

## Study of Effect of NCO/OH Molar Ratio and Molecular Weight of Polyol on the Physico-Mechanical Properties of Polyurethane Plaster Cast

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**Abstract:** Polyurethane plaster cast was an open weave fabric bandage, prepared by coating polyurethane prepolymer on raschel knitted fiberglass and polyester fabric. Curing takes place by coming in contact with water to form hard rigid cast. Polyurethane prepolymers were synthesized by reacting molar excess of diphenyl methane diisocyanate (MDI) with polypropylene glycol (PPG) at 60°C for 2 hours. This effect of different NCO/OH molar ratio and molecular weight of polyol on the tack free time, setting time, diametral compression strength, percent elongation and tensile strength of polyurethane plaster cast were investigated. It was observed that with increase in NCO/OH molar ratio, tack free time and setting time of the cast decreases, whereas diametral compression strength increases. Tensile strength was determined in universal testing machine and was found to increase with increasing NCO/OH ratio while opposite trend was observed in case of percent elongation. With increase in polyol molecular weight, tack free time and setting time of the cast increases, whereas diametral compression strength decreases. Blended polyols i.e. PPG 1000 with PPG 400 in 50/50 ratio gives tensile strength and diametral compression strength in between their unblended counterparts. In comparison to fiberglass cast, polyester cast has higher percent elongation and diametral compression strength.

**Key words:** Polyurethane plaster cast • Prepolymer • Fiberglass cast • Polyester cast

### INTRODUCTION

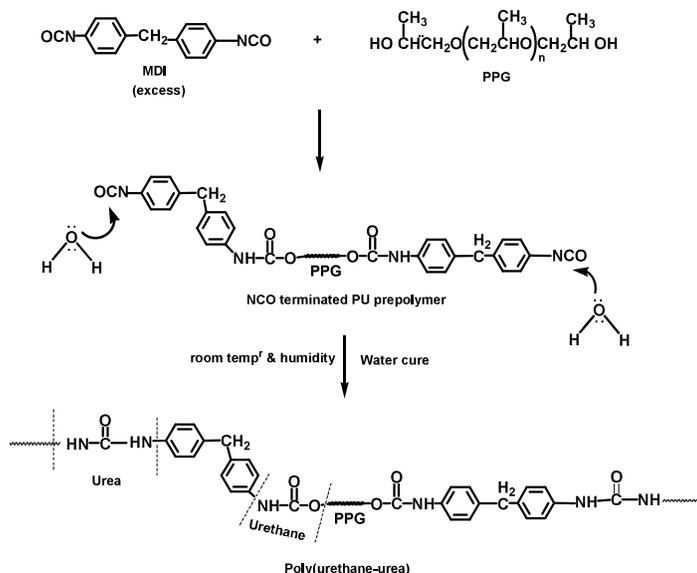
Polyurethanes are considered one of the most versatile classes of polymers for medical applications. By varying the type and amount of polyol, diisocyanate and catalyst, polyurethane with a wide range of physical and mechanical properties can be obtained [1]. One such potential application is in the field of orthopedic plaster cast. Orthopedic plaster cast is used to immobilize injured joints during fracture and for the support and immobilization of ligamentous and muscular structures in case of sprains [2]. Prior to 1980, the vast majority of such rigid casts were made of plaster of paris (POP) [3]. Even though POP cast is largely used, owing to its low cost and easy to apply, it suffers from disadvantages such as long setting times, messy application, low strength to weight ratio and high water permeability. These drawbacks have stimulated research for a better alternative material for this purpose [4].

Synthetic casting materials such as fiberglass impregnated with polyurethane resin are feasible alternatives to POP cast and are gaining popularity. They are stronger, lighter and they may facilitate weight bearing capacity in less time than POP cast. Nowadays, polyester fabric is also being used for making the cast owing to its easy availability, affordable price, good extensibility and less hygroscopicity [5].

Preparation of polyurethane plaster cast involves impregnation of polyurethane prepolymer onto the fabric in a coating machine. Before application, the cast is dipped in water, squeeze slightly to remove excess water and bound around the contours of the patient's limb. The water causes the prepolymer to polymerize, thereby producing a hardening and shaping effect on the relevant part of the patient [6].

For such applications, a moisture sensitive polyurethane prepolymer is the base material, which is finally polymerized in the presence of water to form a

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Scheme 1: Synthesis of poly(urethane-urea)

network of poly (urethane-urea). The reaction scheme for synthesis of poly (urethane-urea) by reacting molar excess of diphenylmethane diisocyanate (MDI) and polypropylene glycol (PPG) is shown in scheme 1. The crosslinking of the prepolymer to a solid end product occurs in the presence of water.

For orthopedic application, an adequate concentration of isocyanate group is necessary to have proper reactivity, workability and strength. Thus, the polyurethane prepolymer for this application is prepared by taking excess of MDI, so as to provide sufficient isocyanate content for reaction with water.

The major considerations for a satisfactory cast material is that it should be easily handleable, shouldn't deleteriously affect the limbs, should have reasonable time or work life, so as to allow a reasonable period of time for molding the cast around the contours of the limb, should be feasible during application [2]. After the resin impregnated scrim has been immersed in water, sufficient work time e.g. 3 to 5 minutes should be given in which wrapping is accomplished and the cast is manually molded into the desired shape. After the cast is shaped, the resin should harden rapidly, typically in 15-30 minutes and preferably less, into a rigid, high strength, weight bearing cast [7].

The properties of the polyurethane plaster cast can be tailored simply by varying the NCO/OH molar ratio and the molecular weight of polyol. The polyglycol moieties which form the soft segment provides elastomeric character to the polymer, while diisocyanate which form

the hard segment provides dimensional stability [8]. According to the literature, for preparing the polyurethane plaster cast, it is preferable to use NCO/OH ratio of the diisocyanate and polyol to about 1.2:1 to 4.5:1 and most preferably 1.8:1 to 3.8:1 [9]. The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO groups and those containing OH group. Also, the preferred molecular weight of polyols is usually below 2000, most preferably between 700 and 1000. It was reported that by using high molecular weight polyol, the rigidity of the cast can be reduced whereas using a polyol with molecular weight less than 400 has been found to be brittle when cured, thus not suitable for use in a supporting bandage [10,11].

In our present study, an effort was made to study the effect of different NCO/OH molar ratio and the molecular weight of polyol on the physico-mechanical properties of the polyurethane plaster cast. The properties studied were tack free time, setting time, diametral compression strength, percent elongation and tensile strength.

### Experimental

**Materials:** MDI was obtained from Sigma-Aldrich, USA. A white solid flakes (melt.pt. 40°C), it was used as such without further purification. PPG was obtained from Sigma-Aldrich, USA. Some properties of MDI and the PPG used for the synthesis of polyurethanes are given in Table 1. Catalysts 2,2' dimorpholino diethyl ether (DMDEE) from Degussa, Germany was procured and used as such without any purification.

Table 1: Properties of MDI and PPG used for the synthesis of polyurethane prepolymer

Property	MDI	PPG400	PPG1000	PPG2000
Average functionality <sup>a</sup>	2.0	2.0	2.0	2.0
OH number (mg KOH/g) <sup>b</sup>	0.0	281	111	56
NCO content (wt%) <sup>b</sup>	33.8	0.0	0.0	0.0
Molecular weight (g/mol) <sup>a</sup>	250	400	1000	2000
Viscosity 25°C, (cSt) <sup>a</sup>	50	99	150	300

<sup>a</sup>Information given by supplier

<sup>c</sup> Estimated by ASTM D2572 - 97(2010)

Table 2: Properties of the fabrics used for preparing polyurethane plaster cast

Properties	Fiberglass	Polyester
Knitting pattern	Raschel	Raschel
GSM (gm/m <sup>2</sup> ) <sup>a</sup>	275	310
Width(cm)	10.2	10.2

<sup>a</sup>Determined as per ASTM D3776/D3776M-09ae2

Table 3: Compositions of the synthesized polyurethane prepolymers

MDI/PPG system	NCO/OH molar ratio	MDI (g)	PPG400 (g)	PPG1000 (g)	PPG2000 (g)	NCO content (%)
MDI/PPG1000	1.2:1	23.1	-	77	-	1.2
MDI/PPG1000	1.5:1	27.3	-	72.7	-	2.9
MDI/PPG1000	2:1	33.3	-	66.6	-	5.4
MDI/PPG1000	2.5:1	38.5	-	61.5	-	7.0
MDI/PPG1000	3:1	42.8	-	57.1	-	8.1
MDI/PPG400	3:1	65.2	34.7	-	-	14.2
MDI/PPG2000	3:1	27.2	-	-	72.7	5.7
MDI/PPGBlend1	3:1	51.7	13.8	34.7	-	7.7
MDI/PPGBlend2	3:1	38.5	10.2	-	51.3	5.3

Blend1= PPG1000 and PPG400 in 50/50 ratio

Blend2= PPG2000 and PPG400 in 50/50 ratio

Methyl ethyl ketone (AR grade), obtained from sdFine Chem Limited, Mumbai was procured and used as received without further purification. Fiberglass was procured from Nickunj Eximp Enterprises Pvt Ld, Mumbai and polyester fabric from Photo Goods Service, Delhi. Some properties of the fiber glass and polyester fabric used in this study are reported in Table 2.

**Synthesis of Polyurethane (PU) Prepolymer:** The preparation of PU prepolymer was carried out in a 5-necked glass reactor equipped with teflon stirrer, thermometer pocket, condenser and nitrogen gas inlet system. The polyol was vacuum dried for 2 hours at 80°C and kept overnight in molecular sieves prior to use to ensure that the material is free from moisture (less than 0.5%). The MDI flakes was melted in a beaker and poured into the reactor under nitrogen atmosphere. Inert atmosphere was maintained throughout the reaction so as

to avoid the ingress of atmospheric moisture. The required amount of catalyst was then added followed by addition of PPG. The PPG was added partwise to the reactor. After that, the system was maintained at 60°C for two hours at 250-270rpm.

After 2hr, a small portion (approx 5gm) of PU prepolymer was taken out from the reactor for determination of %NCO content. The rest amount of the PU prepolymer was then diluted with methyl ethyl ketone (40% of the total wt of the prepolymer) and stirred for 3 to 5 minutes for thorough mixing of the solvent. The prepolymer was diluted with solvent for easy applicability of the prepolymer onto the fabric. If the viscosity of the prepolymer is high enough, sufficient amount of resin will remain in the tape and the desired physical properties will not be obtained.

The composition of the synthesized polyurethane prepolymers was given in Table 3.

**Preparation of the Polyurethane Plaster Cast:** The polyurethane plaster cast was prepared by uniformly coating synthesized PU prepolymer onto the fabric in a roller coating machine at room temperature and relative humidity of 35-40%. Two types of fabric were coated i.e. fiberglass and polyester fabric. The weight of the prepolymer coated onto the fabric range from 216 to 267gm/m<sup>2</sup>.

**Characterization:** The prepared polyurethane plaster casts were tested for various properties.

**Tack Free Time, Setting Time and Diametral Compression Strength:** The setting time and diametral compression strength was determined as per ASTM F 1536-95. A test cylinder was prepared by immersing the casting tape (width 10.2cm) in water, squeezing out the excess water, then wrapping around a cylindrical mandrel with outside diameter of 50mm producing a five layer cylinder.

The tack free time was reported as the time elapsed from the initial immersion, until the test cylinder becomes nontacky to touch. The data given are the average of three measurements.

The setting time was then determined by a manual indentation test, that is the time elapsed from the initial immersion, until the test cylinder cannot be indented by moderate fingernail pressure. The test should be repeated every 15 seconds till all the samples are set. An average of three measurements was taken as the result.

After the test cylinder has set, it was removed from the mandrel taking care not to deform the cylinder. The release liner from the inside of the test cylinder is removed. After 24 hours, the test cylinder is compressed 10mm at a speed of 50mm/min from the initial load position without noticeable failure or a measurable decrease in load in a universal tensile machine. This load at 10mm deflection, called maximum deflection load was noted. The diametral compression strength (in N/mm) was then calculated by dividing the maximum deflection load by the width of the test cylinder. The result given is an average of three measurements.

**Tensile Strength and Percent Elongation:** The tensile strength and percent elongation of the cured casts were determined in a universal testing machine, Tinius Olsen, H5KL. The dimension of the test specimen was 25cm x 7.5cm x 0.15cm and the measurement was performed under load cell of 5kN with a crosshead speed of 50mm/min at room temperature. An average of five measurements was taken as the result.

## RESULTS AND DISCUSSION

Polyurethane prepolymers were synthesized using five different NCO/OH ratio (1.2:1, 1.5:1, 2:1, 2.5:1, 3:1) using MDI and PPG1000 and five different molecular weight of polyol (PPG400, PPG1000, PPG2000, PPG1000 and PPG400 in 50/50 ratio and PPG2000 and PPG400 in 50/50 ratio at NCO/OH ratio of 3:1. Hence, ten polyurethane prepolymers were synthesized. These synthesized prepolymers were then coated onto two types of fabric i.e. fiberglass and polyester to prepare the polyurethane plaster cast. Thus two types of cast were obtained i.e. fiberglass cast and polyester cast and they were in the form of long polyurethane coated fabric of about 1.5mm thickness.

**Tack Free Time and Setting Time:** The tack free time and setting time of the cured fiberglass and polyester cast at different NCO/OH ratio was plotted in Figure 1 and 2, while its effect against molecular weight of the polyol was shown in Figure 3 and 4.

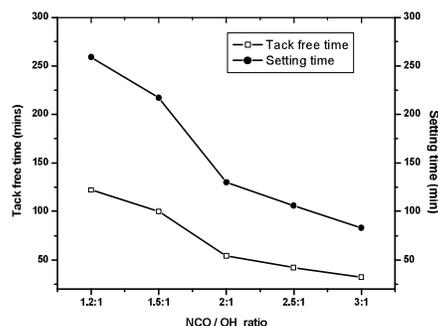


Fig. 1: Effect of increase of NCO/OH ratio for a system of MDI and PPG1000 on the tack free time and setting time of fiberglass cast.

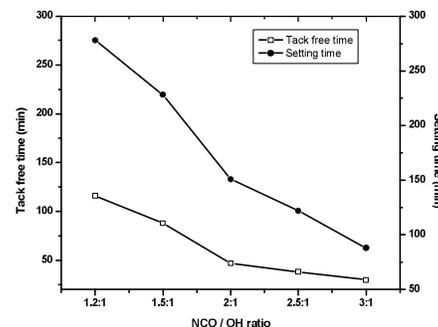


Fig. 2: Effect of increase of NCO/OH ratio for a system of MDI and PPG1000 on the tack free time and setting time of polyester cast.

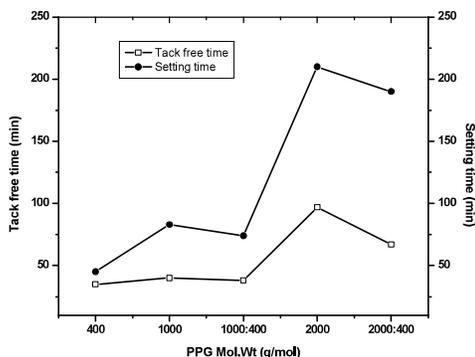


Fig. 3: Effect of polyol molecular weight of PUs with NCO/OH ratio of 3:1 on the tack free time and setting time of fiberglass cast.

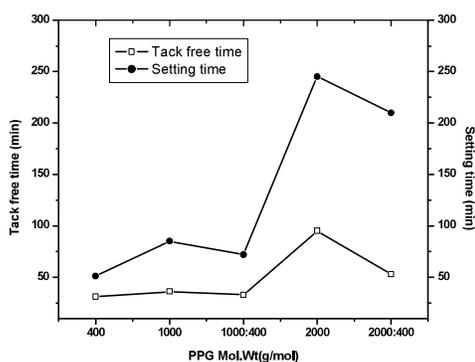


Fig. 4: Effect of polyol molecular weight of PUs with NCO/OH ratio of 3:1 on the tack free time and setting time of polyester cast.

As can be seen from the figures 1 and 2, with increase in NCO/OH molar ratio, tack free time decreases from 122mins to 32mins in case of fiberglass cast and from 116mins to 30 mins in case of polyester cast. Also the setting time decreases from 259mins to 83 mins in case of fiberglass cast and from 278min to 88min in case of polyester cast. This may be due to the fact that increasing NCO/OH ratio, increases the available isocyanate content of the prepolymer, thus generating more reaction site for reaction with water to increase the degree of crosslinking and finally hardening of the cast (as shown in Scheme 1). The increase in available isocyanate content was evident from %NCO content of the synthesized prepolymers (Table 3), which shows an increase with increase in NCO/OH molar ratio.

Thus it was observed that tack free time and setting time can be reduced by increasing the NCO/OH molar ratio. In our present study, the minimum values achieved fall short of the desired targeted values.

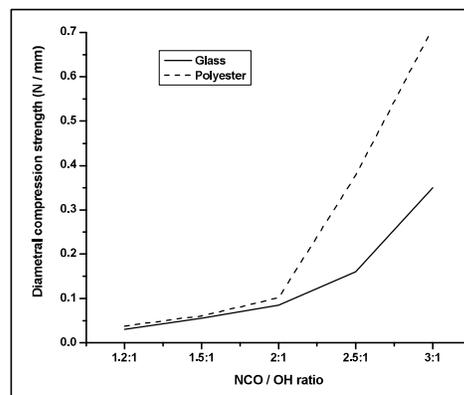


Fig. 5: Effect of increase of NCO/OH ratio of MDI-PPG1000 system on the diametral compression strength of the fiberglass cast and polyester cast

In order to achieve the desired values, it would be necessary to enhance the rate of crosslinking by way of either changing the catalyst or by varying the process parameters.

It was observed from figure 3 and 4 that, as the molecular weight of the PPG was increased from 400 to 2000, the tack free time increases from 28mins to 97mins in case of fiberglass cast and from 26mins to 95mins in case of polyester cast. Likewise, the setting time also increases from 40mins to 210mins in fiberglass cast and from 46mins to 245mins in case of polyester cast. This might be due to the fact that, as the polyol molecular weight increases, the amount of polyol incorporated for a given NCO/OH molar ratio also increases. This results in decrease of % NCO content of the prepolymer (evident from Table 3), which results in less availability of reaction site for reaction with water, thus causing an increase in tack free time and setting time of the cast. The rise in tack free time and setting time was sharp when the molecular weight was more than 1000. This shows that the PPG to be used for the purpose should be of molecular weight within 400 and 1000. Blending of PPG 1000 with PPG 400 and PPG 2000 with PPG 400 in 50/50 ratio, gives tack free time and setting time in between their respective counterparts.

**Diametral Compression Strength:** The effect on diametral compression strength of the fiberglass and polyester cast at different NCO/OH molar ratio was plotted in Figure 5, while its effect against polyol molecular weight was shown in Figure 6.

It was observed that with increase in NCO/OH molar ratio, the diametral compression strength of the cast increases from 0.01N/mm to 0.24N/mm in case of fiberglass

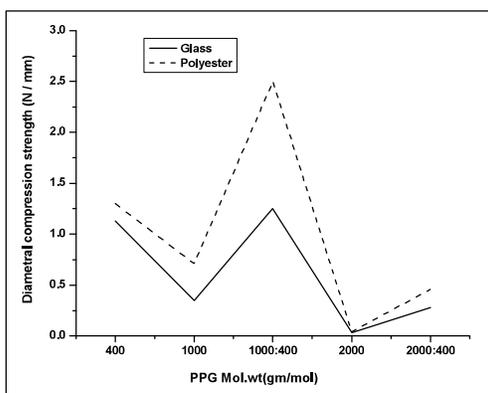


Fig. 6: Effect of polyol molecular weight of PU with NCO/OH ratio of 3:1 on the diametral compression strength of the fiberglass cast and polyester cast

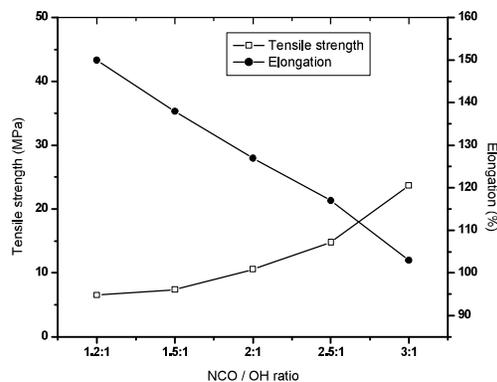


Fig. 8: Effect of increase of NCO/OH ratio of MDI-PPG1000 system on the tensile strength and percent elongation of the polyester cast.

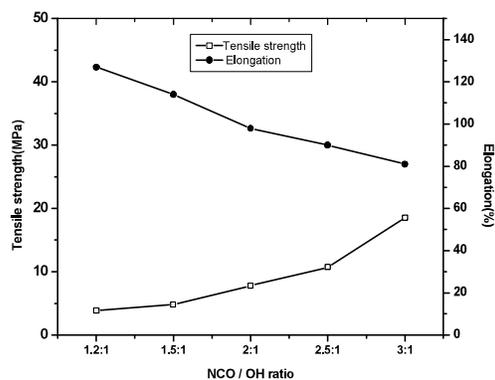


Fig. 7: Effect of increase of NCO/OH ratio of MDI-PPG1000 system on the tensile strength and percent elongation of the fiberglass cast.

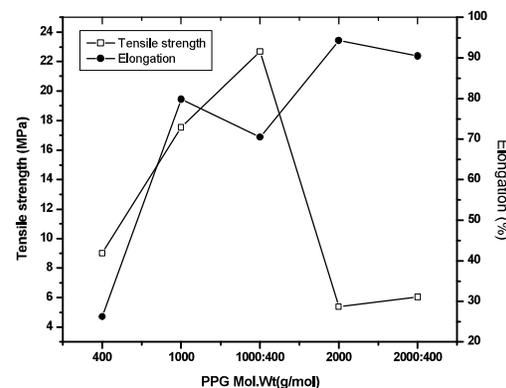


Fig. 9: Effect of polyol molecular weight of PU with NCO/OH ratio of 3:1 on the tensile strength and percent elongation of the fiberglass cast.

cast and from 0.02N/mm to 0.62N/mm in case of polyester cast. As the NCO/OH molar ratio increases, the available isocyanate content of the prepolymer increases. These free NCO group will react further to form three dimensional allophanate or biuret crosslinks or polar urea structure thus increasing the number of urethane groups [7,12]. The increase of intermolecular attraction of hard to hard segment by the increase of NCO/OH ratio tends to increase the diametral compression strength of the cast.

Also with increasing molecular weight of the polyol, diametral compression strength of fiberglass cast decreases from 1.03N/mm to 0.025N/mm and from 1.2N/mm to 0.03N/mm in case of polyester cast. As the polyol molecular weight increases, the soft segment content increases for any given NCO/OH molar ratio.

This decreases the rigidity of the cast and lowers the diametral compression strength. Prepolymers having blended polyols i.e. PPG 1000 with PPG 400 and PPG 2000 with PPG 400 in 50/50 ratio, gives diametral compression strength in between their respective counterparts. In comparison to fiberglass cast, polyester cast has higher diametral compression strength, this may be due to the fact polyester substrate used here has higher GSM (as mentioned in Table 2).

**Tensile Strength and Percent Elongation:** The tensile strength and percent elongation of the fiberglass cast and polyester cast at different NCO/OH ratio was plotted in Figure 7 and 8, while its effect against polyol molecular weight was shown in Figure 9 and 10.

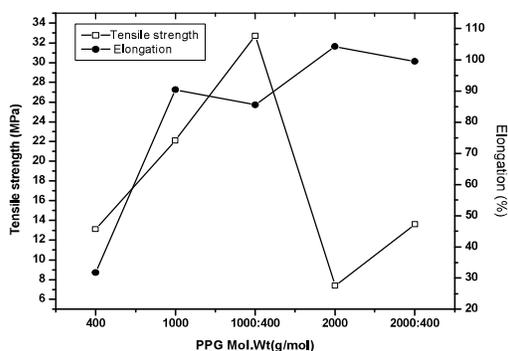


Fig. 10: Effect of polyol molecular weight of PUs with NCO/OH ratio of 3:1 on the tensile strength and percent elongation of the polyester cast.

It was seen from the figures 7 and 8 that the tensile strength of the fiberglass cast varied from 3.85MPa to 18.53MPa and in polyester cast, it was varied from 6.5MPa to 23.7MPa with increasing NCO/OH molar ratio. But with increase in NCO/OH molar ratio the percent elongation of the fiberglass cast decreases from 127% to 81% and from 150% to 103% in case of polyester cast. This is due to the same reason as described in case of diametral compression strength, which increases the tensile strength and decreases the percent elongation as the NCO/OH molar ratio was increased. Polyester cast was observed to have higher percent elongation in comparison to fiberglass cast, due to the fact that polyester substrate is more flexible and can give under load rather than cracking and spitting, which sometimes occur in fiberglass substrate due to its rigidity [13, 14]. Tensile strength is nearly the same in case of both the cast.

From the figures, it was observed that with increase in polyol molecular weight from 400 to 2000, percent elongation increases from 27.5% to 95.7% in fiberglass cast and in polyester cast it increases from 40% to 116%. Tensile strength of both the cast increases upto PPG 1000, thereafter decreases. This is due to the fact that increasing polyol molecular weight, increases the chain length of the soft segment, which in turn make the urethane chain more flexible. This results in increasing the percent elongation of the cast, whereas the higher content of soft segment results in lowering the tensile strength with increasing molecular weight of the polyol. Blended polyols i.e. PPG 1000 with PPG 400 in 50/50 ratio gives highest tensile strength in case of both the cast. Here also, in comparison to fiberglass cast, polyester cast has higher percent elongation. The reason behind this is same as discussed above.

## CONCLUSION

The studies reveal that the tack free time and setting time of the cast can be decreased by increasing the NCO/OH molar ratio of the prepolymer, whereas opposite trend was observed on increasing the molecular weight of the polyol. Lowest tack free time and setting time was observed in PU system having NCO/OH molar ratio of 3:1 and polyol molecular weight 400. The PU system having NCO/OH molar ratio of 3:1 gives highest tensile strength and diametral compression strength to the cast. The tensile strength increases with increasing the NCO/OH molar ratio, whereas percent elongation follows opposite trend. Blended polyol i.e. PPG1000 with PPG400 in 50/50 ratio gives highest tensile strength. The percent elongation of the cast increases with increasing the molecular weight of the polyol. In comparison to fiberglass cast, polyester cast has highest elongation and diametral compression strength.

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