which phase predominates (Vancaeyzeele *et al.*, 2005). Other applications to date include ion exchange ultra-filtration membranes (M'Bareck *et al.*, 2006), electrolyte membranes (Elmer and Jannasch, 2006, 2005), gas and liquid separation membranes (Byun *et al.*, 2006; Matsuguchi and Takahashi, 2006), coatings and paint in latex form (Venkatesan *et al.*, 2006), liquid crystalline polymer (Zhao *et al.*, 1999), electrical conductive materials (Jeevananda and Siddaramaiah, 2003), polyelectrolyte gels (Kalapala and Eastes, 2005) and sound and vibration damping materials (El-Aasser *et al.*, 1999). Recently, an interesting application is in the medical field, as devices for drug delivery systems (Matricardi *et al.*, 2006; Rokhade *et al.*, 2006; Liu *at el.*, 2006; El-Sherbiny *et al.*, 2005), biomaterials (Diez-Pana *et al.*, 2002; Zhang and Peppas, 2002) and hydrogels [Chivakula *et al.*, 2006; Kaewpiron and Boonsang, 2006). A number of IPNs are now commercially available.

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