Synthesis and Characterization of Nano Silica filled Polyurethane and Polystyrene (PU/PS) Interpenetrating Polymer Network (IPN)

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Abstract— Interpenetrating polymer network (IPN) of castor oil based polyurethane (PU) and polystyrene (PS) was prepared by sequential polymerization. The polyurethane was prepared by reacting hydroxyl groups of castor oil with toluene diisocyanate (TDI) and polyurethane was swollen in polystyrene monomer and subsequently polymerized in the presence of the initiator benzoyl peroxide. The effect of different amount of nano silica (0–5%) on the properties of polyurethane (PU)/ polystyrene (PS) (50/50) IPNs, such as mechanical properties like tensile strength, modulus and percentage elongation at break have been reported. In past few years numerous work has reported on the polymer/ silica composite because of its special surface chemistry and reinforcing effects. Nano silica filled IPNs shows improved tensile strength than the unfilled interpenetrating polymer network (IPN) of castor oil based polyurethane (PU) and polystyrene (PS) system. Different properties of these samples were determined like resistance to chemical reagents, tensile strength, water absorption and surface hardness.

Index Terms— Castor oil, Chemical reagent resistivity, Interpenetrating polymer network, Nano silica, Polyurethane, Polystyrene, Toluene diisocyanate, surface hardness.

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1 INTRODUCTION

From the beginning of the material science to the present latest research, one objective is common that is, to combine numerous unique properties in one material. For this purpose, different combination techniques developed. These techniques based on the chemical as well as physical interaction of polymeric materials. These techniques provide the most effective way for the modification of properties of polymeric materials and to get a material with a desired unique set of properties for specific engineering applications. Among these combination techniques, IPN is most effective because of its numerous advantages over the other conventional techniques. IPN provides the best way to combine two or more mutually incompatible material efficiently.

According IUPAC (2007 Recommendations) IPN can be define as polymer comprising two or more networks that are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken [1]. IPN is a combination of two polymer networks where at least one polymer is synthesized or cross-linked in the presence of another polymer.

However, no covalent bonds exist between polymer structures in IPN only physical interaction exists between these structures, so during formation of IPN the monomers belongs to different polymer systems can't react with each other [2], [5].

Due to applications of IPNs in numerous fields of daily life, it is very attractive subject for the research. In IPN the polymer structures cannot be separated unless chemical bonds of individual polymer structure are broken because during polymerization, two different polymer structures developed such a

strong physical interaction that it is almost impossible to separate these structures until or unless bonds are broken[2], [5]. IPNs are classified into different classes based on the type of material, polymerization technique and sequence of polymerization. Based on polymerization sequence could be classified as sequential or simultaneous IPN. In sequential IPN, networks formed one after another. In simultaneous IPN, both networks formed at the same time. Another type of IPN is semi IPN in which one polymer is cross linked and one is leaner [2], [6], [7].

In this research work polystyrene interpenetrating polymer network has made with the polyurethane to get combination of distinct properties of both materials. PU is a distinctive polymer material with splendid physical and chemical properties because of its unique chemical structure[8], [9]. Properties of PU depend mainly depend upon the monomer from which it is synthesize here the term monomer represent the polyole and isocyanate type [9], [10]. Because of PU versatility, it is the most suitable material for various domestic and industrial applications like coatings, adhesives, fibers and foams [11], [12]. PU but it also has some disadvantages like poor mechanical strength and less thermal stability [13], [14], [15]. Numerous efforts had done to improve the mechanical as well as thermal stability of the PU. In the present research castor oil used as a polyole and toluene diisocyanate (TDI) used as a isocyanate for the formation of PU. Castor oil obtained from the natural source and it is renewable. It is biodegradable and nontoxic. It is basically vegetable oil and only natural source of this oil is the castor plant. It is triol, means it has three OH functionality. During the formation of carbamate linkage in polymerization reaction of polyurethane the OH group reacts with NCO group. In this reaction hydroxyl, functionality is provided by the castor oil [16], [17].

In this research we selected filler is nano silica. It is precipitat-

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ed nano silica powder white in color. Due to its some of unique properties like high surface to volume ratio, splendid surface chemistry, purity and extremely small size, nano silica is widely used in commercial applications. In past few years numerous works has reported on the polymer/ silica composite because of its special surface chemistry and reinforcing effects. Hydrophilic nature of the nano silica is due to presence of silanol and siloxane groups on the surface And these groups are responsible for the high degree of interaction between the silica filler and polymer matrix. Three type of silanol groups are present on the surface of nano silica; isolated silanols, vicinal silanols and geminal silanol [18]. Shown in Fig 1.

Fig 1: Silanol and siloxane groups are present on the silica surface;isolated silanols; vicinal silanols; geminal si-lanols[18].
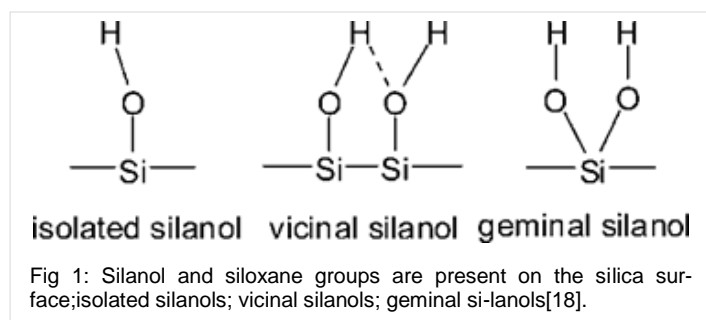
1.1 Previous Research Work:

In the literature several work have been reported on the synthesis, development and characterization of IPN of castor oil derived PU with different polymers and fillers. In 1999 Siddaramaiah with his coworker studied the effect of composition of castor oil derived PU/PS IPNs on the physical and mechanical properties. In this research physical, thermal and mechanical properties of castor oil derived PU/PS IPNs were described [19]. In 2001 and 2003 Jeevananda, Siddaramaiah studied the effect of concentration of conductive filler (PAni)CSA on the physical ,mechanical and chemical properties of castor oil derived PU/MMA IPN [20], [21]. In this research work mechanical analysis, thermal response and surface morphology of IPNs were studied. In 1999 Brovko observed the effect of Fe2O3 on PU IPN [22]. In 2006 Trakulsujaritchok and D.J.Hourston studied the Damping properties of silica filled PUR/PEMA IPN [23].In the present research our aim was to enhance the thermal, physical, and mechanical properties of PU/PS IPN by using silica as filler, where castor oil based PU used in this research. Different basic properties of IPN like tensile strength, percentage elongation, tensile modulus, water absorption, thermal analysis, surface morphology, surface hardness, resistance to chemical reagents have been described.

2 MATERIALS AND METHODS

2.1 Materials

Specifications of all chemicals are given in Table 1. Castor oil, TDI and DBTL were used for PU synthesis. BPO and styrene monomer were used for PS synthesis. EGDMA used as a cross linker. In this DBTL act as a catalyst and BPO was used as initiator.

TABLE 1

DETAIL OF CHEMICALS USED FOR THE SYNTHESIS OF NANO SILICA FILLED PU/PS (50/50) IPNS)

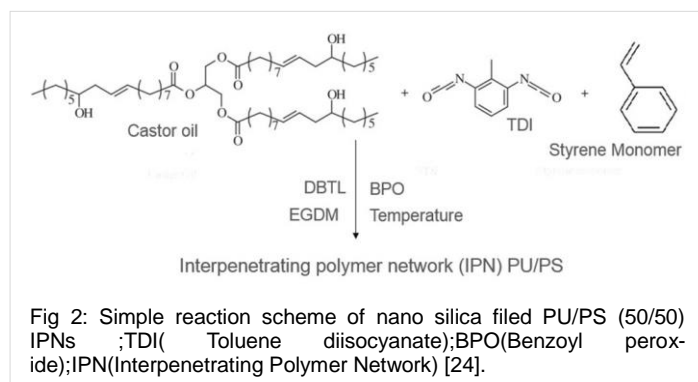|	Chemicals		Country
A	Castor oil	--------	Lahore, Pakistan
B	Styrene monomer	--------	Korea
C	Toluene diisocyanate	TDI	Germany
D	Benzoyl peroxide	BPO	UK
E	Dibutyltin dilaurate	DBTL	Germany
F	Ethylene glycol dimethacrylate	EGDMA	USA
G	Nano-silica	--------	Korea

2.2 Preparation of IPN

2.2.1 Preparation of PU/PS IPN

The IPN of PU/PS was formed by using sequential polymerization technique so synthesis procedure of IPN was started with the reaction of castor oil with TDI. The polyurethane is formed due to the reaction of NCO group with the OH group. In this research work NCO is provided by TDI and OH provided by castor oil and ratio of NCO to OH was kept 0.6.The reaction OH with NCO was occurred at room temperature in 1hr duration, in the presence of gentle and continuous stirring. Then styrene monomer with 0.5% dissolved initiator was added in PU and gentle mixing was applied for 10 min. BPO selected as an initiator for the Styrene monomer. 1% DBTL was added in the mixture, which act as a catalyst. 1% cross linker was added. In this research EGDM selected as a cross linker for PU and PS system. The mixture of PU and PS system was mixed at room temperature for 20–30 min. After this mixture poured into mold [19]. Provide specific time and temperature for the polymerization of PU and styrene monomer. These conditions are explained in next section.

2.2.2 Preparation of nano silica filled PU/PS IPN

As explained in above section pre polymer of PU and styrene monomer with BPO mixed in one beaker. Different weight percentage of nano silica added in the beaker and mixed with above mentioned mixture. 1% DBTL was added in the mixture, which act as a catalyst. 1% cross linker was added in this specific research work EGDM act as a cross linker. The mixture of PU, styrene monomer, initiator, catalyst and cross linker was stirred at 30℃ for about 30 min. After this stirring, mixture was poured into a mold. PU took 24 hr for the completion of polymerization at room temperature. The styrene monomer present in this flexible material was polymerized at 80 ℃ temperature. Then mold was kept at 110 ℃ for 10 h, to ensure complete polymerization and removal of unreacted monomers. PS was produced in this IPN through polymerization of Styrene monomer. The IPN sheet was cooled slowly and removed from the mold. In the present study up to 5% nano silica can be conveniently filled because after this certain agglomerates of nano silica appear within the samples. Simplest scheme of the process displayed in Fig 2.

Fig 2: Simple reaction scheme of nano silica filed PU/PS (50/50) IPNs ;TDI(Toluene diisocyanate);BPO(Benzoyl peroxide);IPN(Interpenetrating Polymer Network) [24].

2.3 Measurements

Brief over view of the standards, techniques and methods used for the characterization of the nano silica filled PU/PS (50/50) IPNs are following.

2.3.1 Tensile properties:

In tensile properties were measured according to ASTM D 638 using a TIRA-2810 UTM (at Department of Polymer & Process Engineering, UET Lahore, Pakistan) at ambient conditions. Three samples of single composition were tested and the average of measured values was calculated. The speed at which testing is performed was 50 mm/min. Tensile strength and percentage elongation at break was simply calculated from the data obtained from test. Modulus of elasticity was calculated by draw a line on the linear part of stress/strain curve. The slope of this line provided the modulus of elasticity [25].

2.3.2 Surface hardness:

Shore A scale is used for testing of sample. Shore hardness tested with an instrument called Durometer. Shore hardness measurements based on very simple principle, which is to measure the resistance of the indentation of a pin into the test specimen in the presence of standard load. ASTM standard D2240 used for measurement of surface hardness [26], [27].

2.3.3 Density:

Density is measured by using ASTM D 792. First of all measure the mass of sample in air. Then sample was immersed in water and mass of this sample in water was determined. By using these measurements specific gravity of these samples were determined [28]. To convert specific gravity to density multiplied the specific gravity with density of water.

2.3.4 Chemical reagent resistivity:

Percent loss in weight of samples of nano Silica filled PU/PS (50/50) IPNs in acids was examined by using Sperling and Mihalakis's method [21], [29]. In this specific procedure IPN samples remained in contact with acid solution at 25°C for 7 days. Than all samples were the dried at 60°C. After this by

using any weight balance percent loss in weight was determined.

2.3.5 Water absorption:

For the water absorption testing of the nano Silica filled PU/PS (50/50) IPN, ASTM standard D570 was used. Comparison of water absorption values of IPN samples made on the basis of values obtained in accordance with twenty four hour immersion method [30].

3 RESULTS AND DISCUSSIONS:

3.1 Tensile properties:

Data related to the tensile properties of the nano-silica filled PU/PS (50/50) IPNs is given in the Table 2. Increasing nano silica content in the IPN systems resulted in improved, mechanical behavior. Results showed an increase in the modulus. But decrease in elongation at break was observed. Tensile strength initially increased with the increase in filler concentration after certain amount of filler it showed gradual decrease.
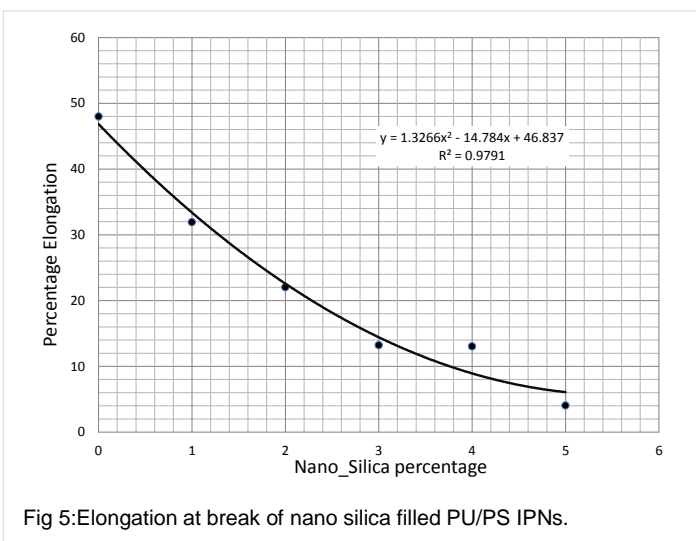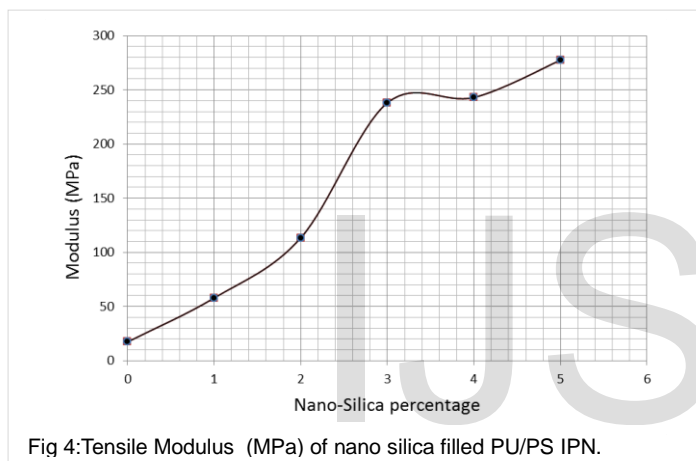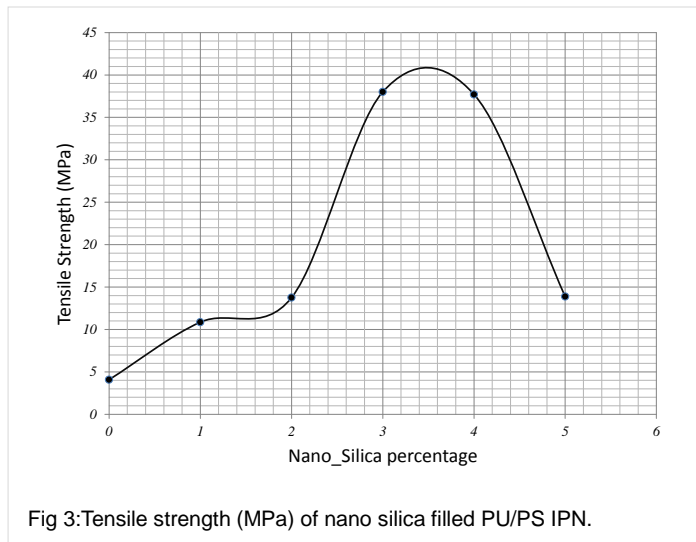
Tensile strength increased with filler concentration (Fig 3). This increase in the tensile strength is due to reinforcement of nano silica because high reinforcement can be achieved from those filler which have of very small particle size. Nano silica because of fine size made extensive adhesion with polymeric chains [23]. Decrease in tensile strength due to formation of agglomerates of nano silica [31]. Modulus increased with increase in nano silica (Fig 4). The particulate of the silica are rigid, when these particulate added in polymer caused an increase in modulus.[32], [33] The magnitude of this increase depends on the quantity of silica filler [34]. A decrease was observed in percentage elongation with increase in silica filler because flexibility of chains was decreased due to filler content (Fig 5)[33], [35].

The trend of the mechanical properties showed the high degree of possibilities of development in physical and mechanical properties by using proper ratio of filler. By using appropriate filler content increment from 4.08 to 38 MP observed. IPN samples showed maximum tensile strength at 3% nano silica content.

TABLE 2

MECHANICAL PROPERTIES OF NANO SILICA FILLED PU/PS (50/50) IPNs)

	Composition	Tensile Strength	Elongation at Break	Tensile Modulus	Density	Hardness
		MPa	%	MPa	g/cm³	Shore A
a	PU/PS+0% Silica	4.08	48	17.33	1.051	79
b	PU/PS+1.0% Silica	10.86	31.92	57.94	1.075	83
c	PU/PS+2.0% Silica	13.75	22.02	113.4	1.092	85
d	PU/PS+3.0% Silica	38.00	13.22	238.0	1.112	87
e	PU/PS+4.0% Silica	37.71	13.03	243.0	1.131	88
f	PU/PS+5.0% Silica	13.87	4.04	277.4	1.158	89

(a) PU/PS+0% Silica; (b) PU/PS+1.0% Silica; (c) PU/PS+2.0% Silica;(d) PU/PS+3.0% Silica; (e) PU/PS+4.0% Silica; (f) PU/PS+5.0% Silica

Fig 3:Tensile strength (MPa) of nano silica filled PU/PS IPN.

Fig 4:Tensile Modulus (MPa) of nano silica filled PU/PS IPN.

$y = 1.3266x^2 - 14.784x + 46.837$
$R^2 = 0.9791$

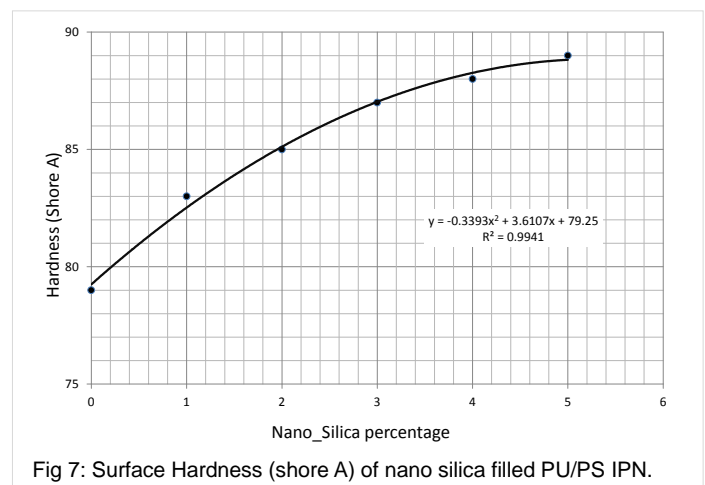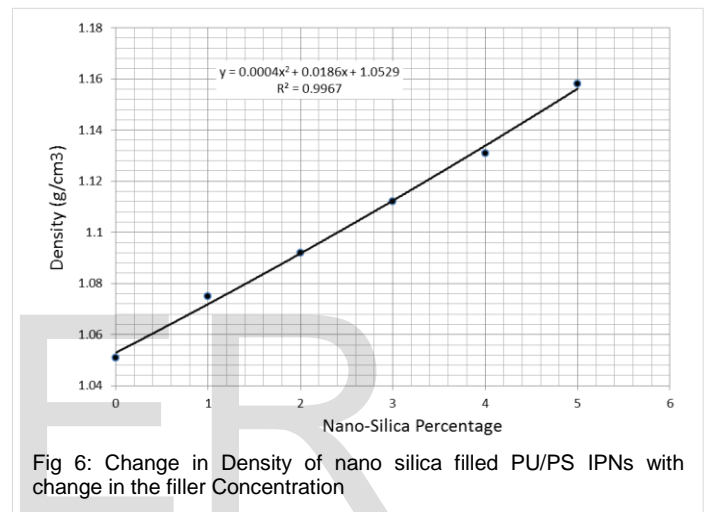Fig 5:Elongation at break of nano silica filled PU/PS IPNs.

3.2 Density:

Density of silica filled, castor oil based PU/PS IPN increased with the increase in the silica concentration (Fig 6). Results represented in Table 2. Particle density of the nano silica is greater than the density of the pure IPN of castor oil

based PU/PS IPN. So with the increase in the silica concentration overall density of the nano silica filled PU/PS IPN was increased [36], [37].

3.3 Surface hardness:

Nano silica filled PU/PS IPN samples showed improved surface hardness. These results showed high degree of dimensional consistency of IPNs samples. This result also supports the concept reinforcement of nano silica filler. Hardness value of IPN samples were fell in the range 79–89 Shore A. Results shown in Table 2 and Fig 7. Nano silica as filler increases the hardness. As the size of nano-silica is very small, it can be easily dispersed so nano silica filler established certain physical interaction with the base polymer which reduced the mobility of the chains and hence the hardness increased [38], [39].

$y = 0.0004x^2 + 0.0186x + 1.0529$
$R^2 = 0.9967$

Fig 6: Change in Density of nano silica filled PU/PS IPNs with change in the filler Concentration

$y = -0.3393x^2 + 3.6107x + 79.25$
$R^2 = 0.9941$

Fig 7: Surface Hardness (shore A) of nano silica filled PU/PS IPN.

3.4 Water absorption:

Water absorption of the nano silica filled PU/PS (50/50) IPNs increase with the increase in filler content. Significant change in water absorption was observed due to change in concentration of nano silica from 0% to 5%. This can be attributed to the hydrophilic nature of nano silica and polar groups present at the surface of nano silica Fig 1. These groups

have a high inclination to absorb water and increase the amount of water uptake [40]. Results are represented in Table 3.

TABLE 3

PERCENTAGE INCREASE IN WEIGHT OF NANO SILICA FILLED PU/PS (50/50) IPNs AT; 24°C

	Composition	% change in weight at 24℃ for 24h
a	PU/PS+0% Silica	1.6
b	PU/PS+1.0% Silica	2.1
c	PU/PS+2.0% Silica	2.6
d	PU/PS+3.0% Silica	3.2
e	PU/PS+4.0% Silica	3.6
f	PU/PS+5.0% Silica	4.2

3.5 Chemical resistivity:

The percentage loss in weight of IPNs was determined in H_2SO_4, CH_2O_2, HCl. IPN samples remained in contact with above mentioned acids at normal room temperature for 7 days, after this these samples were examined for the percent loss in weight and the results obtained from the experiment were furnished in Table 4. The results showed that there was no significant loss in weight and no change or deformation in the physical appearance of any sample of the silica filled PU/PS IPN. PU undergoes hydrolytic degradation (Fig 8). The hydrolytic degradation of the PU on exposure to the hostile chemical environment may be attributed to the increased hydrolytic potential. But high temperature is required for the hydrolysis. This reaction leads to the formation of secondary amine and CO_2 is evolved. The reaction is accelerated by acids like H_2SO_4, CH_2O_2, HCl. In case if hydrochloric acid solution amine hydrochlorides, polyols and CO_2 are produce (Fig 8) [41], [42]. With the increase in silica percentage weight loss decreased, because silica is resistance against acids and it prevented the weight loss up to some extent (Fig 9).

TABLE 4

PERCENTAGE CHANGE IN WEIGHT

Chemical Reagents		Silica contents in PU/PS IPNs (%)					
		0	1.0	2.0	3	4	5
a	HCl	1.42	1.35	1.33	1.20	1.14	1.06
b	CH_2O_2	0.89	0.85	0.70	0.75	0.60	0.60
c	H_2SO_4	1.50	1.46	1.38	1.35	1.35	1.30

Percentage change in weight on treatment with different chemicals reagents(after 7 days at room temperature);chemical reagents consist of 10% solution of;(a)HCl;(b) CH_2O_2;(c) H_2SO_4.

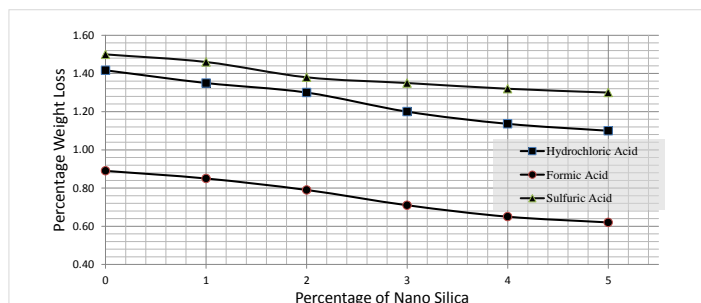Fig 8: Reaction involve in the degradation of Nano-silica filled IPN

Fig 9: Percentage loss in weight on treatment with different chemicals reagents (after 7 days at room temperature) chemical reagents consist of 10% solution of;HCl; CH_2O_2;H_2SO_4

4 SUMMARY & CONCLUSIONS:

Silica filler consisting of very fine powders was added in the IPN. The different effects of silica filler were detected by changing the concentration of silica from 0 to 5% weight percent. In mechanical testing, modulus of elasticity, tensile strength, and the percentage elongation at break were three basic parameters observed. These all parameters shown variation by changing silica concentration, but the trends of variation are different for all parameters. Mechanical properties of silica filled PU/PS IPN, improved with the increase in silica content. Incorporation of the silica filler in IPN caused stiffening in the polymeric chains so the modulus of the IPNs showed increasing trend. Elongation at break was decreased, because the flexibility of chains was decreased due to filler content. Particle density of the nano silica is greater than the density of the pure IPN so with the increase in the silicon concentration overall density of the IPN increases. Filler contents form physical interaction with the base polymer which reduces the mobility of the chains and hence the hardness increased. Mechanical testing of PU/PS IPN exhibit greatly improved mechanical strength due to filler loading. Thermal analysis of these samples showed high degree of improvement.
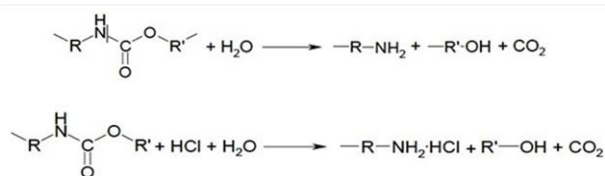
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