Interpenetrating polymer networks for coatings – properties, characterization, applications and current status

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Abstract

As the protective mechanism of an organic coating is largely dependent on its polymer used as binder, blending of polymers has long been practised to improve end use properties. Polymer alloys, in particular interpenetrating polymer networks [IPNs], offer a variety of improved coating properties. IPNs represent a mode of blending of two or more polymers to produce a mixture in which the phase separation is not as extensive as in polymer blends. The combination of varied chemical types of polymeric networks in different proportions, often resulting in different controlled morphologies, has produced IPNs with synergistic behavior.

The physical properties of the IPNs fall into two classes: The first class contains those properties, which vary monotonously as the composition is varied from one pure network to the other. The second class of properties includes those which at least in certain IPNs can exhibit maxima or minima at an intermediate composition between the two networks. IPNs offer a broad range of applications including protective coatings. IPN technology has surprisingly covered almost all sorts of applications and, in the coatings areas also, quite a good number of commercial products based on full, semi- and pseudo-IPNs are already available in the market, although they are rarely identified as such. In this paper, the noteworthy IPNs so far published have been cited.

Introduction

AS the protective mechanism of an organic coating is largely dependent on its barrier property, i.e., on the film forming polymers, the selection/choice of the such polymers as binders/film formers is the primary task while designing /selecting a coating system for an anticipated corrosive environment. Each film-forming polymer has its characteristic physical and chemical properties, which recommend themselves for specific uses in coatings.

Natural resins and unmodified synthetic resins [known as 'neat polymers'] have long been used as such. Later, using co-polymerization techniques, co-polymers [a polymeric material synthesized from more than one monomer] were largely produced. These neat and co-polymers, while possessing advantageous properties, still lack some of the basic requirements. Hence, attempts to produce more durable polymer classes for various applications are constantly being carried out, and this has resulted in the development of polymer blends, polymer alloys and specifically interpenetrating polymer networks, among others.

Polymer blends and alloys

Polymer blends [referred to also as 'polyblends'] include a broad category of polymeric mixtures and generally refer to a mixture of at least two polymers or co-polymers.[1] Technically, polymer blends may be well classified into miscible and immiscible polymer blends according to a thermodynamic property, i.e. change in entropy while mixing takes place.[2]

A miscible polyblend is a polymer blend, homogeneous down to the molecular levels, and is associated with the negative value of the free energy of mixing, i.e. $\Delta G \approx \Delta H_m < 0$, and an immiscible polyblend is any polymer blend with $\Delta G \approx \Delta H_m > 0$. The latter class is a commercially attractive polymer mixture, normally homogeneous to the eye and often with

enhanced physical properties over the constituent polymers.[2]

Polymer alloys, a specific sub-class of polymer blends, are a compatibilised immiscible polymer blend, wherein compatibilisation refers to a process of modification of interfacial properties of an immiscible polymer blend, leading to polymer alloys.

Interpenetrating polymer networks

The physical and chemical combination of two or more structurally dissimilar polymers provides a convenient route for the modification of properties to meet specific needs. It facilitates processing and may impart flexibility, tensile strength, chemical resistance, weatherability, flammability resistance and other required properties.[3-5] The physical properties of the combined polymers depend on the properties of the polymers and the way they are combined.

Interpenetrating polymer networks, shortly *IPNs*, a novel type of polymer blend composed of cross-linked polymers, are more or less intimate mixtures of two or more distinct cross-linked polymer networks with no [or few] covalent bonds between the polymer components, i.e. polymer A crosslinks predominantly only with the other molecules of the polymer A, and so is the case with polymer B. Thus, IPNs may be described as combinations of chemically dissimilar polymers in which the chains of one polymer are completely entangled with those of the other polymers, where upon the entanglements are permanent in nature and are made so by this homo-crosslinking of the two polymers.[6-7]

Thus IPN formation represents a third kind of mechanism [other than mere physical blending and co-polymerization] by which different polymers can be physically combined by inducing polymer blends compatibility through polymer structure modification.

An IPN can be distinguished from simple polymer blends, block or graft co-polymers in two ways:

i. IPNs swell but do not dissolve in solvents
ii. Creep and flow properties are considerably suppressed

Formation of IPNs

IPNs represent a mode of blending of two or more polymers to produce a mixture in which the phase separation is not as extensive as it would be, otherwise, in the case of polymer blends made out of simple physical mixing. It is the only way of combining cross-linked polymers. Normal blending or mixing of polymers results in multi-phase morphology due to the well-known thermodynamic incompatibility of polymers. This incompatibility is due to the relatively small gain in entropy upon mixing the polymers due to contiguity restrictions imposed by their large chain length. However, if mixing is accomplished on a lower molecular weight level, and then polymerization accomplished simultaneously with crosslinking, phase separation may be kinetically controlled somewhat, since the entanglements will have been made permanent by the crosslinking. In other words, phase separation cannot occur without breaking the covalent bonds in the individual component polymers. An interesting analogy of an IPN is given by *George Gamov*, as that two worms eat out independently tunnels in an apple.

Till now, the IPNs synthesized have exhibited various degrees of phase separation, dependent principally on the compatibility of the polymers.

i. With highly incompatible polymers, the thermodynamics of phase separation are so powerful that it occurs substantially before the kinetics of crosslinking can prevent it. In these cases, only small gains in phase mixing occur.
ii. In cases where the polymers are more compatible, phase separation can be almost completely circumvented. But the complete compatibility, which is almost an impossible situation, is not necessary to achieve complete phase mixing, i.e. interpenetration, since the 'permanent' entanglements produced by inter-penetration prevent the phase separation.
iii. In cases where the polymers are intermediately compatible, intermediate and complex phase behavior results.

Thus IPNs with dispersed phase domains ranging from a few microns [the largest part][8] to a few hundred angstroms [intermediate],[9] finally to those with no resolvable domain structure [complete mixing][10] have been reported in the literature.

Topological isomerism of IPNs

IPNs represent a special example of topological isomerism in macromolecules.[11-12] Some permanent entanglements between the different cross-linked networks are inevitable in any sufficiently intimate mixture of the cross-linked networks. These represent examples of catenation in polymer systems, i.e. different ways of imbedding these molecules in three-dimensional space. Permanent entanglements act as constraints to the motion of segments[13] and simulate covalently bound chemical cross-links. Simplified theoretical models of such permanent entanglements[14] exhibit a surprisingly large non-linear elastic restoring force, unlike that expected with chemical cross-links from the ideal rubber elasticity theory.

Synergistic behavior of IPNs

The combination of varied chemical types of polymeric networks in different proportions, often resulting in different controlled morphologies, has produced IPNs with synergistic behavior. An example of this is that, if one polymer is glassy [i.e. the glass transition temperature T_g > room temperature] and the other polymer is elastomeric [i.e. T_g < RT], an IPN resulting out of it will be either a reinforced rubber in case the elastomeric phase is predominant and a high impact plastic in case the glassy phase is predominant. In the case of more complete phase mixing, enhancement in numerous mechanical properties is due to the increased physical cross-link density. IPNs have been synthesized with intermediate maxima vs. network composition in bulk properties such as tensile strength[15-23], impact strength[17-18] and thermal resistance[17-19,21] and minimal surface properties. Others such as thermal resistance may result from the fact IPNs are usually blends of different types.[24]

Morphology of IPNs

The morphology of IPNs [molecular orientation] is related to physical properties such as modulus and glass transition temperature [T_g] and provides an insight into the latter. The morphology of IPNs is controlled by chemical

compatibility [solubility parameters], interfacial tension, cross-link densities, mode and kinetics of polymerization, and component types. The IPNs synthesized to-date show different morphologies with varying degrees of phase separation. Phases vary in size, shape, sharpness at the interfaces, and degree of continuity. Based on morphology, IPNs can be classified as having large structures with domain sizes of a few microns [15-16] intermediate structures with sizes around 1000 angstrom[9,25] and no resolvable domain structures at all.[10]

As the polymers are cured, they phase-separate due to their thermodynamic incompatibility. This phase separation is naturally diffusion controlled and requires time. If the curing reactions are accelerated, less time will be available for diffusion and subsequent phase separation to occur. When fully cured, further phase separation cannot take place due to topological constraints. Thus faster crosslinking would be expected to yield less phase separation.[25]

The compatibility of IPNs can be enhanced because the polymers are interlocked in a three dimensional structure during polymerization before phase separation can occur. Nearly all two-polymer compositions form two immiscible phases. This arises from the unusually low entropy of mixing obtained on blending the polymers. The Gibbs free energy of mixing DGM is expressed as $\Delta G_M = \Delta H_M - T \Delta S_M$; where ΔHM is the enthalpy of mixing and ΔS_M the entropy of mixing. Separation occurs because ΔG_M changes from negative to positive as the molecular weight increases due to crosslinking of polymers. The decrease in entropy [or randomness] occurs because before polymerization, all individual molecules are interchangeable with each other. However after polymerization, the monomers are bound by covalent bonds and can only move in co-ordination with other monomer units of the same polymer. They cannot physically pass through each other. This decreases the randomness of the system. The ΔH_M for mixing monomer and monomer or monomer and polymers changes in either negative or positive direction after polymerization. Thus, in most cases at least to some extent, phase separation results. IPNs can be

compatibilised by carefully choosing monomers of similar solubility parameters as well as choosing other parameters mentioned above.

In general, the smaller the phase domains, the more compatible the systems. Compatible IPNs mix on a molecular level with 5.0 nm domains, and semi-compatible IPNs from 5.0-30 nm and incompatible IPNs have domain sizes of 30 nm and greater, i.e. very coarse morphology.

More crosslinks in the IPNs indicate a smaller negative value of the free energy of mixing ΔG_M. In sequential IPNs, the network-I controls the entire morphology and the network-II has little effect on it. This has been confirmed by increasing the cross-link density of network-II which produced no changes in morphology of the IPN.[26]

The highly grafted IPNs wherein grafting was induced deliberately displayed poorly defined morphologies with irregular structures; phase- domain boundaries were characterized by fibrillar and interphase regions. A single glass-transition peak has been also observed.[27]

A core-shell morphology has been observed in sequential latex IPNs based on polyvinyl chloride / poly butadiene-co-acrylonitrile. This type of morphological structure within the latex particles may be explained by smooth gradation of composition from core to shell, by an abrupt composition boundary between the core and shell with phase separation within the core.[6]

Low cross-linked IPNs and semi-IPNs are characterized by dual phase continuity. The electron micrographs show that an increase in cross-links of both polymers produces a finer morphology with greater regularity. When both polymers are cross-linked, the indications are stronger that two continuous phases are evolved, with the domains decreasing in size with increasing crosslinking density.

In the case of pseudo-IPNs, the phase mixing is less due to the presence of temporary entanglements, since only one polymer is cross-linked. In the case of linear blends, even less mixing can be expected, since there

are no topological constraints at all, for neither polymer is cross-linked.

Glass transition behavior of IPNs

All amorphous polymers have a glass transition temperature [Tg] depending upon the chemical nature of the polymer. Glass transition increases with increase in cross-link density. In the case of IPNs, the glass transition may be broadened or shifted depending upon the mixing of the polymer in the IPNs. In highly incompatible IPNs [which is highly phase separated] each phase retains its individual Tgs. In the totally compatibilized IPNs where complete mixing takes place, only one transition is observed in the range between the glass transitions [Tgs] of the component polymers.[28] Usually glass transition of the polymer alloys shift inward from the glass transition temperatures of the individual components.

The Tg of the IPN is always lower than the Tg [av] as defined by

$$Tg_{[av]} = W_1 Tg_1 + [1 - W_1] Tg_2$$

where W_1 is the weight fraction of component 1 and Tg_1 and Tg_2 are the Tgs of components 1 and 2 respectively.

The Tgs also differ from the value calculated according to the Fox equation,[29-30]

$$1/Tg = W_1/Tg_1 + [1- W_1] / Tg_2$$

This observation may be related to a theoretical equation in which the shift in the Tg is a function of the degree of crosslinking.[30] Generally, chemical crosslinking in the conventional polymers raises the Tg. If Tg is the glass transition temperature of the cross-linked polymer, Tg_0 is the glass transition temperature of the uncrosslinked polymer, X_c, the mole fraction of monomer units which are crosslinked in the polymer, F_x/F_m the ratio of segmental mobilities for the same two polymers and E_x/E_m the ratio of the lattice energies for cross-linked and uncross-linked polymer respectively, then the *DiBenedetto* [30] equation becomes

$$[Tg-Tg_0]/ Tg_0 = \frac{[E_x/E_m - F_x/F_m] X_c}{1-[1- F_x/F_m] X_c}$$

Any co-polymer effect due to crosslinking is accounted for by modifying Tg_0. For chemically cross-linked polymers $E_x/E_m = 1$ [DiBenedetto estimates this to be about 1.2] and the mobility of a chemically cross-linked segment $F_x << F_m$ so that $F_x/F_m = 0$. Hence the DiBenedetto equation may be simplified to

$$[Tg-Tg_0]/\, Tg_0 \approx 1.2\ X_c\,/\,[1-X_c]$$

which exhibits the often experimentally observed increase of Tg with X_c.

For an IPN, the DiBenedetto equation must be modified by replacing the Tg_0 with $Tg_{[av]}$. This should account in first approximation for the co-polymer effect present in IPNs. The monomer units of both networks are not chemically modified on forming an IPN as a result of forming permanent entanglements by topological interpenetration $E_x - E_m = 1$. Therefore, the equation now becomes

$$Tg-Tg_{[av]}\,/\,Tg_{[av]} = \frac{[\,1-[1-F_x/F_m]\ X_c\,]}{[\,1-[1-F_x/F_m]\ X_c\,]}$$

with X_c the entanglement mole fraction. In general, secondary intra-molecular bonding of a network, Vander Walls or hydrogen bonding [if present], is reduced by the permanent entanglement of portions of two different networks. Hence, the mobilities of the segments of an IPN, F_x are larger than in the non-interpenetrating separate networks, F_m [i.e. $F_x/F_m > 1$]. Setting

$$\theta = [\,F_x/F_m - 1\,]\ X_c > 0,\quad 1 \ge X_c > 0$$

the above equation can be rewritten as

$$Tg-Tg_{[av]}\,/\,Tg_{[av]} = -\,\theta\,/\,[1+\theta\,]$$

which would predict that the Tg of an IPN will be less than or equal to the $Tg_{[av]}$

The values of F_x/F_m and X_c depend upon the chemical nature, cross link densities and weight fraction [W] of the constituent networks of the IPNs. For a series of IPNs of differing values W made from the same two constituent networks, θ is expected to reach a maximum not far from the maximum of X_c as a function of W.

Physical properties of IPNs

The physical properties of the IPNs fall into two classes: The first class contains those properties, which vary monotonously as the composition is varied from one pure network to the other. Examples are the glass transition temperature, density, and elongation at break and water vapor permeability. The second class of properties are those which at least in certain IPNs can exhibit maxima or minima at an intermediate composition between the two networks.[31-32] Thus, for example, the tensile strength at break in certain IPNs [based on polyurethanes, for example] appears to exhibit this property. On the other hand, this does not appear to be the case with the systems studied by Sperling and his collaborators. It appears that the PU based IPNs which exhibit such a maximum do this both when the apparent more continuous phase is more rubbery or less rubbery than the remaining phase. Thus it is possible that this maxima is a true reflection of an optimal extent of interpenetration.

Other properties, which fall in this second-class, are lap shear and peel strength. Since the failure in these materials is easily seen to be cohesive in the polymer phase and since both peel strength and lap shear are proportional to the tensile strength, the maximum in the tensile strength is observed.[33] Other desirable properties of IPNs are the toughening and increased impact resistance observed when one component network is glassy and the other elastomer.[34] The very broad glass transition region observed in some of the semi-compatible IPNs yield damping materials and acoustical damping coatings suitable for a wide variety of use temperatures. K.C. Frisch et al [35] have mentioned that a number of IPN combinations exhibit significant improvement in thermal resistance over the component networks.

Characterization of IPNs

The ultimate properties of the IPNs synthesized with various degrees of interpenetration have been extensively characterized using the modern instrumental techniques. In IPN literature, a greater variety of instrumental characterization techniques have been reported in order to determine the morphology, thermal properties, physical properties and other characteristics of IPNs.

Till now, no single method is available to prove the existence of interpenetration. However the interpenetration may be identified by

i. comparing the morphologies and distribution of phase domains, sizes for these IPNs with their corresponding homo-polymers.
ii. comparing the shift of dynamic Tgs of IPNs with their homo-polymers or pseudo-IPNs, linear polymers or grafted-IPNs.

The existence of interpenetration is generally better judged through the combination of the above inferences.[33]

Morphology by electron microscopy

The morphological properties of IPNs are best characterized by using the Scanning Electron Microscopy [SEM] and Transmission Electron Microscopy [TEM] using various staining methods and in particular Kato's staining and sectioning techniques.[36-39] The micrographs obtained using the SEM and TEM appear to be useful in detecting the interpenetration, phase domains, shape and structures of the order of magnitude of a micron to a tenth of a micron and the degree of molecular mixing. The presence of a single phase at about 5000x magnification would confirm the good molecular mixing.

In the Kato's technique, a small piece of IPN is taken and is stained overnight in 1% aqueous solution of osmium tetroxide, after which the sample is rinsed twice with acetone and dried and subsequently embedded in Spurr varnish.[39-41] The sample is then thinned and all the sections are stained with uranyl acetate and lead citrate before being observed by SEM. In another technique, film of an IPN is cryogenically fractured [called freeze-fracturing] in liquid nitrogen and is mounted vertically on a SEM stub by silver adhesive paste. The specimen is coated with gold to about 200-angstrom thickness using vacuum system like EPS/Carl Zeiss at about 10-5 torr.[42]

Thermal measurements

The real morphology of an IPN is

the sum of the observations from electron microscopy and thermal measurements. Differential Scanning Calorimetry [DSC], Differential Thermal Gravimetric Analysis [TGA], Differential Thermal Analysis [DTA] have all been extensively used to study the true thermal behavior of the IPNs.[43, 43-44]

Differential Scanning Calorimetry often exhibits one or two or two inwardly shifted or three [and in principle one] T_gs. All of the reported T_gs lie at or between the T_gs of the pure networks. The observation of a single T-g for an IPN implies that the interpenetration has occurred by segmental mixing [i.e. complete mixing]. In many cases, two distinct Tgs as T_g1 and T_g2 corresponding to those individual component networks have been observed. This confirms the phase domain interfaces become more distinct and phase separation results due to poor compatibility and very weak physical interactions between the component networks. Such behavior has been reported by *Sperling* and others.[45-46] It has been reported that the calculated T_gs [according to the Fox and co-polymer equation] are almost always higher than the T_g values measured for the IPNs. Apart from the Tg values, the weight loss of IPNs indicates the thermal stability character of the IPNs. In most reports the thermal stability of the IPNs have been found to be more than their homo-polymers.

An interesting information obtained from the thermal measurements is the oxidation index [OI] of IPNs. The OI values calculated are based on the weight of the carboneous char [CR] related to an empirical equation;[47] OI x 100 = 17.5 + 0.4 x CR. Higher OI values imply that the IPNs can be a good fire-retardant material.

Generally, thermograms are obtained from a thermo-gravimetric analyzer under nitrogen or air [to find the weight loss along with the oxidation index] at a heating rate of 5-10oC /min or less or as required. The sample in the shape of a thin disc weighing around 5 to 10 mgms. is placed in a platinum sample pan under a continuous nitrogen flow of 1-5 ft³ / hr.

Mechanical properties

Mechanical properties of IPNs like tensile strength have been extensively studied using the familiar testing methods. The mechanical properties of IPNs mostly depend upon the composition and nature of the constituent polymeric networks. Varying the composition from one end to other end results in changes in the mechanical properties of the IPNs.

Tensile strength, Young's modulus and elongation at break [the stress-strain properties] are measured using an *Instron* Tensile Tester at a cross head speed of about 2-5 in./min.. Specimens used are of 0.125 to 1 inch wide dumbbells. An ASTM standard D 638-1971 is used for this purpose. Lap shear strength and peel strength [180°] are measured on an Instron Tensile Tester with 3 x 0.5 in Al/steel plates lapped 0.5 in. from their edges. The failure is observed as adhesive or cohesive.

The hardness of the IPNs are generally measured by means of a Shore A and D Durameter [ASTM D 785-1965 and 2240-1975]. Pencil hardness has also been reported elsewhere. Both direct and indirect impact strengths [as impact resistance] are obtained from a Gardner SPI modified variable height impact tester using ASTM D 2794-1969.

Kinetic measurements of IPN formation

The kinetics of the formation of IPNs from its constituent polymeric networks has been studied using simple methods. In a test tube [of 12 cm long and 8 mm diameter] sample polymers are taken and the tubes are sealed subsequently. These capsules are then placed in an oil bath at about 110°C. The samples are taken out at different intervals and are quenched in a dry ice-acetone bath and examined for flowability. The time at which the polymerizing mass does not flow at room temperature is noted as 'Gel Time'.

For any IPNs of two component systems, after mixing the networks, the 'gel time' is measured as the time required for an IPN mixture to reach a viscosity level of 100,000 cps. When the reaction mixture is touched with a steel spatula and if found solidified, then the time required for such state is noted as 'solidification time'. In the polymerization process, the increase in the viscosity first leads to gelling point followed by solidification point and further accompanied by shrinkage of the mass, known as the 'crystallization time'.

Barrier properties of IPNs

Barrier properties of IPNs are directly measured as water permeability or more accurately as moisture vapor transmission rates [MVTR] using either sorption or diffusion methods. For ease of operation, generally diffusion methods are employed, which makes use of Payne's cup method. In this method a film of IPN is placed in between the cup containing water and the moisture free environment developed in a desiccators. The constant loss in weight of water per unit time indicates the rate of diffusion and hence the diffusion co-efficient of the IPNs.

Chemical and corrosion resistance properties of IPNs

Chemical resistance of IPNs is carried out by immersing the IPN samples in different chemicals [usually in the aqueous solutions] for a specified period. The changes in the films during the test period are noted and their resistance is comparatively assessed. The corrosion resistance properties are best judged by placing films of IPN [as coatings applied over steel surfaces] in a salt spray chamber as per the ASTM B-117. The corrosion resistance property is also assessed using the AC Impedance spectroscopic technique.

Solvent resistance properties of IPNs

Solvent resistance properties are measured directly as MEK solvent resistance and by swelling measurements. In the former, the IPNs are rubbed with cotton soaked in Methyl Ethyl Ketone [and / or xylene] solvent. The effect is noted as gloss loss or material loss to determine the IPNs resistance to MEK. In the case of swelling measurements, data regarding the volume equilibrium degree swelling [Q] and molecular weight between cross link [Mc] are obtained from which the solvent resistance of IPNs is measured. For this, specimens are immersed in solvents with increasing order of solubility parameter [δ] from 6.6 to 14.5 cal. cm². [n-decane [δ=6.6], n-heptane [7.5], carbon tetrachloride

[8.6], benzene [9.2], acetone [9.7], fur-
fural [11.2], nitro methane [12.7] and
methanol [14.5].

Visco-elastic measurements of IPNs

Visco-elastic measurements are
determined using Viscot Test Appara-
tus for determining the dimensional
stability of IPNs under heat. Needles
having 1 mm^2 of circular cross section
are kept over the IPN sample. A load
of 5 kg. is applied vertically over the
needles and the specimen is uniformly
heated. The temperature is noted when
the needle penetrates a depth of 1 mm
in the specimen.

Electrical properties of IPNs

The electrical properties of IPNs
like dielectric nature and electrical
conductivity have been studied by a
few authors according to ASTM D1531-
1962.[48-50] The intrinsic electrical con-
ductivity [σ_0], electrical conductivity at
room temperature [σ], and activation
energy [E] of some selected IPNs and
their constituent homo-polymers have
been studied by some of the authors.[51]
It has been found that the intrinsic
electrical conductivity of IPNs ranges
from 1.0×10^{-9} to 2.08×10^{-10} ohm^{-1}
cm^{-1} while their individual homo-poly-
mer networks have values of $1.12 \times
10^{-11}$ [for polyurethanes] and $3.90 \times
10^{-16}$ ohm^{-1} cm^{-1} [in the case of polyethyl
methacrylate]. It is evident from these
observations that IPNs behave like
poor semi-conductors as compared
with the insulating behaviour of their
individual homo-polymers.

Infra-Red [IR] and Fourier Transform Infra-Red [FT-IR] spectroscopy

IR and FT-IR spectroscopic tech-
niques have been widely used for iden-
tifying the components with their spe-
cial groups in IPNs. This forms addi-
tional tool to confirm the completion
of reaction. The FT-IR technique has
been successfully employed to deter-
mine the kinetics of the formation of
the IPNs by observing the appearance
and disappearance of functional
groups present in the polymeric net-
works.[52]

Gel Permeation Chromatography

Gel Permeation chromatographic
measurements have been reported for
IPNs to determine the molecular

weights of the polymers along with the
polydispersity of the low molecular
weight components.[53] It has been
shown that this technique is very much
useful in determining the molecular
weights of the component polymeric
networks used in the coatings and
adhesives.

Density and wettability

Density of the IPN materials has
been found using hydrostatic tech-
nique by immersing in water [sample
dimensions are 0.125 x 1.25 x 2.5 cm].
The thickness of the IPN films have
been found using a standard gauge or
a dry film thickness meter operated by
eddy current or electromagnetic prin-
ciples.

The wetting ability of the IPNs have
been determined using 'contact angle
measurements' and surface tension.
Lipatov[54] and his collaborators have
applied a thermodynamic method of
obtaining the cross link density of an
IPN from the measured retention vol-
ume in gas chromatography of the IPN.

Application of IPNs

Many types of IPNs, SINs, Semi-
IPNs etc. are available in the commer-
cial market of polymers, although they
are rarely identified as such. Because
the term interpenetrating polymer net-
works was coined even before the full
significance of phase separation was
recognized and since most IPNs are
phase separated, the term *interpen-
etrating phase* may more accurately

describe some systems. However, dual
phase continuity is not required in the
definition of an IPN. From the broad
range of applications of the IPNs, a
few are represented in *Table 1*.

Other than the above, there are
other IPNs used for various applica-
tions and a few among them are given
below.

IPNs as leather coatings

To improve strength, elastic prop-
erties, and water penetration and to
minimize surface defects, the animal
skins are treated with polymer precur-
sors by an emulsion polymerization.
In this process the skin is immersed in
water, initiator, redox system and sur-
factant. After flushing with carbon-di-
oxide, monomeric vinyl, styrene, or
acrylic moieties are added and the
system is tumbled. Semi-I and full IPNs
are formed.[64-65] These leather IPNs can
be made dry-cleaned without loss of
polymer.[66]

IPNs as dental fillings

In 1945, acrylic plastics were intro-
duced as restorative materials[67] which
were semi-II IPNs based on linear
polymethyl methacrylate as polymer-I
with polymethyl methacrylate plus
crosslinking agents as network-II.
These IPNs were sold and used as
two component packages for dental
fillings. Silanes are also used in ortho-
pedic applications for joining bones,
i.e. by using 85% inorganic fillers plus
ethylene glycol dimethacrylate as
crosslinking agent for the network-II.[68]

TABLE 1: APPLICATIONS OF IPNS

Applications	Type of IPNs
Ion Exchange resin[55-56]	Sulphonated polystyrene / Polyacrylic acid Sulphonated polystyrene / Polychloro methyl styrene
Impact resistant plastics[57-59]	Polybutadiene / Polyacrylonitrile-co-ethyl acrylate Polybutadiene / Polystyrene Polybutadiene / Polybutyl acrylate-co-styrene Polybutadiene / Polybutyl acrylate-co-acrylonitrile
Optically smooth plastic surfaces[60-61]	Polymethyl methacrylate / Poly ethyl vinyl ketone, Polystyrene / Polystyrene
Noise damping coatings[62]	Polyethyl methacrylate / Poly [n-butyl acrylate]
Adhesive/surface coatings[63]	Epoxy resin / Polyester resin, Polyacrylate / Polyurethane, Olysiloxane / Polysiloxane Any water soluble resin / Poly styrene Polyester / Polystyrene, Epoxy resin / Polyacrylate Polysulphide rubber / Epoxy resin, Olyurethane / Epoxy resin / Polyacrylates

IPNs as sheet-moulding compounds [SMCs]

IPNs as sheet-moulding compounds are used in transportation, appliances and electrical devices. These IPNs impart stiffness and high temperature properties, which can only be obtained through the use of modifiers in the conventional moulding compounds. Cross-linked polyurethanes, poly-styrene and unsaturated polyesters with minimized shrinkage and warpage during the moulding are used for this purpose.[69]

IPNs as noise and vibration damping materials

Semi-compatible, IPNs of low and high Tg polymers dampen noise and vibration over the intervening transition range. The motion of flexible chains over their stiffer neighbours may be the basis of the phenomenon[70] Epoxy resin, Polyurethanes and Methacrylic-acrylate based latex IPNs have been extensively studied for this purpose.[71] For use as coatings, IPNs are applied in latex form rather than in bulk form. The IPN elastomers and foams prepared by the simultaneous technique from polyurethanes and epoxies [both filled and unfilled, plasticized and un-plasticized are excellent noise and vibration dampers over a broad temperature and frequency range.

IPNs as rimplast thermoplastic resins

This class of thermoplastic interpenetrating polymer networks is made by reaction of functional silicone fluids in thermoplastic melts [called rimplast]. These IPNs are a combination of thermosetting and thermoplastic IPNs. They exhibit properties of both resin components as well as unusual composite behavior including three times the tear strength of high performance silicones, better tensile and flexural strength, lower specific gravity and surface wear, and reduced oxygen permeability and moisture vapour transmission.[72] Current applications include PTFE lubricated nylon-6,6 IPN moulded in a bearing for use in high speed paper handling equipment, typewriter key board frames, etc.

IPNs as automobile parts

Thermoplastic IPNs composed of hydrogenated butadiene-styrene block co-polymers with a molecular weight range from 9,000 to 47,000 as one component and polyamide such as nylon-6, -11, or -6,6 as the other are used as automobile parts with improved visibility, exterior, decorative automotive parts like *fascia* and bumper parts. These IPNs possess the combined properties of an engineering polymer with the processing benefits of a thermoplastic polyolefins like polyethylene.

Current status

In the field of polymer science and engineering, hundreds of different types of IPNs have been prepared from various polymer components and their properties have been characterized to some extent. These IPNs have been reported mostly as polymeric materials and their applications in various fields have been seldom mentioned.

The coatings industry has adopted the IPN technology because of its good features as excellent coating materials. Only recently, about two decades ago, the introduction of IPNs into coatings has been reported.[73-74] Earlier the polymer blends and graft polymers have extensively been used in order to improve the final film properties.

IPN technology, as mentioned earlier, has surprisingly covered almost all sorts of applications and in coatings areas also, quite a good number of commercial products based on full-, semi- and pseudo-IPNs have already become available in the market although they are rarely identified as such. While most of the literature citations and patents on IPNs for coatings have dealt with the synthesis and characterization, a complete study of an IPN as coating materials, either as clear or pigmented or both, is seldom reported.

As most of the IPNs so far reported basically lack the property of ambient temperature curing due to their complex chemistry and physics of alloying, their complete entry into the coatings industry has long been struggling. However with the flourishing of baking enamels as OEM coatings, these IPNs have been well considered.

Frisch, K.C., Frisch, H.L., Sperling, L.H., Klempner.D and other co-workers are the pioneers in this field and have extensively studied the IPNs. They have also attempted to develop organic coatings based on IPNs as both pigmented and unpigmented. The introductory attempts were all related to IPNs synthesized using simultaneous techniques and cured at elevated temperatures for a specified period [usually much higher than the conventional baking type enamels] and the study of their properties confined to the examination of their suitability for use in coatings as film formers in comparison with their homo-polymers.

The results obtained thereafter have confirmed that IPNs including full-, semi- and pseudo-types provide improved film properties in all aspects including the valuable protective properties when compared to the conventional ones. But they still remain as high temperature curing material hindering the field application possibilities, and for this reason, it has not gained much attention among the coatings industries.

The IPNs that have been specifically cited as coating materials in the literature of scientific publications and patents are summarized below.

Howard Lucas et al.[75] have prepared a series of IPNs based on thermoplastic polyurethane dispersions by reacting a difunctional aliphatic diisocyanate [TMXDI] with long or short chain polyesters containing terminal hydroxyl groups. When characterized, the flexible -OH polymers were found to lower the tensile module and increase elongation. [Typically these thermoplastic polyurethane dispersions of non-IPN types do not have both high strength and high elongation]. Also the attack by solvents was the primary drawback of an aqueous polyurethane dispersion, which was overcome with these IPN, based materials which cross linked internally.

Chin-Ping Yang et al.[76] have synthesized six urethane modified cationic resins by reacting half blocked polyglycol - TDI-Urethane and 2-ethyl hexanol blocked TDI [2-ethyl hexanol blocked TDI] modified epoxy resins with methoxy ethanolamine and subsequent neutralization with acetic acid. These cationic resins were dissolved in suitable solvents and mixed with de-ionized water to form emulsions.

The cross link density properties and cathodic electro-deposition of these resins were studied.

Rao et al.[77] have prepared a series of IPNs based coatings for high performance application based on phosphate ester of epoxy-novalac and phenolic resins. Phosphate ester epoxy or epoxy novalac and phenolic resin based on bisphenol-A and cardanol [from the CSNL oil] were prepared for IPNs. Polyamide adduct was used as curing agent with zinc oxide as catalyst in the case of phosphate ester epoxy. The IPNs prepared were found to be highly resistant to different chemicals as compared to conventional neat epoxy systems.

Jain et al.[78] also have attempted to prepare an IPN polymer system based on epoxy and phenolic resins for use as coatings for building materials in aggressive environment. The individual resin with their respective crosslinking agents and catalysts were sheet cast and subsequently cured to IPN at an elevated temperature for a specified period. These IPNs were found to be useful as barrier coatings for anti-corrosive application of different building materials including one in the fertiliser industry.

Kordamenos et al.[73] have reported coating compositions of IPNs of simultaneous type based on acrylic polyurethanes. The IPN was prepared from two-component polyurethane and unsaturated urethane modified acrylic copolymer. The two-component polyurethane was earlier prepared from hydroxy ethyl acrylate-butyl methacrylate co-polymer cured with a biuret triisocyanate of hexamethylene diisocyanate. The unsaturated acrylic copolymer was made from the hydroxyl functional acrylic co-polymer modified with isocyanato-ethyl methacrylate. Simultaneous IPNs with different network ratios have been prepared by mixing the networks together and heating at 80°C for 30 minutes and post cured at 120°C for another 30 minutes. The resulting IPNs were characterized and found to attain good molecular mixing as evidenced by the Tg and SEM measurements.

J. Shaw et al.[79] have prepared a series of heat-cured IPNs based on poly[epoxy-urethane-acrylate] for use in coatings as primers. These IPNs were prepared using simultaneous technique of solution polymerization. These IPNs are obtained by mixing a urethane triol acrylic macro-monomer [cross-linked by free-radical polymerization of the pendent double bonds] and an amine terminated epoxy resin cross-linked through a blocked isocyanate curing agent [like methyl ethyl ketoxime as blocking agent]. The IPNs showed good corrosion protection as tested in salt spray chamber test, beside higher tensile strength and adhesive strength as compared to their homo-polymers. In a continued publication, the authors also studied the influence of the amino groups terminating the epoxy resin as well as the molecular weight of the epoxy resins on such physical and other properties of the coatings as corrosion resistance, impact strength, adhesive strength, etc.

H.X.Xiao & K.C.Frisch[80] in an extensive publication on IPNs for coatings have reported to have prepared four different IPNs using simultaneous technique of solution polymerization and studied their properties. The four IPNs were as follows: IPN-A: Polyurethane-acrylic IPNs with similar polymer backbones but cured by means of different crosslinking mechanisms. This type of IPNs consisted of two different series of IPNs: IPN-1 and IPN-2. IPN-1 was made from polybutyl methacrylate hydroxy ethyl acrylate, which was prepared by co-polymerizing butyl methacrylate and hydroxy ethyl acrylate and polybutyl methacrylate-hydroxy ethyl acrylate-isocyanato-ethyl methacrylate, which was made by reacting polybutyl methacrylate-hydroxy ethyl acrylate with isocyanato-ethyl methacrylate. IPN-2 was made from the poly butyl methacrylate-hydroxy ethyl acrylate-caprolactone, which was prepared by reaction of polybutyl methacrylate-hydroxy ethyl acrylate with caprolactone, and polybutyl methacrylate-hydroxy ethyl acrylate-caprolactone- isocyanato-ethyl methacrylate, which was prepared by reacting polybutyl methacrylate-hydroxy ethyl acrylate with isocyanato-ethyl methacrylate. Both polybutyl methacrylate-hydroxy ethyl acrylate- isocyanato-ethyl methacrylate and polybutyl methacrylate-hydroxy ethyl acrylate-caprolactone-isocyanato-ethyl methacrylate are cross-linked by free radical polymerization of the pendant double bonds, while polybutyl methacrylate-hydroxy ethyl acrylate and polybutyl methacrylate-hydroxy ethyl acrylate-caprolactone are cured by reaction with a biuret triisocyanate forming urethane crosslinks.

1. IPN-B: Polyurethane [PU]- methacrylate copolymer IPNs with opposite charge groups IPN-B consisted of two series of IPNs, viz. IPN-B1 and IPN-B2. IPN-B1 was made from polyurethane which was prepared from 4,4' methylene bisphenyl isocyanate [MDI] and polyoxy tetramethylene glycol [PTMO 1000], and polymethyl methacrylate [PMMA], which was prepared by homo-polymerization of methyl methacrylate [MMA]. IPN-B2 was made from NPU, which was prepared from PTMO 2000, MDI, and bis [2-hydroxy propyl] aniline [BHPA], and P[MMA-MAA], which was prepared by co-polymerisation of MMA and methacrylic acid [MAA]. PMMA and P-[MMA-MAA] were cross-linked by free radical polymerisation with ethylene glycol dimethacrylate [EGDMA] as crosslinking agent. Both PU and NPU were cured with 4,4' methylene bis [2-chloro aniline] [MBCA].

2. IPN-C: [PU-vinyl chloride copolymer [VMCC] ionomer semi-IPNs]. IPN-C consisted of two types IPN-C1 and IPN-C2. IPN-C1 was made from PU, which was prepared from PTMO 1000, a cyclo-aliphatic diisocyanate [H₁₂MDI] chain extended with 1,4-butane diol [1,4-BD], and VMCC, which was a copolymer of vinyl chloride, vinyl acetate, and maleic acid. IPN-C2 was made from NPU, which was the same as used in the preparation of IPN-C1 [except that it was chain extended with N-methyl diethanol amine] and VMCC. Both PU and NPU were cross-linked with 1,4-BD and trimethylol propane [TMP] [at 4:1 of equivalent weight ratio].

3. IPN-D: [Ionomer IPNs from PU-isocyanurate and PU anionomer] IPN-D consisted of a PU anionomer, which was prepared from a polyether polyol and MDI, chain extended with dimethylol propionic acid and neutralized with zinc

acetate. The PU-isocyanurate was made by trimerization of an NCO-terminated polyether prepolymer employing a substituted hexahydro-triazine catalyst [Polycat ®41].

All the four IPNs were thermally cured and post cured at elevated temperature. They have shown good molecular mixing as evidenced by the SEM and Tg measurements. The study has not been extended to any type of corrosion resistance tests.

Sm Krishnan et al [81-82]. in their patents have dealt with the synthesis of full- and grafted IPNs of poly-[-epoxy-urethane-acrylate] type. These ambient curing IPNs have been synthesized via sequential polymerisation techniques and have been characterized for their properties. The authors have reported that the IPNs possess significant improvements in corrosion and chemical resistance, along with improved mechanical properties. The films of IPNs have also shown better UV resistance than epoxy system, as found from the QUV weatherometer, making the IPNs to be used as better top coat binder materials.

Tehranisa et al.[83] have reported an acrylic-polyurethane for coatings application. They prepared an IPN from two networks P[UA]-1 and P[UA]-2. P[UA]-1 was a self-curing polymer synthesized from butyl methacrylate and hydroxy ethyl acrylate. The hydroxy groups of this acrylic polymer were reacted with caprolactone monomer to generate flexible side chains [PBHC]. The hydroxyl groups of this polymer [PBHC] were then capped with isocyanato-ethyl methacrylate to produce an acrylic backbone with pendant flexible side chains carrying double bonds which in the presence of initiators could be cross-linked P[UA]-1. P[UA]-2 was formed by reacting PBHC with an isocyanate crosslinker [biuret of hexamethylene diisocyanate]. In both P[UA]-1 and P[UA]-2, the reactive sites for crosslinking were at the end of flexible chains to improve the overall flexibility of the IPN networks. The IPNs cured thermally at 80°C for 30 minutes and post-cured at 130°C for another 30 minutes showed improved weather resistance, higher tensile strength and adhesive strength when compared with original components. The authors have

also studied the morphology and Tgs of the IPNs.

A. Patsis et al.[74] have presented a novel type of ionomer/semi-IPN based coatings from polyurethane and vinyl chloride co-polymers. The ionomer/semi-IPN was prepared from a carboxyl containing vinyl chloride co-polymer [vinyl chloride, 84%, vinyl acetate 15% and maleic anhydride 1%] and polyurethanes with and without tertiary amine nitrogen in the polymer backbone at various polyurethane / vinyl chloride co-polymer ratios. The IPNs were cured thermally at 80°C for 2-3 hours and post-cured at 100°C for 16 hours. The evaluation tests revealed that the chemical and solvent resistance properties of the IPNs were very much improved over the homo-polymers and also the miscibility of the component polymers has well been enhanced by introducing oppositely charged groups to form ionic bonds.

A coating material based on epoxy and poly-chloro vinyl polymers claimed to be of polymer alloy type was developed and applied as paints in tons over rail transports systems in Moscow [Russia] in a single step spray method to a total dry film thickness of 60-120 microns. The performance of the IPN coating, as reported, was found to be excellent as an effective substitute to a multi-layer protective coating system of about 300-400 microns thick.[84]

Roesler et al.[85] have formulated a high solids coatings based on IPNs. In this work the authors have prepared a two-component polyurethane and acrylic cross-linked polymers and combined them to form an IPN with good performance. Though 100% reactive, the system was solvent reducible for spray application to over 80% solids. Quick drying time was achieved if the reactive diluent, a multi-functional acrylate, was radiation cured prior to the urethane curing.

A European patent[86] deals with a semi-IPN based on a linear vinyl or acrylic and a cross-linked polyester which could be better used as film former in coatings.

A Japanese patent[87] described an IPN based on polymerizing an alkyl acrylate or an alkyl acrylate and co-

polymerisable monomer in presence of a fumarate polymer. The IPN was claimed to be useful either as film former in coatings or as adhesive.

A patent filed by Koseino et al.[88] described an abrasion and corrosion resistant IPN based coating with improved adhesion and processability. This was based on an IPN of an irradiated and modified fluoro-polymer and an unnamed thermosetting resin.

Menorex corporation[89] in one of their patents have dealt with an aqueous thermoset type magnetic coating based on IPNs along with the method of preparation. The composition with improved toughness and stability comprised a pigment suspended in a polymeric binder having hard and soft segments and dispersant to disperse magnetic pigments. The polymeric binder was a semi-IPN with a soft segment, i.e. an acrylic emulsion with carboxyl groups which were cross-linked with the hard segment, i.e. urethane or vinyl emulsion. The dispersant used was a sodium polyphosphate of anionic electrolytic type.

Curable coating compositions based on acrylic and polyalkylene oxide polymers as IPNs have been reported in a European patent[90] with good storage stability and ability to form coatings and adhesives with improved mechanical properties, transparency and weather resistance. The polymer composition consisted of a co-polymer of alkyl methacrylate units, oxyalkylene polymer and curing accelerators. Both polymers contained silicon containing functional groups capable of crosslinking by forming siloxane bonds.

Patel et al.[91] have prepared IPNs from castor oil based polyurethanes and polyacrylate. The castor oil based polyurethane was prepared by reaction of the castor oil with a diisocyanate of either aliphatic or aromatic at varying NCO/OH ratios. The IPNs were prepared simultaneously by mixing the urethane pre-polymer along with the acrylic monomers, their crosslinking agents and initiators to form films after heat curing. The IPNs were reported to be resistant to various chemicals and had better mechanical properties.

Hitachi Chemical Corporation[92] have patented an IPN based on phe-

nolic resins for use in coatings as varnishes. The composition consisted of a phenolic resin together with an unsaturated rubbery polymer or oligomer and an azo- type initiator, which on heating formed an IPN. The material was claimed to possess satisfactory coating properties.

Ma.S et al.[193] have published a theoretical calculation for selecting the amount of crosslinking agents for castor modified epoxy/polyurethane based IPNs. In the publication, the authors have developed a sample IPN with improved properties as a proof to their theoretical data agreeing with the experimental data. R.S.Tu in a communication[94] explained the measurements of reaction rate and stoichiometry of several proprietary hydroxylated binders and water towards a polyisocyanate adducts of trimethylol propane.

Essex Speciality Products Inc. in USA have patented[95] an IPN based on one-component composition. The composition contained urethane/ epoxy/silicone polymeric networks. The networks were prepared by thermo-reversibly blocking of some of the isocyanate groups of a polyurethane prepolymer, reacting the remaining NCO-

with a silicone polycarbinol and a polyol and combining the resulting NCO- free prepolymer with a polyepoxide resin and a thermo-reversibly blocked polyamine curing agent.

Sequa Corporation[96] in a patent has reported paper-coating compositions based on IPN emulsion. The compositions were obtained by polymerizing poly vinyl acetate or an ethylene vinyl acetate or vinyl acetate/acrylic co-polymer with second polymer as polystyrene or styrene/butadiene or styrene/acrylic co-polymer. The physical properties of the dried films might be adjusted by varying the type and properties of the constituent polymers. This type of IPN was reported to possess high heat resistance.

Conclusion

IPNs, a sub-class of polymer alloys, possess interesting properties for use in coatings. They exhibit improved qualities over that of the neat polymers from which they are made. They find applications in many fields including protective coatings. They may be characterized using the modern instrumental techniques.

All the IPNs, exclusively studied as coating materials, convincingly show improvements as far as the essential coatings properties are concerned. While there is an IPN of ambient curing in the patent literature, not many IPNs cited possess this advantageous property, which is yet to be distinctively solved.

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