

**INTERPENETRATING POLYMER NETWORKS BETWEEN
NATURAL RUBBER AND POLYMETHYL METHACRYLATE:
EFFECT OF CROSSLINK DENSITIES ON THEIR
MECHANICAL AND PHYSICAL PROPERTIES**

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Abstract. Interpenetrating polymer networks (IPNs) were synthesized using natural rubber (NR) and polymethyl methacrylate (PMMA) via the sequential mode of polymerization. Dicumyl peroxide and divinyl benzene were used as the crosslinker of NR and comonomer/crosslinker for methyl methacrylate monomer, with benzoyl peroxide as the initiator. IPNs were prepared and characterised by evaluating their mechanical properties, swelling behaviour, density and the effect of solvents, by varying the degree of crosslinking of the base matrix NR. The results showed higher tensile strength, density and a lower percentage of swelling for IPNs. This is due to an increase in the number of crosslinks, calculated using Flory-Rehner equation for crosslinked polymers. The resultant IPNs was found to have a good resistance against most common solvents, thus showing great potential in the medical field as well as in the polymer industry, as films and coatings.

1.0 INTRODUCTION

Two polymers are believed to be miscible when they have the same (or similar) polarity, contain similar molecular fragments, form donor-acceptor (hydrogen) and other bonds and the components have similar stereo configurations and solubility in common solvents. Normal blending or mixing of polymers results in a multi-phase morphology due to the well known thermodynamic incompatibility of polymers mainly due to the low values of mixing entropy, (Sperling & Paul Newman [1-2]). As a result, the mixed polymer components separated into individual macroscopic phases with low adhesion towards each other. Consequently, such composites have poor aggregative stability and physico-mechanical properties. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains. The synergistic effects, (Sperling [1], Paul and Newman [2] & Mason and Sperling [3]) resulting from the threading and entanglement between the two networks not only influences compatibility and morphology, but also imparts new synergistic physical properties.

An extension of blending is to prepare mixtures of polymers where at least one component is crosslinked. When both polymers are crosslinked and intermeshed, the resulting product

is known as a 'true' interpenetrating polymer network (IPN). They represent an interesting approach to polymer blends (Paul and Newman [1] & Mason and Sperling [3]). IPN can be synthesized by either 'sequential' or 'simultaneous' techniques, (Sperling [1], Mason & Sperling [3], Klemmner, Yoon, Frisch & Frisch [4] and Sperling [5]). They will then exhibit a unique combination of properties.

It is thus the aim of this study, to synthesize IPN based on natural rubber (NR) with polymethyl methacrylate (PMMA) via the sequential mode of polymerization. Subsequently by varying the crosslink densities of NR, their mechanical and physical properties were determined.

2.0 EXPERIMENTAL

2.1 Materials Used

Natural rubber (NR) of SMR5 grade was used as supplied. Monomer, methyl methacrylate (MMA) and divinyl benzene (DVB), used as the crosslinker for PMMA, were supplied by Merck. They were prewashed with 10% aqueous NaOH and dried over molecular sieve 4A for one week and stored in the dark. Dicumyl peroxide (DCP) supplied by BDH was used as the crosslinker for NR. Benzoyl peroxide of BDH grade was recrystallized in chloroform and used as the initiator for the polymerization of MMA.

2.2 Preparations of IPN Samples

The preparation of IPN requires network I, NR, to be mixed with DCP on the 2-roll-mill. Curing takes place on the Brabender Plasticorder mixer at a temperature of 150°C. Subsequently the network is swelled into the monomer, MMA, crosslinker, DVB, and initiator, BPO, to form network II.

Table 1 Ratio of DCP in NR and NR/MMA in IPN

Samples	DCP in NR (phr) %	NR in IPN %	MMA in IPN %	NR/MMA Ratio in IPN
DCP-1	0.4	33	67	1:2
DCP-2	0.6	37	63	1:1.7
DCP-3	0.8	32	68	1:2
DCP-4	1.0	32	68	1:2
DCP-5	1.2	35	65	1:1.8
DCP-6	1.6	33	67	1:2
DCP-7	2.0	33	67	1:2
DCP-8	3.0	31	69	1:2.2
DCP-9	5.0	32	68	1:1.9
DCP-10	7.0	32	68	1:1.9
DCP-11	10.0	42	58	1:1.3

The samples were prepared according to the formulation in Table 1, whereby, samples of NR with different doses of DCP (0.4–10 phr) were swelled into MMA (50 ml), BPO (0.5

% by wt. of MMA) and DVB (6% by wt. of MMA) for a period of 15 minutes in a closed 500 ml bottle. After 15 minutes the samples were taken out to dry off excess MMA using filter papers. The samples were then weighed and kept in close bottles in the freezer for 24 hours for equilibrium to be achieved before being moulded at $\pm 120^\circ\text{C}$ for 4 hours.

2.3 Tensile Testing

The mechanical properties of the resultant samples produced were studied using the LLOYD 1000R tensometer (ASTM D412-87), using Type 2 dumb-bell test pieces and with a crosshead speed of 50 mm/min. For each DCP dose, 2 samples were prepared and for each sample 5-6 pieces were cut and tested. The results are the averages of all the samples tested.

2.4 Swelling test

Swelling tests were carried out to determine the swelling ratio, percentage of swelling, network-chain segment concentrations, η and molecular weight between crosslinks, \bar{M}_c .

A known weight of the samples, 1 cm by 1 cm, were placed in a stoppered bottle of freshly distilled toluene and replaced every 3 days for a period of one week. The sample weights were taken each day, until constant weight has been achieved.

Swelling Ratio, $Q = \text{Swollen weight}/\text{Initial weight}$

$$\text{Percentage of Swelling} = \frac{\text{Difference in weight}}{\text{Initial weight}} \times 100$$

2.5 Density Measurements

The densities of the samples were determined using an Electronic Densimeter, ED-120T. A known weight of the sample was immersed in the water and the density of the samples can thus be directly determined from the densimeter.

2.6 Solvent Effects

The effect of different solvents, both organic and inorganic were studied. However, for this purpose only one type of IPN samples (DCP-4) were evaluated by swelling into 40 ml of the different solvents and the percentage of swelling and swelling ratios calculated.

3.0 RESULTS AND DISCUSSION

3.1 Mechanical Properties

The results obtained from the tensile tests gave values for initial modulus, tensile strength and percentage of elongation at break are given in Table 2. Figure 1 shows the variation of stress versus strain at DCP concentrations varying from 0.4 to 10%. The modulus increases with increasing DCP, however, as the DCP concentration increases above 2.0 phr (DCP-7), the modulus decreases. The same is observed with the tensile strength curve in Figure 2, whereby there is an optimum between 0.8-3.0 phr DCP.

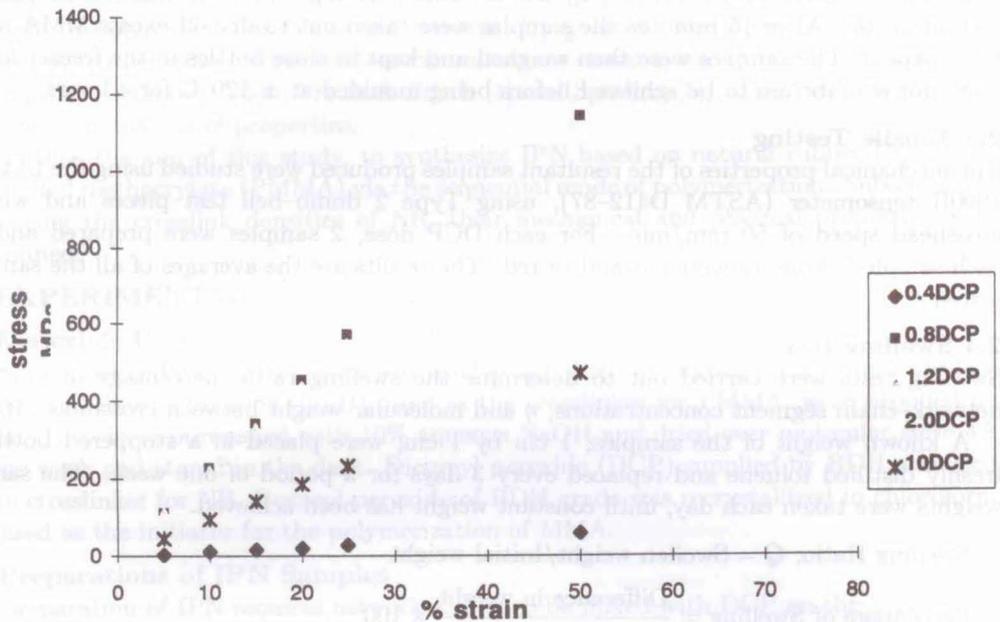


Fig. 1 Influences of DCP on the Stress-Strain curves for IPN

The dependency of tensile strength on the DCP concentration can be related to the phase homogeneity and the number of effective crosslinks of NR component in the NR-PMMA system. The higher the DCP concentration, the higher the number of crosslinks in NR matrix.

Crosslink densities (CLD) influences the morphology and properties of the resultant IPNs, Djomo [6] thus by increasing the DCP concentration, more crosslinks is being introduced into the rubber matrix. This in turn enhances the formation of interlocking ring structure or catenanes, Olabishi [7] resulting in interpenetration between the two networks formed. The excess DCP either promote chain-scission in NR or covalently bonded to PMMA chains. The second assumption is unlikely true because one will observe an increase in tensile strength when more PMMA are crosslinked. Therefore, the enhancement of tensile strength is a combined result of reinforcement by the glassy dispersed phase, increased physical entanglements and adhesion at phase boundaries due to interpenetration at higher crosslink densities of NR. However, as the DCP concentration increases beyond an optimum value (3.0 phr), the compatibility of components become less, the NR matrix could possibly be overcured, degraded or underwent reversion whereby it became soft and loses its strength, resulting in a decrease in tensile strength. Thus phase separation may proceed simultaneously with chain-scissions (Hoffman [8]) in NR.

Table 2 Influences of DCP concentration on tensile properties of NR-PMMA IPN

SAMPLES	MODULUS at 25% Elongation (MPA)	TENSILE STRENGTH (MPa)	% of Elongation at Break (mm)
DCP-1	28.59	5.44	10.28
DCP-2	332.94	17.21	61.92
DCP-3	570.48	25.40	22.92
DCP-4	493.48	22.87	26.04
DCP-5	542.37	19.97	49.39
DCP-6	272.32	19.70	21.92
DCP-7	374.72	20.29	24.50
DCP-8	368.07	23.17	24.95
DCP-9	88.32	15.28	22.90
DCP-10	374.63	18.99	43.28
DCP-11	235.82	15.07	94.39
NR*	0.071	0.274	523.9
NR10DCP*	0.237	0.429	367.2

*Tensile tests were also done on samples NR only and NR10DCP without PMMA.

3.2 Swelling Behaviour

The extent to which a network swells in a given solvent is inversely proportional to the polymer segment concentration. The swelling tests gave values for the swelling ratios and percentage of swelling for the IPN system. A graph of the DCP concentration against the percentage of swelling is described as in Figure 3. It is observed that IPN has a low percentage of swelling as compared to NR homopolymer network, which is an indication that tighter networks are formed due to an increase in the number of crosslinks contributed by the PMMA network.

We can determine the value of η network-chain segment concentration by measuring the equilibrium swelling behaviour of both crosslinked NR and the IPN samples. Thus applying the Flory-Rehner equation for crosslinked polymers, the values of η can be calculated, Sperling [9]. The value of χ_1 , interaction parameter used was for NR-toluene system, as the values of η calculated will represent the active network-chain segment of the rubber matrix.

The Flory-Rehner equation for crosslinked polymers can be written as:

$$- [1n(1 - V_2) + V_2 + \chi_1 V_2^2] = V_1 \eta [V_2^{1/3} - V_2/2]$$

$$\therefore \eta = - [1n(1 - V_2) + V_2 + \chi_1 V_2^2] / V_1 [V_2^{1/3} - V_2/2]$$

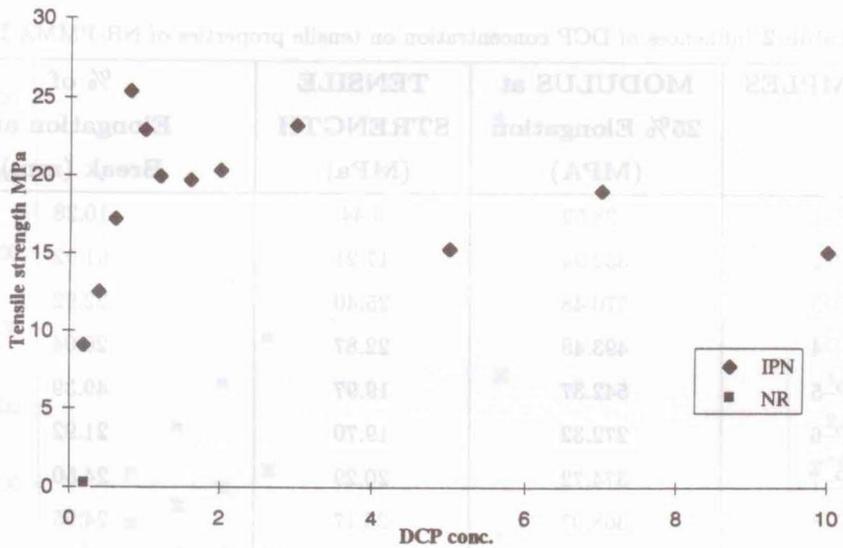


Fig. 2 Influences of DCP on tensile strength of IPN

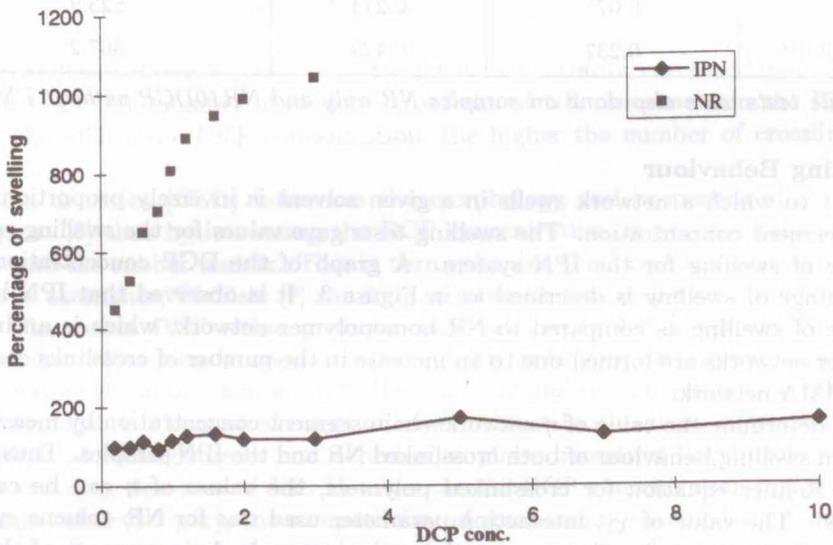


Fig. 3 Percentage of swelling for IPN and NR

where, η is the network-chain segment concentration, mol per cm^3 ; V_2 is the volume fraction of polymer in the swollen areas; V_1 is the molar volume of solvent and χ_{11} is Flory-Huggins

polymer-solvent interaction parameter (0.36 for NR-toluene at 25°) (Brandrup & Immergut [10]).

The crosslink densities were then calculated as follows: Crosslink Density (CLD) = $2M_c^{-1}$; whereby $\eta = \rho M_c^{-1}$ where M_c^{-1} is the molecular weight between crosslinks and ρ is the density of the sample.

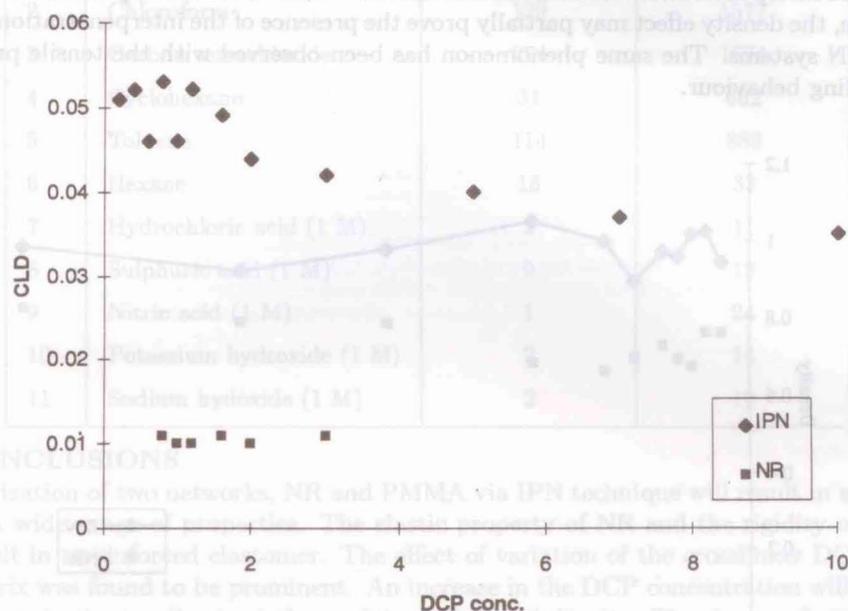


Fig. 4 Crosslink Densities of IPN and NR

An increase in the values of CLD is observed in Figure 4, the IPNs showing values four times higher than vulcanized NR. This can also be described in terms of the degree of penetration whereby the extent of molecular mixing will be higher when the values of crosslink density is also high resulting in finer domain sizes, thus smaller phase separation.¹¹ The fine domain sizes indicates greater mixing between NR and PMMA and hence more interpenetration on a molecular scale takes place, therefore increasing the compatibility and miscibility between them. However, for values of DCP greater than 3.0 phr, the extent of penetration between NR and PMMA decreases as the number of effective crosslinks decreases. The same phenomenon has been observed with the tensile properties of this IPN system.

3.3 Density

The density of NR (SMR5) was measured to be 0.891 g/cm^{-3} , and 0.970 g/cm^{-3} for vulcanized NR, (Brandrup & Immergut [10]). Figure 4 shows density versus DCP concentration curves for NR homopolymer and NR-PMMA IPN. It was observed that the densities of IPNs are greater than that of crosslinked NR homopolymer.

Most of the IPN system show a density effect (Kim, Klempner, Frisch & Frisch [12]). Millar [13] found that the measured values of the densities were higher than the theoretical

values based on volume additivity in his IPN systems. He explained that this phenomena was attributed to the interpenetration between two networks filling the relatively loose and amorphous molecular structure and the formation of more compact molecular structure. The experimental results in Kim and Klempner's work, (Kotaka, Nishi & Adachi [11]) revealed that there was a density effect and it was more apparent in the PU-PS IPN system than in the PU-PMMA system. As a result, if an IPN system consists of a rubber and a plastic and interpenetration between the two networks occurs, the density effect will appear. Therefore, the density effect may partially prove the presence of the interpenetration in some of the IPN systems. The same phenomenon has been observed with the tensile properties and swelling behaviour.

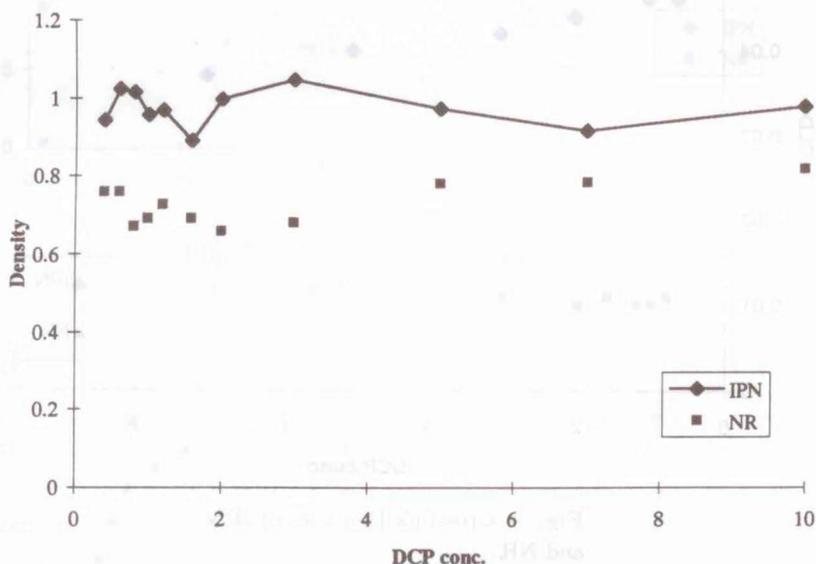


Fig. 5 Density of IPN and NR

3.4 Solvent Effects

The effect of different solvent on NR-PMMA system is tabulated in Table 3. IPN samples showed low percentage of swelling compared to NR indicating good solvent resistance.

The percentage of swelling is small in organic hydrocarbon like hexanes but increases with increasing chlorine concentrations of the solvent. However, it is still much less than that of NR homopolymer. Inorganic solvents exert little effect on the NR-PMMA IPN and NR samples.

Table 3 Effect of different solvents on NR-PMMA IPN system

No	Solvents used	% of swelling	
		IPN	NR
1	Chlorobenzene	187	1016
2	Chloroform	129	1577
3	Carbon tetrachloride	274	1694
4	Cyclohexane	31	662
5	Toluene	114	889
6	Hexane	15	32
7	Hydrochloric acid (1 M)	2	11
8	Sulphuric acid (1 M)	9	12
9	Nitric acid (1 M)	1	24
10	Potassium hydroxide (1 M)	2	14
11	Sodium hydroxide (1 M)	2	15

4.0 CONCLUSIONS

Polymerization of two networks, NR and PMMA via IPN technique will result in a polymer having a wide range of properties. The elastic property of NR and the rigidity of PMMA will result in a reinforced elastomer. The effect of variation of the crosslinker DCP on the NR matrix was found to be prominent. An increase in the DCP concentration will result in an increase in the tensile strength, modulus, CLD and density. The degree of crosslinking of the NR matrix influences the degree of penetration of PMMA networks. Increasing the concentration of the crosslinker, DCP resulted in the formation of higher concentration of effective crosslinks in the NR matrix. This in turn increases the mechanical and physical properties of the whole system. Increased miscibility is observed which in turn reduces phase separation for the IPN system. The mechanical and physical properties of the IPN will thus depend upon the crosslinking of the NR matrix. IPN shows great potential as films and coatings in the polymer industry and also in the medical field due to their very good resistance to most common solvents. As a result of new material technology, IPN has a great future in the rubber and polymer industries as the new polymer of the next century.

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