INTERPENETRATING POLYMER NETWORKS

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ABSTRACT

Interpenetrating Polymer Networks (IPN's) are shown to be applicable to solving a broad spectrum of difficult requirements in the reinforced plastics field. From a highly rigid, water impermeable sheet molding compound to corrosion resistant lab bench tops to tough resin rich areas capable of withstanding high speed impact, Interpenetrating Polymer Networks have done the job. Interpenetrating Polymer Networks (IPN's) adapt admirably to the fabrication of advanced composites. Pultruded unidirectional aramid and graphite fibers are processed with the ease of polyesters and give properties comparable to those found for epoxy systems.

1. INTRODUCTION

In the late 1970's, Freeman Chemical Corporation developed an SMC thickening process based on urethane chemistry. This system is defined as an Interpenetrating Polymer Network (IPN). An Interpenetrating Polymer Network in its simplest terms is any material containing two or more polymers which are synthesized or crosslinked in the immediate presence of each other.[1] These reactions may be simultaneous or sequential and may or may not result in separate phases. In many cases the end result of these reactions is a synergistic improvement of properties over those found for the polymer components individually.

Utilizing the company's acrylic polymer technology in conjunction with isocyanates an IPN system was patented.[2]. The first commercial application for this IPN system has been in containers for telecommunications equipment. In addition to the telecommunications application the IPN system has been expanded to a broad range of applications.

The application of the acrylic-isocyanate IPN concept has been applied to the following systems:

- A rigid water impermeable sheet molding compound.
- Corrosion resistant polymer concrete for laboratory bench tops.
- A very tough system which allows resin castings to withstand high speed impact.
- Pultruded unidirectional aramid fibers with IPN resins which process like polyesters and show properties similar to epoxies.
- Pultruded unidirectional graphite fibers mixed with IPN resins which give properties similar to epoxies.
- Thick laminates based on IPN resins and S-2 glass which give ballistic quality armor.

Each of the above systems shows unique properties applicable to the use intended. These observations are the basis for this publication. The resins used contain both vinyl and hydroxyl groups and have been designed specifically for reaction with isocyanates for the IPN applications noted.

REFERENCE: Weldon N. Reed and Michael Kallaur, **Interpenetrating Polymer Networks**, *SAMPE Quarterly, Volume 18, No. 3, April 1987, pp 16-20.*

2. SHEET MOLDING COMPOUND

Description and Properties of Various IPN Systems

As was noted above, Freeman Chemical patended an IPN system based on urethane chemistry for thickening Sheet Molding Compound (SMC). It was soon discovered that SMC panels molded from these formulations showed exceptional resistance to moisture absorption and high temperatures. The first commercial application for this system has been in containers for telecommunications equipment. Projected figures indicate that these containers when exposed to the elements will withstand moisture penetration for over forty years. A detailed description of this IPN SMC system is found in references.[3]

3. CORROSION RESISTANT RESIN CEMENT

Products such as sinks, troughs, laboratory bench tops, and furniture are subject to many corrosive chemical environments. The staples of this industry have long been epoxy cast composites or other fabrications which are treated with a chemically resistant gel coat. These products often take long periods of time to fabricate to a final cure.

A major manufacturer of laboratory furniture approached us to see if we could come up with a polymer concrete casting which would show good chemical resistance and be easy to fabricate. An IPN resin system was recommended. A silica filled, black pigmented composite based on an IPN resin system worked very well.

The formulation used in the polymer concrete casting is shown in Table 1. Component A is a resin with both vinyl and hydroxyl groups dissolved in styrene. Component B is a peroxide catalyst. C is a pigment additive. Component D is a medium molecular weight polyisocyanate, E is a two mesh grade silica and D is dimethyl aniline, used to initiate the vinyl polymerization at ambient temperature. The above ingredients were mixed with a Hobart mixer, then poured into a mold. After one hour of ambient temperature cure the casting was post cured for one hour at 120° C. The resultant casting was a shiny black slab.

Polymer concrete castings made by the above described process were evaluated for corrosive attack using forty nine chemicals commonly found in a chemistry laboratory. This evaluation was carried out by the Pittsburg Testing Laboratory using a commercial product as a control standard. The IPN and the control epoxy were comparable in properties. Thirty three of the reagents showed no detectable change in the working surface for the IPN system as compared to thirty two for the control. Fourteen of the reagents were rated as good to excellent for the IPN to fifteen for the control. These good to excellent ratings showed only a slight detectable change in color. Each system was rated as having two failures defined as pitting of the working surface.

Table 2 lists some highly corrosive acids, bases, oxidants and solvents which showed no detectable effect on either the IPN or the control standard working surface. Also listed are the reagents which caused a failure in each system. Although these are not the same chemicals for the two systems, they are very highly corrosive reagents and it is of no surprise that they would cause damage to most working surfaces.

TABLE 1
POLYMER CONCRETE FORMULATION
PARTS BY WEIGHT

A.	Resin	16.35
B.	Catalyst	0.32
C.	Pigment	0.40
D.	Polyisocyanate	8.16
E.	Filler	74.75
F.	Co-Catalyst	0.02

TABLE 2
THE EFFECT OF VARIOUS REAGENTS
ON IPN AND COMMERCIAL LAB BENCH TOPS

	RATING	
REAGENT	IPN	COMMERCIAL
Hydrochloric Acid 37%	NE	NE
Sulfuric Acid 77%	NE	NE
Phosphoric Acid 85%	NE	NE
Acetic Acid 98%	NE	NE
Ammonium Hydroxide 28%	NE	NE
Sodium Hydroxide 40%	NE	NE
Zinc Chloride Saturated	NE	NE
Tincture of Iodine	NE	NE
Ethyl Alcohol	NE	NE
Xylene	NE	NE
Chloroform	NE	NE
Ethyl Ether	NE	NE
Nitric Acid 70%	FAIL	FAIL
Hydrofluoric Acid 48%	G-E	FAIL
Dichloro Acetic Acid	FAIL	G-E

The IPN concrete castings have been shown to tolerate many highly corrosive chemical exposures without damage to the working surface. This resistance to corrosive attack along with the ease of fabrication make the IPN resin a viable candidate for polymer concrete type systems which are subject to harsh chemical exposures.

High Speed Impact Resins

Earlier work on the effect of molecular weight of the diisocyanate portion of an IPN system was reported earlier.[4] That study indicated that very tough products were achievable. When an application for a product that could withstand slamming into a concrete curb and not show any evidence of cracking was requested, it was decided to apply one of our very tough IPN systems.

When deciding on a resin to give the toughness properties required for the above application, two properties in particular are considered, Tensile Elongation and Izod Impact. Table 3 shows these properties for castings made from an acrylate resin with varying molecular weight diisocyanate components. The 78.3 percent tensile elongation and the unnotched Izod impact of 25.4 ft.lbs./in. indicated that the system utilizing the ultra-high molecular weight diisocyanate should be the system of choice.

The ultra-high molecular weight diisocyanate system was used to surround a compressed foam core which is expanded during the cure cycle.[5] Although a very tough resin rich edging resulted which would pass the impact test, considerable gassing resulted from the isocyanate and the expanding foam. Here is a case where the resin system

TABLE 3
THE EFFECT OF DIISOCYANATE MW ON
CLEAR CASTING PROPERTIES

	ISOCYANATE MOLECULAR WEIGHT		
PROPERTY	MEDIUM	HIGH	ULTRA-HIGH
Flexural Strength, psi	21,312	9,775	4,272
Flexural Modulus, 10^6 psi	0.57	0.27	0.13
Tensile Strength, psi	11,594	5,000	2,334
Tensile Modulus, 10^6 psi	0.50	0.26	0.13
Tensile Elongation, %	3.64	39.4	78.3
Unnotched Izod, ft. lb/in.	1.26	16.5	25.4
Hardness, Shore "D"	89	85	80
HDT, °C	97	68	43

Isocyanate Index = 90

itself has the properties desired but is not adaptable to the application.

IPN-Aramid and Graphite Pultrusions

As we move into the high-tech area where reinforced plastics will play a significant role, we find that the properties required must far surpass those found in todays systems. Often when one moves to high strength reinforcement such as aramid and graphite fibers it is discovered that these materials are often difficult to wet out. With some matrix systems, which do give good properties, the method of fabrication is often long and tedious. IPN resins on the other hand are easy to fabricate and give excellent properties when used with aramid and graphite reinforcements.

Freeman Chemical has developed several IPN resins which wet out aramid and graphite fibers exceptionally well. One resin system called, INTERPOL 47-1000, is based on a thermosetting acrylic used in conjunction with diisocyanate system of varying molecular weights. The IPN system has the distinguishing characteristics of having low viscosity, excellent wet out of aramid and graphite, good retention of physical properties at elevated temperature and excellent resistance to moisture absorption.

The INTERPOL 47-1000 IPN resin was pultruded with unidirectional aramid and with unidirectional graphite fibers into rectangular strips 0.5 inch wide by 0.085 inch thick. Table 4 compares the properties of the aramid

TABLE 4
PROPERTIES OF PULTRUDED ACRYLIC IPN -
UNIDIRECTIONAL KEVLAR™*

IPN - KEVLAR (58% by wt.)	RT	210°F	300°F
Flexural Strength (psi)	87,860	71,280	48,074
Flexural Modulus (psi x 10^6)	9.0	----	----
Short Beam Shear (psi)	5,490	5,100	3,195
Vinyl Ester Resin**			
Flexural Strength (psi)	80,000		
Flexural Modulus (psi x 10^6)	9.0		
Short Beam Shear (psi)	6,800		

* IPN = INTERPOL 47-1000
KEVLAR = 7400 DENIER - 17 STRANDS UNIDIRECTIONAL

**Data From: Diversified Fabricators, Inc.
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Winona, Minnesota 55987
Phone: (507)454-3799

system at room temperature to those found for a commercial vinyl ester system.[6] These data show the IPN resin system to be superior to the vinyl ester in flexural strength, equal in flexural modulus and lower in short beam shear. Properties at 210° F and 300° F are also shown for the IPN system. These data indicate that good properties are maintained even at 300° F.

In Table 5 the properties of the INTERPOL 47-1000 IPN resin system when pultruded with unidirectional graphite fibers are compared to those found for an epoxy-graphite and a vinyl ester system at room temperature and at 300°F.[6] Here we see that across the board the IPN system is comparable to the epoxy system and higher than the vinyl ester system. These properties and the ease of fabrications make the IPN system a viable candidate for use in graphite reinforced systems.

Pultrusions of another Freeman IPN resin INTERPOL 47-1050 which is based on an isophthalic resin system give equally good properties at room temperature but do not maintain the excellent high temperature properties or the resistance to moisture penetration observed for the acrylic system. The room temperature properties of the INTERPOL 47-1050 IPN resin based pultrusion of unidirectional aramid are compared to those found for a vinyl ester system in Table 6.

IPN-Ballistics Armor

The application of reinforced plastic materials on inner and outer portions of military vehicles is being explored. A major consideration is the reduction in weight while maintaining a high level of armor protection. IPN resins in conjunction with high tensile S-2 glass fit this application exceptionally well. Glass roving impregnated with IPN resin is collected in a roll with the layers separated by a film layer. After aging at ambient temperature for several days the system matures to a tacky state. The matured sheet is then cut to size and stacked. The fabricated part is nearly two inches in thickness and requires 67 plies of

TABLE 6
TYPICAL PREPREG FORMULATION FOR AN ACRYLIC IPN

		Parts By Weight
A)	INTERPOL 047-1050	82.0
B)	USP-245 (Peroxide Cat.)	1.0
C)	STYPOL 040-7263	17.0

VISCOSITY BUILD

Time (hrs)	CPS
Zero	140
0.5	175
1.0	250
2.0	500
20.0	48,000
72.0	900,000

TABLE 5
PROPERTIES OF PULTRUDED ACRYLIC IPN - UNIDIRECTIONAL GRAPHITE*

IPN-Graphite** (70% by wt.)	RT	210°F	300°F
Flexural Strength (psi)	233,000	188,000	124,000
Flexural Modulus (psi x 10^6)	17.7	----	----
Short Beam Shear (psi)	14,200	10,000	5,370
Epoxy Graphite**			
Flexural Strength (psi)	260,000	----	165,000
Flexural Modulus (psi x 10^6)	18.5	----	15.0
Short Beam Shear (psi)	14,000	----	7,500
Vinyl Ester**			
Flexural Strength (psi)	210,000	----	100,000
Flexural Modulus (psi x 10^6)	17.0	----	16.5
Short Beam Shear (psi)	12,000	----	4,100

* IPN = INTERPOL 47-1000
GRAPHITE = 35 STRANDS 12K UNIDIRECTIONAL

**See Table IV

material. The application of vacuum bag pressure and gradual heating results in an essentially void free laminate.

Physical properties for a laminate made with 24 oz. S-2 woven roving glass and an isophthalic IPN INTERPOL 47-1050 resin are shown in Table 7. These properties show that exceptional strength is generated by the IPN-S-2 glass composite. Outstanding is the tensile strength of 88,000 psi.

Ballistics testing indicates a close to 2500 ft/sec. V-50 value for the 1¾ inch thick laminate.

Additional studies using unidirectional glass banding tapes are also underway.

The more applications that we investigate the more new ones seem to develop. We at Freeman Chemical feel that only the surface has been scratched with the potential for Interpenetrating Polymer Network systems in the reinforced plastics field.

TABLE 7
PHYSICAL PROPERTIES OF IPN* - S-2 GLASS
ARMOR PLATE

PROPERTY	TEST METHOD	VALUES
Compression Strength	ASTM D695	38,309 psi
Tensile Strength	ASTM D638	88,110 psi
Short Beam Shear	ASTM D-2344	5,270 psi
Density		1,89 gms/cc
Glass 24 oz. Woven Roving		73.2%
Voids		3.3%

* IPN = INTERPOL 47-1000

4. CONCLUSION

The many applications of IPN resins in conjunction with various reinforcements or as casting materials show the versatility of using Interpenetrating Polymer Networks in solving many hard to fabricate problems. In addition to the systems described, Freeman Chemical IPN resins are being marketed or tested in many applications such as:

- Sound vibrational damping rods
- Low shrink additives
- Controlled shrinkage castings to replace metal parts
- Low smoke and flame retardant panels
- High strength wheel applications
- High performance bowling ball veneers
- High tensile polyethylene reinforced ballistics armor
- Resin transfer molding
- Corrosion resistant valves and bench tops

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