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Abstract. Organic inorganic hybrid coating possess superior coating properties. In the current paper studies have been carried out to compare the coating properties of pure organic polyurethane and inorganically modified polyurethane. By changing the concentration of Si in polyurethane matrix various results were compared for hardness, flexibility, adhesion, scratch resistance, storage stability. Our results concluded that inorganically modified polyurethane with 8% Si has optimum coating properties.

INTRODUCTION

Surface coatings are at the leading edge of advance technology as well as part of the traditions of old craft. Despite the fact that surface coatings have been known since the beginning of time, the subject is still very present today in research laboratories worldwide. Coatings play a significant role in modern technology, and this role is escalating as expectations for coating's quality of performance and range of applications increases. Coatings are no longer just passive barriers, but increasingly play an active role, chemically, electrically and biologically. For instance, they are designed to release inhibitors for corrosion prevention, to release biocides. It is clear that there is growing scope for research and development in an area of coating technology that continues to expand.

Surface coatings are classified on basis of elements present in backbone chain which can be organic coatings, inorganic coatings and organic-Inorganic hybrid coatings [1-3]. It is observed that organic coating and inorganic coating have few drawbacks like lower durability, dependence on substrates, less U.V. resistance, etc. Some of these drawbacks can be eliminated by using organic inorganic hybrid coatings. Hybrid coatings are known to exhibit superior coating properties as compared to organic coatings and inorganic coatings. Hence, in the current paper we have concentrated on hybrid coatings. There are various methods for preparation of organic-inorganic hybrid materials. One of them is SOL-GEL method [4]. The sol-gel process is a convenient means of producing hybrid nanocomposites. Hybrid nanocomposites rely on the history of organic and inorganic phases incorporated into the material.

Polyurethane has better crosslinking properties as compared to polyester [4]. Hence, we have used polyurethane as an organic component which is prepared by reacting polyester with polyisocyanate. Polyester was prepared using trimethylol propane, neopentyl glycol and azelaic acid. This polyester was then inorganically modified using TEOS to enhance its coating properties, which was further reacted with TMP-TDI adduct to give polyurethane. From thermodynamics, it is known that polyester is directly incompatible with TEOS hence MEMO is used as a coupling agent. TEOS can be directly hydrolyzed and it can be used to modify polyester, but this would yield inferior coating properties [6,7]. Hence use of coupling agent is preferred. In the present study we have compared coating properties of pure organic polyurethane and inorganically modified polyurethane. By varying the concentration of inorganic component we have determined the concentration at which optimum properties were obtained.

A. Experimental

Raw materials

Raw materials used in this project are Tetraethoxy methasilane (TEOS), 3methaacryloyloxy propyl trimethoxy silane (C.R) (MEMO), Methanol, (A.R), Hydrochloric acid (A.R), Azelaic acid (A.R),



Neopentyl glycol (A.R), Trimethylol propane (A.R), Toluene diisocyanate (A.R), Dibutyltin dilaurate (A.R)

Synthesis of materials

1. Synthesis of sol

52 g TEOS was dissolved in 42.2 g of absolute ethanol at 52⁰ C and was hydrolyzed with 2.25 g of water and 0.55 g nitric acid. The sol was then heated at 53⁰ C for 60 min before addition of 2.25 g of water. After heating another 10 min at 53⁰ C, 31 g of MEMO was added resulting in silane/silica ratio of 1:2. The sol was heated for 30mins before adding another 4.5 g of water and heated at 53⁰ C continuous for another 30 mins and solvent was removed by vacuum distillation. [U.S. Patent no. 5231156]

2. Synthesis of gel (Polyester)

A 500 mL capacity three necked flask, equipped with motorized stirrer, a nitrogen gas inlet tube and a reflux condenser, was placed with weighed quantities of azelaic acid, trimethylol propane and neopentyl glycol. Depending upon the calculated Hydroxyl value (OHv) accurate weights of all the above were taken. Initially glycol components were charged in a reaction vessel and mixture was heated at about 70⁰ to 80⁰ C till it melts. After the complete melting of glycols, measured quantity of azelaic acid was added to the mixture and the reaction temperature was further raised to 235-240⁰ C and the reaction was continued for another 6-7 hours till the calculated amount of water is being removed.

Final traces of water were removed in the form of azeotrope using xylene as a solvent. The reaction mixture was stirred continuously and a slow stream of nitrogen gas was passed through the mixture at a constant rate to provide inert atmosphere. Once the required temperature was reached the heating was discontinued. Condenser tube was then placed in distillation position and the polyester so formed was heated under reduced pressure and at a temperature which was maintained at 70⁰ C. The polyester so formed was then cooled to room temperature and stored in an air – tight bottle. However, just prior to use, polyester formed was dried again under vacuum at about 100⁰ C to 110⁰ C. To remove any traces of water, which might have got in during storage. The polyester so formed was stored in an airtight bottle.

1. Synthesis of sol-gel hybrid i.e., inorganically modified polyester:

A 500 mL capacity three necked flask, equipped with motorized stirrer, was placed with weighed quantities of SOL and GEL which was obtained from above process. Varying quantity of SOL, it was added to GEL and calculated amount of ethyl acetate was added. Resulting solution was stirred for 30 mins at 160⁰ C to obtain SOL-GEL hybrid. This hybrid was inorganically modified polyester. SOL concentration were varied as 0%, 3%, 8%, 10% and 15%

2. Synthesis of polyisocyanate:

A 500 mL capacity three necked flask, equipped with motorized stirrer, nitrogen gas inlet tube and a reflux condenser, was placed with weighed quantities of trimethylol propane and toluene diisocyanate. TMP was taken in small batches and was added to total weight of TDI taken. TMP was taken in batches in order to avoid any increase in temperature as this is an exothermic reaction and has to be carried out around 60⁰ C. The reaction mixture was heated to a temperature of about 60⁰ C to 70⁰ C for about 4 to 5 hours. The reaction mixture was stirred continuously and a slow stream of nitrogen gas was passed through the mixture at a constant rate to provide inert atmosphere. Calculated amount of solvent i.e. ethyl acetate was added. Solvent was added to ensure proper mixing of TMP and TDI. As the temperature increases above 60⁰ C, heating was discontinued. Condenser tube was placed in distillation position and the polyisocyanate was heated under reduced pressure. The polyisocyanate so prepared was stored in airtight bottle.

However, just prior to use, the polyisocyanate was dried again in an oven maintained at 100⁰ C to 110⁰ C to remove any traces of moisture, which might have got in during storage.

3. Synthesis of inorganically modified polyurethane:

Prepared polyisocyanate and inorganically modified polyester were weighed accurately and was directly mixed. 2-3 drops of DBTDL catalyst was added. Synthesis of inorganically modified polyurethane is described in Fig. 1.

RESULT AND DISCUSSION

Characterization

1. Characterization of SOL (Particle size analysis):

Particle size is an important factor in deciding the final industrial use of siliceous soil. Particle size was measured using 'Malvern Instrument India Ltd' at 25°C. Mean intensity particle size diameter of TEOS-MEMO adduct i.e. SOL was found to be 90.1 nm as depicted in Fig. 2. The sol is considered to consist of nano particles of silica.

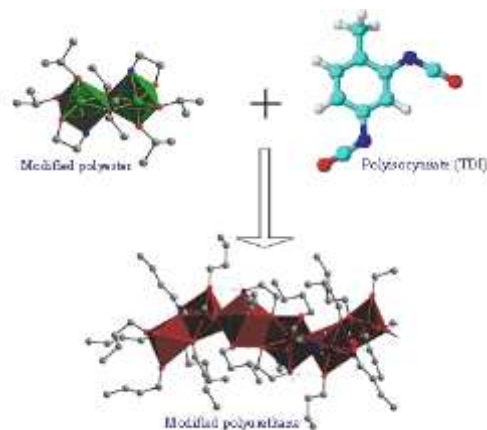


Fig. 1. Synthesis of Polyurethane

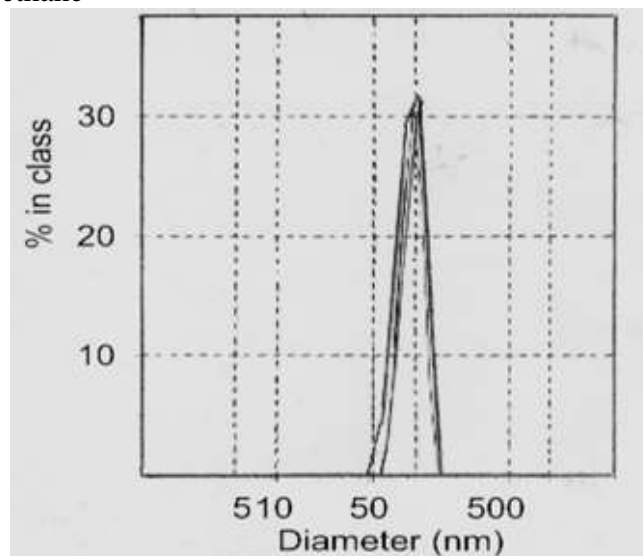


Fig. 2. Graph of particle size analysis

2. Using IR spectroscopy:

IR spectroscopy has been found to be highly useful in the field of polymer chemistry. It is used to indicate the functional groups present and also give information about H-bonding, conformation orientation.



Shimadzu FTIR – 4200 dual beam spectrophotometer was used to record IR Spectra of the polymer in the range of 4000-400 cm^{-1} . The tentative assignments of observed bands in modified polyurethane (8%Si) is shown in table 1.

Table 1. IR Spectra of polyurethane

Assignments	Wavenumber (cm^{-1})
-OH	3430-3300
-CH ₂ stretching	2961-2967
Free C=O and hydrogen bonded C=O	1729,1731
C-N-C	1146
C-C skeleton vibration	1055
Si-O-Si	761, 735

1. Thermo-gravimetric analysis

Using 'Diamond' Perkin Elmer Analyzer, the decomposition profile of silica modified PU film were thermogravimetrically analyzed. Film samples extending from 4-6 mg were placed in platinum sample pan and heated from 30-800°C, under N₂ atmosphere at a heating rate of 100 C/min. Temperature difference and weight loss were recorded as a function of temperature. The table 2 displays the initial degradation temperature (IDT) and temperature at 50% (T₅₀) weight loss for different silica hybrids.

Table 2. TGA thermogram data

Sample	Si (0%)	Si (5%)	Si (8%)	Si (10%)	Si (15%)
IDT	160 ⁰ C	185 ⁰ C	210 ⁰ C	210 ⁰ C	210 ⁰ C
T ₅₀	285 ⁰ C	315 ⁰ C	385 ⁰ C	360 ⁰ C	344 ⁰ C

From the thermogram data it can be observed that initial degradation temperature was maximum for 8 % Si sample and then remained constant. Temperature at 50 % weight loss was found to be maximum for sample with 8 % Si which, clearly indicates that sample with 8 % Si has maximum thermal stability.

Analysis of coating properties of inorganically modified polyurethane

Mild steel panels of size 6'x 4' and glass panels used for coating were used after pre-treatment as described below:

1. Preparation of mild steel panels for testing of coating films:

The 24 – gauge mild steel panels of size 6'x 4' were first cleaned free of greasy materials by treating them with hot 10% sodium hydroxide solution, followed by rinsing with cold water. Rust that might have been present was removed by rubbing with sandpaper. Any emery particles left over, were cleaned off by cloth. The panels were dipped in phosphoric acid solution (1:1) at room temperature for one minute and then rinsed immediately with distilled water for a minimum of 15 secs. Next, these panels were sprayed with 95



% denatured alcohol containing 1 % by volume of ammonium hydroxide. Finally, the panels were dried at 80-90^o C and stored in a desiccator until needed.

Glass panels of size 6'x 4' were degreased in an alkali (sodium hydroxide) solution and swabbed subsequently with water and xylene before film application.

Method of Application of Resins on to the panels: All the samples of resins were applied onto mild steel and glass panels using a bar coater (18-cm film width, 50 μ m film thickness, Sheen Instruments Ltd., Surrey, England). Drying times (air drying and baked drying at 120^o C) of all the compositions was determined. The dried film obtained was approximately of about 35 \pm 2 μ m thickness.

The samples were studied for the various coating properties like hardness, flexibility, adhesion, impact resistance, chemical resistance and storage stability [8]. The results of all the tests thus performed are mentioned in the table 3.

Table 3. Coating properties at different percentage of Si

Coating properties	AA+ NPG+ TMP				
	Si (0%)	Si (5%)	Si (8%)	Si (10%)	Si (15%)
Pencil Hardness	H	2H	5H	4H	4H
Scratch Resistance (g)	1200	1400	>2000	1500	1500
Shore Hardness ^A	67	73	92	81	80
Flexibility	Passes	Passes	Passes	Passes	Passes
Adhesion (%)	100%	100%	100%	100%	100%
Impact resistance Direct/ Reverse (inch-lb)	100/100	120/120	160/160	140/160	140/160
Storage stability	>8 months	>8 months	>8 months	~4 months	~4 months
Chemical Resistance					
Water ^a	No effect	No effect	No effect	No effect	No effect
1% H ₂ SO ₄ ^b	Slight blush	Slight blush	No effect	No effect	No effect
1% NaOH ^c	High blush	Slight blush	No effect	No effect	No effect

Where, a = immersed for 24 h in water.

b = immersed for 24 h in acid.

c = immersed for 24 h in alkali

CONCLUSION

By varying the different concentration of Si in PU matrix it was observed that the hardness properties (shore A and pencil hardness) were minimum for pure organic coatings but increases in hybrid coatings.



Maximum hardness was observed for hybrid coating containing 8% Si. Adhesion was found to be 100 % at all concentration and each and every sample passes the flexibility test. But impact resistance (direct/reverse) as well as scratch resistance was found to be minimum for pure organic coating and increased in hybrid coating. Impact resistance was 160 inch-lb (both direct as well as reverse) for sample with 8% Si and was found to be maximum. The scratch resistance was found to be more than 2000 for coating with 8% Si which clearly shows that hybrid coating (with 8% Si) have better property as compare to any other sample. Storage stability was found to be maximum for sample with 8% Si. This sample remained unaffected when tested with acid and alkali and have successfully passed water immersion test. Hence, it can be concluded that inorganically modified polyurethane with 8% Si has optimum coating properties.

REFERENCES

- [1] R. Zandi, A. Rahimi, "Silica based organic–inorganic hybrid nanocomposite coatings for corrosion protection," *Prog. Org. Coat*, vol. 53, pp. 286-291, 2005.
- [2] A. D. Wilson, J. W. Nicholson, H. J. Prosser, Elsevier Applied Science, 1987.
- [3] C. Sanchez, B. Julia'n, P Belleville, M. Popall, "Applications of hybrid organic–inorganic nanocomposites," *J. Mater. Sci.*, vol. 15, pp 3559-3592, 2005.
- [4] D. Randall S. Lee, *The polyurethanes handbook* Wiley, 2003.
- [5] Y. Chen, S. Zhou, G Chen, "Preparation and characterization of polyester/silica nanocomposite resins," *Prog. Org. Coat*, vol. 54, pp. 120-126, 2005.
- [6] N.G. Cave, A.J. Kinloch, "Self-assembling monolayer silane films as adhesion promoters," *Polym J.*, vol. 33, pp 1162-1170, 1992.
- [7] Sajjadi, S. Pooyan. (2005). Sol-gel process and its application in Nanotechnology. *J Polym Eng .*, vol. 13. pp38-41, 2005.
- [8] J. V. Koleske, *Mechanical Properties of Solid Coatings*. Encyclopedia of Analytical Chemistry, 2006.