Synthesis and Characterization of Poly (urethane-urea) based on Functionalized Polystyrene and MDI

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Abstract: *The poly(urethane-urea) based on α, Ω, hydroxy terminated polystyrene (OH-PSt-OH), 4,4'-methylenediphenyldiisocyanate(MDI) and three different diamines is prepared by a melt polymerization method. The length of the soft segmentis varied from 2310 to 9366 g/mol using MDI as a chain extender. The synthesized copolymer is characterized by viscosity measurements, FT-IR,temperature dependent FTIR,DSC, TGA,swelling ratio and solvent resistivity. The inherent viscosity of the polymeris found to be in the range of 0.5-2.3dL/g is suggesting that the polymerare of high molecular weight. Differential scanning colorimetry (DSC) data'sare confirming that the melting temperature of the polymer varies from 237°C to 263°C. From the temperature dependent FTIR, the crystallinity obtained for hard segment is around85%. The TGA data reveal that the polymer shows single stage decomposition center around 414°C.The solubility in chloroform and swelling ratio of the polymer depending on the concentration of the hard segment.*

Keywords: *Poly(urethane- urea), decomposition, crystallinity, swelling ratio, solvent resistivity.*

I. Introduction

Segmented copolymer consists of alternating hard and soft segments. The hard segments are in either glassy or crystalline state and upon phase separation they form physical crosslinks with the amorphous

(soft)segments. This morphology accounts for the typical thermoplastic elastomer behavior[1].Generally, phase separation occurs in most TPUs due to the intrinsic incompatibility between the hard and soft segments: the hard segments[2], composed of polar materials, can form hydrogen bonds and thus tend to cluster or aggregate into ordered hard domains, whereas the soft segments form amorphous domains. Phase separation, however, is often incomplete, i.e., some of the hard segments are dissolved in the soft domains.In many TPUs, the hard domains are immersed in a rubbery soft segment matrix. Depending on the hard segment content, the morphology of the hard domains changes from isolated to interconnected domains. The presence of hard domains in segmented polyurethanes is very important parameter which affects the mechanical properties. In segmented polyurethanes, the hard domains act as physical crosslinks which playing a role similar to chemical crosslinks in the vulcanzation of rubber and imparting the material's elastomeric behavior. Since hard domains also occupy a significant volume and are stiffer than soft domains, they also function as effective nano-scale fillers and rendera material behavior similar to that of a composite[2]. A wide variety of combinations in property can be achieved byvarying the molecular weight of the hard and soft segments, their ratio and chemical type. At present, thermoplastic polyurethanes are an important group of polyurethane products because of their advantage in abrasion and chemical resistance, excellent mechanical properties, tissue compatibility and structural versatility[3,4].

There are a wide variety of aromatic or aliphatic diisocyanates are used depending on the desired thermal and mechanical properties of the final material. Among the most commonly used aliphatic diisocyanate is 1,6-hexamethylene diisocyanate (HMDI). This diisocyanate is often used due to their greater UV stability when compared to aromatics.[5] 1,4 trans-cyclohexyldiisocyanate (CHDI) is used less frequently due to its cost, toxicity, and volatile organic compounds (VOCs). Aromatic diisocyanates include para-phenylenediisocyanate (*p*PDI), meta-phenylenediisocyanate (*m*PDI), 4,4'-methylenediphenyl diisocyanate(MDI). Such aromatic species are generally chosen because they are more reactive than the aliphatics and as such, the latter often require the need for catalysts during the chemical reaction[6,7]. Chain extenders are low molecular weight amine terminated compounds that play an important role in polymer morphology. The choice of chain extender and diisocyanate determines the characteristics of the hard segment and to a large extent the physical properties of polyurethane. Diamines react faster with isocyanates and result in the formation of the hard segment with a high density of secondary bonding, high *T*g, and high thermal stability of the polymer[8].

Polystyrenes are high Tg (100°C) materials extensively used in electrical, electronics, medical, home application, packaging industry, etc. The amorphous polystyrene like other amorphous polymers possesses poor solvent resistance and environmental stress cracking. To improve the solvent resistance of amorphous polymers, they are often blended with a high melting semi-crystalline material at a higher quantity (>40 wt. %).[9,10] Also

amorphous polystyrene has been modified by reacting with diisocyanates to form semi-crystalline polyurethane. In this way a semi-crystalline copolymer is obtained and it found to have both amorphous soft segment (SS) and crystalline hard segment (HS) phases having different chemical structures. However, the low crystallization window of high Tg materials decreases the crystallization rate of the HS and crystallinity. [11]

The present work deals with the synthesis and characterization of poly(urethane-urea) prepared using MDI and PSt_{2000} prepolymers with various chain extenders having different chain lengths. The aim of this work is to synthesize the dihydroxy terminated low molecular weight polystyrene and to modify the amorphous polystyrene to a semi-crystalline copolymer using crystallizable hard segments. The synthesized PUUs are expected to show excellent solvent resistivity and low water absorption behavior.
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II. Experimental

2.1. Materials

1,6-Hexamethylenediamine(HMDA),4,4'-methylenediphenyldiisocyanate(MDI),1,2-ethylenediamine(EDA),1,4-butanediamine(BDA),deuterated trifluoroaceticacid (TFA-d), phenol and 1,1,2,2 tetrachloroethaneare purchased from Aldrich Chemical Co.Tetrahydrofuran, toluene, methanol, dimethyl formamide are purchased from S.D fine chemicals and used as such without further purification.The functionalized hydroxy terminated polystyrene (OH-PSt-OH) is synthesized using the known route.[12]

2.2. General procedure for the synthesis of block copolymer

Segmented block copolymer are synthesized using various mole ratios of soft to hard segments with three different chain extenders. The synthetic route for the synthesis of copolymer is presented in the scheme 1. The preparation of the **1a** copolymer is here given as an example and similar procedure is followed for other ratios.Functionalized polystyrene of weight average molecular weight (Mw) (2000g/mol) (6g , 0.003mol) is placed in a 100ml three-necked round-bottom flask fitted with mechanical stirrer, nitrogen inlet, a dropping funnel and heated in an oil bath. The first stage of the reaction is carried out in the melt (without solvent) at 120°C. When the temperature reached 120°C, a small excess of MDI (1.5, 0.006mol) is added with stirring for 3h. After 3h, the temperature is raised to 150°C and then 0.35g (0.003mol) of HMDAis added with constant stirring for a period of 2h. Thus the polymer is formed.In the solid state, the polymer is transparent, brittle while being semi crystalline. The materials have a slightly cream in hue.Yield: 6 g (82 %). ^{1}H NMR (δ, ppm): 7-7.5 (b, aromatic proton), 4.9
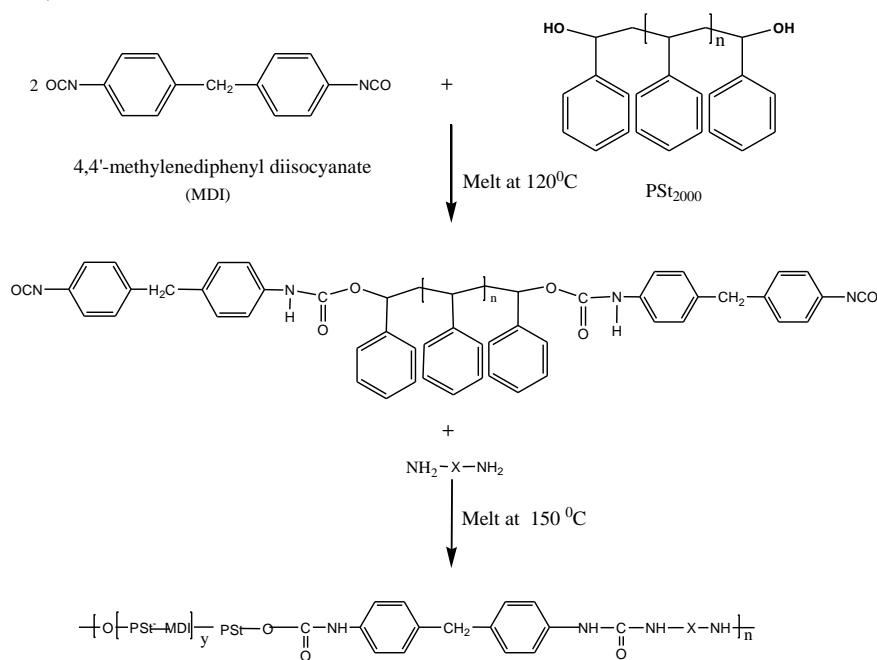
where,

1a, PSt=2000, Y=0 and X= $-(CH_2)_2-$
1b, PSt=2000, Y=2000 and X= $-(CH_2)_2-$
1c, PSt=2000, Y=4000 and X= $-(CH_2)_2-$
1d, PSt=2000, Y=6000 and X= $-(CH_2)_2-$

2a, PSt=2000, Y=0 and X= $-(CH_2)_4-$
2b,PSt=2000, Y=2000 and X= $-(CH_2)_4-$
2c,PSt =2000, Y=4000 and X= $-(CH_2)_4-$
2d, PSt=2000,Y=6000 and X= $-(CH_2)_4-$

3a,PSt=2000, Y=0 and X= $-(CH_2)_6-$
3b, PSt=2000, Y=2000 and X= $-(CH_2)_6-$
3c.PSt=2000, Y=4000 and X= $-(CH_2)_6-$
3d,PSt=2000, Y=6000 and X= $-(CH_2)_6-$

Scheme1. The reaction pathway for the synthesis of semi-crystalline copolymers

(b, >N$\underline{H}$), 3.9, aliphatic -C$\underline{H}_2$ present in MDI, 3.0 (b, -C$\underline{H}_2$- connected to urethane group), 2.7 (b, -C$\underline{H}_2$- connected to urea group), 1.3-1.8 (b, aliphatic proton).

2.3. Fourier-Transform Infrared Spectroscopy
Infrared spectra are recorded using Alpha Bruker FT-IR with a resolution of 2 cm^{-1}. Samples are prepared by adding a droplet of a polymer solution (HFIP (1 g/L)) on a pressed KBr pellet and the measurements are carried out at room temperature.

The temperature dependent FT-IR measurements are recorded on aAlpha Bruker instrument connected with alpha-T accessory and recorded between 30°C to120ºC under a nitrogen flow. The samples investigated for the purpose of this work, is prepared from the 5 wt. % solution of PUU in HFIP. The films are prepared by pouring the solution onto a potassium bromide pellet and by evaporating the solvent.These conditions allow the polymer films to have a stable morphology with desirable properties[13].

The degree of crystallinity of the rigid segments in the polymers could be estimated with the following equations:

$$Xc = \frac{crystalline\ urethane\ peak}{amorphous\ +\ crystalline\ urethane\ peak}$$

$$Xc = \frac{h(1733)}{[C \times h(1747)] + h(1733)} \times 100\% \qquad \text{Equ.----} \quad (1)$$

The heights (h) of the amorphous and crystalline urethane peaks are related by the factor ''C'' with a value of 2.4. [14]

2.4.   Inherent Viscosity Measurements
The inherent viscosity of the copolymer at a concentration of 0.1 g dL^{-1} in a 1:1 (molar ratio) mixture of phenol/1,1,2,2-tetrachloroethane is determined at 25°C by using a capillary Ubbelohde.

$$\eta_{inh} = \ln (t / t_0) / c \qquad \text{Eqn. ----- (2)}$$

t = Elution time of the polymer solution
t_0 = Elution time of the solvent
c = Concentration of the polymer solution (g/dL)

2.5.Differential Scanning Calorimetry
DSCspectra are recorded on a Perkin Elmer DSC 7 apparatus equipped with a PE 7770 computer and TAS-7 software. 10-15mg of dried copolymer sample is heated at a rate of 20°C/min for recording DSC spectra.The second heating is used to evaluate the Tg and Tm of soft and hard segments respectively.

2.6.Thermo gravimetric analysis
Thermal stability of the polymer is done using a thermo gravimetric analysis (TGA) method using Dupont 951 thermogravimerticanalyser. The sample weight is 8-10mg. The work is performed from 30 to 600°C at the heating rate of 10 ^{0}C/min in a nitrogen atmosphere with a gas flow rate of 100ml/ min.

2.7.Swelling Ratio of polymer
The equilibrium swelling ratio is measured on pieces of injection-moulded polymer bars. The samples are placed in desiccators with a layer of demineralised water for four weeks at room temperature. The swelling ratiois defined as the weight gain of the polymer according to Eqn. (3):

$$\text{Swelling Ratio} = \frac{m - m_0}{m_0} \times 100\ [wt.\%] \qquad \text{Eqn.---(3)}$$

Where m$_0$ is the weight of the dry sample and m the weight of the sample after conditioning to equilibrium.

2.8.   Solvent Resistivity
Injection moulded sample of dimension 10x10x2 mm are used for solvent resistance measurements. Previously weighed sample is dipped in 50ml of organic solvents taken in a flask and shaken for 60 mints. After that, the solvent is decanted and the flask is dried for 24 h at 70^{0}C. It is weighed again and from the weight loss, the amount of polymer sample dissolved in that solvent is calculated by using Eqn. (4).

$$Solvent \ Resistivity \ (\%) = \frac{m - m_o}{m_o} \ X \ 100 \ \text{Equ.--------(4)}$$

Where, m is the weight of dry the substance (mg) before solvent treatment, m_o- weight of the substance (mg) after solvent treatment.

III. Results And Discussion

3.1 Synthesis of Polyurethane-urea

The poly(urethane-urea) used in this study are prepared by a two-step procedure as compared to a "one-shot" method[15]. In the first step of the procedure the polyols are reacted with a diisocyanate (MDI) to create isocyanate end-capped prepolymers. These end-capped prepolymers will become the soft segments for the poly(urethane-urea) and possess urethane linkages which will ultimately reside at the interface between hard and soft segments. It is possible that some polyols will be joined together by the diisocyanate, but largely they willexist as single end-capped polyols. The prepolymer will then be reacted with a chain extender diamine which leads to poly(urethane-urea).

Chain extender used in this study are EDA,BDA and HMDA. In each series, the molecular weight of the soft segment is varied using MDI as an chain extender thereby changing the hard segment concentration PUUs.The chemical structure of PUUs is shown in the scheme 1.

3.2.Molecular weight measurements

The synthesized polymer are capable of form hydrogen bonding itself and also with other substrates. Therefore GPC could not carry out without any discrepancies in elution time. Inherent viscosity of the copolymer is determined in Phenol/1,1,2,2-tetrachloroethane (1:1 molar mixture) to get an idea about the molecular weight. The PSt shows the inherent viscosity of 0.1dL/g.The copolymer shows high inherent viscosities (0.5-2.3dL/g), suggesting that the polymer are of high molecular weight.HMDA based copolymer (series 3)has shown higher inherent viscosities than that of polymer obtained based on EDA (series 1) and BDA (series 2) chain extenders. The inherent viscosities (η_{inh}) of series 3 have ranged between 0.7-2.3dL/g whereas the inherent viscosities (η_{inh}) of series 1 and series 2 ranged between 0.5-1.5 and 0.6-1.9dL/g respectively.
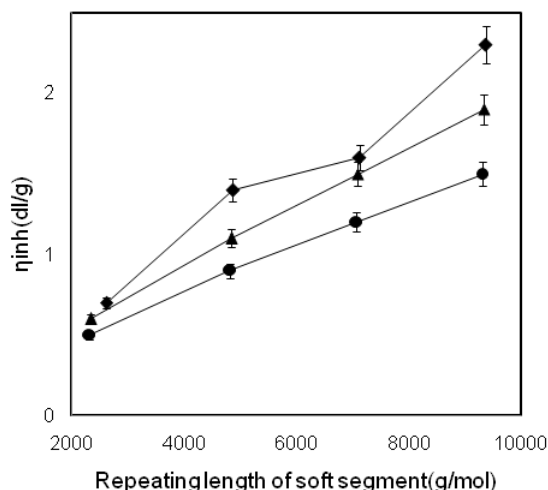
Figure 1. Effect of soft segment length on the molecular weight of the polymer.

Increase in the molecular weight of the polymer is evident from the increase in inherent viscosity.The datais shown in table 1 and the correlation between the SS length to that of the inherent viscosity is linearly increasing with

Table 1. Mole fraction in feed, length of the repeating length and the inherent viscosities of the polymers.

Polymer code	Mole fraction			SS length (g/mol)	η_{inh} (dl/g)
	PSt	MDI	NH$_2$-X-NH$_2$		
PSt$_{2000}$	--	--	--	2000	0.1
1a	1	2	1	2310	0.5
1b	2	3	1	4810	0.9
1c	3	4	1	7060	1.2
1d	4	5	1	9310	1.5

2a	1	2	1	2338	0.6
2b	2	3	1	4838	1.1
2c	3	4	1	7088	1.5
2d	4	5	1	9338	1.9
3a	1	2	1	2616	0.7
3b	2	3	1	4866	1.4
3c	3	4	1	7116	1.6
3d	4	5	1	9366	2.3

Where X= can be either -$(CH_2)_2$- or -$(CH_2)_4$-, or -$(CH_2)_6$-

Increasing the molecular weight as shown in the Fig.1. It shows that as the length of the soft segment increasesfrom 2310 to 9366g/mol, the molecular weight of polymer increases evident from the increase in inherent viscosity.

3.3.FT-IR spectra

Infrared spectroscopy is used to study hydrogen bonding in PUU systems. The absorption bands of C=O and N-H groups depend on extent of hydrogen bond formation. Hydrogen bonding in PUs plays a vital role in determining their macroscopic properties. The hydrogen bonding interaction produces physical crosslink's and thereby reinforces the PU matrix which in turn increases strength and stiffness [16,17] .Two different carbonyl groups that can form hydrogen bonds are urethane and urea groups. Urea groups can form either bidentate or monodentate hydrogen bonds. The FT-IR spectra of PUU(EDA), PUU(BDA), and PUU(HMDA)'s polymers at 30˚C are shown in Fig. 2.
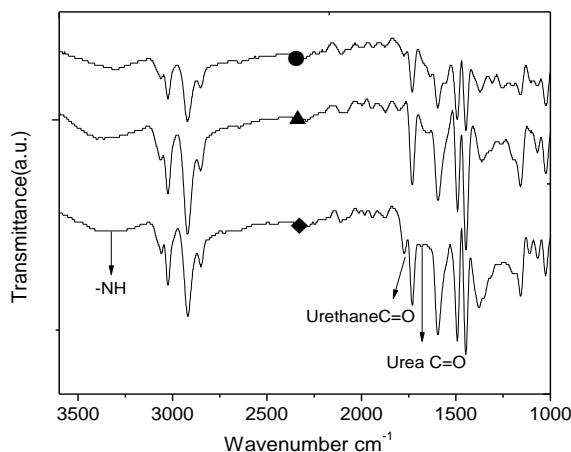

Figure 2. FT-IR spectrum of three copolymer at room temperature. ●;,1a, ▲;,2a, ♦;3a

The IR spectra shows absorption peaks at 3330-3345, 2947 and 2862 corresponds to N-H, C-H of methyl and methylene group respectively. The amorphous and crystalline urethane carbonyls appear around 1748 and 1733 cm^{-1} respectively. The monodentate crystalline urea carbonyl group appears at 1686-1661 cm^{-1} group and aromatic C=C stretching frequency appears at wave number of 1596cm^{-1}.The absence of absorption peak around 3400 cm^{-1}for hydroxyl group in the prepolymer. It is confirms that the prepolymer is effectively encapped with MDI. Similarly, the appearance of new absorption peaks at 3330 and 1596 cm^{-1} indicating the presence of urethane (–NH–) and aromatic groups in the polymer chain respectively. These absorption peaks confirms the chemical structure presented in the Fig.2.

Temperature dependent infrared spectroscopy is used to study the crystallinity of the urethane segments as a function of temperature and shown in the Fig.3.The samples are heated from 30 to 120°C and the spectra
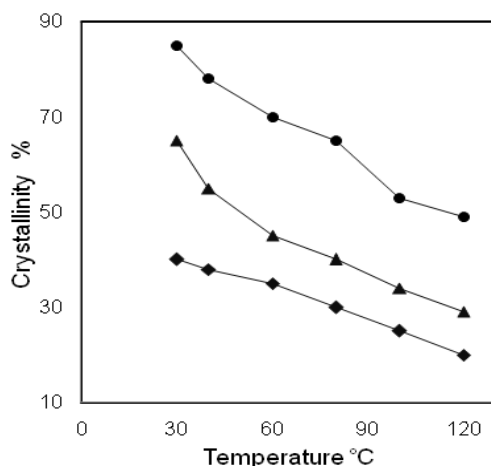

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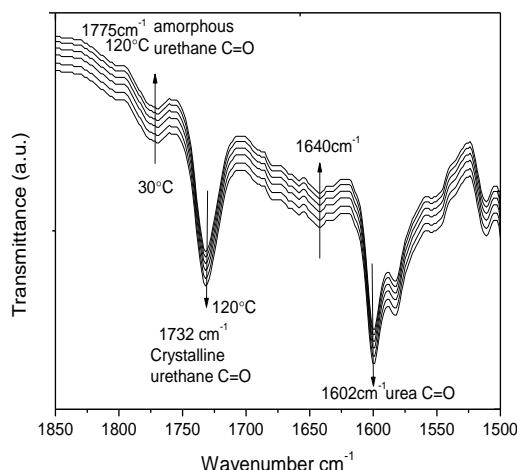
Figure 3. Temperaturedependent FTIR spectrum of 1a copolymer at different temperatures.

recorded at 20^oC intervals. The experiment is designed to follow the infrared absorption as a function of temperature in order to directly study the extent and strength of hydrogen bonding provided by the hard segment.

In PUU-EDA, upon heating, the peak intensity of H-bonded urethane C=O groups and urea groups decreases. Upon cooling the sample from 120°C to 30°C, the H-bonded urethane C=O peak intensity increases and the peak at the free urethane C=O groupintensity decreases. Fig.3 shows the temperature dependent IR spectra of PUU(EDA) 1a present in the carbonyl region of 1500 to 1800cm^{-1}. Some of the H-bonded urethane in PUU dissociate during heating to form non-bonded free urethane. The hydrogen bonded urethane carbonyl peak will appear at lowerwave number around 1732cm^{-1}and highest intensity, which is attributed to a reduction in the electron density of the carbonyl groups due to hydrogen bonds. Since the hard segments contain the less flexible EDA species, they can pack more efficiently and promote the highest level of hydrogen bond interaction[18].The peak around 1775cm^{-1} is assigned to stretching of non-bonded

Table 2. FT-IR data of the multiblock copolymer at room and different temperature.

| Polymer Code	HS (wt.%)	η_{inh} (dL/g)	N-H Urea (cm^{-1})	C=O Urethane(amor) (cm^{-1})	C=O Urethane (cry) (cm^{-1})	C=O Urea (cry) Monodentate	Crystallinity (%)
PSt$_{2000}$	0	0.1	-	-		-	
1a	22	0.5	3330	1748	1733	1686	85
1b	17	0.9	3329	1726	1732	1685	70
1c	15	1.2	3328	1725	1732	1685	62
1d	14	1.5	3327	1725	1731	1684	58
2a	23	0.6	3345	1744	1735	1678	65
2b	17	1.1	3344	1733	1733	1678	60
2c	15	1.5	3343	1732	1732	1677	56
2d	14	1.9	3342	1731	1732	1676	49
3a	24	0.7	3337	1743	1734	1669	40
3b	18	1.4	3336	1747	1733	1668	36
3c	16	1.6	3335	1746	1733	1668	31
3d	15	2.3	3334	1745	1732	1667	25

Figure 4. Crystallinity studies of three polymers.(⬤;, 1a, ▼;,2a ♦;,3a)

urethane carbonyl groups. The peak around1710 cm^{-1}is due to amorphous urea carbonyl and the H-bonded urea carbonyl groups are centered around 1660-1690cm^{-1} corresponds to bidendate and monodendate assemblies.

The effect of temperature on the crystallinity of the hard segment is given in the Fig 4. . The crystallinity of the PUU(EDA) (85 %) are higher than the other two series like PUU(BDA) (65%) and PUU(HMDA)(40%). Remarkably, the crystallinity of the PUU (EDA) is constant up to 120°C. Whereas, the crystallinity of the PUU(BDA) and PUU(HMDA) decreases with increasing the temperature clearly suggesting that the former is formed much stable hydrogen bonding than the latter two polymers. It is concluded that the physical crosslinks decreases as the length of the carbon chain increases i.e.,close packing between hard and soft segment decreases,so as the crystallinity decreases in PUU (HMDA)andPUU(BDA)with respect toPUU(EDA).

3.6 DSC

The thermal properties of poly(urethane-urea) are studied using differential scanning colorimeter. The second heating curve of the polymers1a, 2a and 3a series are given in the Fig.5. Heating curve of the polymer samples shows Tg of soft segment and melting(Tm) of hard segment. The cooling curve exotherm is not observed in all three samples namely1a,2a and 3a and therefore not presented here.
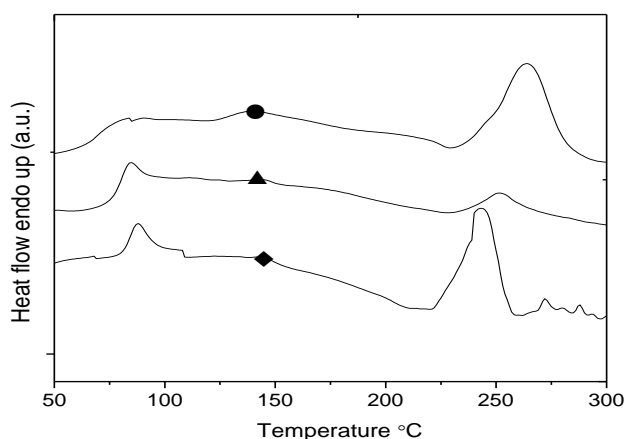
Figure 5. DSC heating curve and cooling curve of three polymers (⬤;,1a,▲ ;,2a, ♦;,3a)

**Table 3. DSC, TGA, swelling ratio and solubility data for PUU Copolymers**

Polymer code	HS (Wt. %)	SS (Wt. %)	η_{inh} (dL/g)	DSC(°C)		TGA$^\blacklozenge$ °C	Swell.# (Wt. %)	Solub. (Wt. %)
				Tg	Tm			
PSt$_{2000}$	--	100	0.1	58	-	412	0	100
1a	22	78	0.5	83	263	415	25	35
1b	17	83	0.7	82	261	416	23	45
1c	15	85	0.9	81	260	417	22	49
1d	14	86	1.1	80	259	418	20	54
2a	23	77	0.6	85	252	413	24	38
2b	17	83	0.8	84	251	414	22	51
2c	15	85	1.1	82	249	415	21	55
2d	14	86	1.5	81	248	418	19	59
3a	24	76	0.7	87	242	410	21	44
3b	18	82	1.4	85	240	411	19	52
3c	16	84	1.6	84	239	413	18	58
3d	15	85	2.3	83	237	414	17	61

$^\blacklozenge$ = Decomposition temperature
= Swelling ratio in 28 days

The Tg and Tm of poly(urethane-urea) of three series is given in the Table 3. The poly(urethane-urea) has various glass transition temperatures ranging from 83 to 87°C, and it tends to increase with increase in the chain length of prepolymer used in the polymerization process. From the DSC curves, it can be seen that, upon increase the chain length of the extender from EDA to HMDA, shifts the glass transition to higher temperatures. PUU (HMDA) has higher *Tg* value due to the higher hard segment contents and lower crystallinity.

The relationship between hard segment content to that of the Tg of the polymer is shown in the Fig.6. From the Fig.6 it is concluded that as the length of the soft segment increases, Tg value decreases. Melting temperature of the hard segment for the polymer 1a, 2a and 3a are 263, 252 and 242°C respectively. Melting temperature decreases with decrease in HS concentration which means that the % of crystalline region decreases.
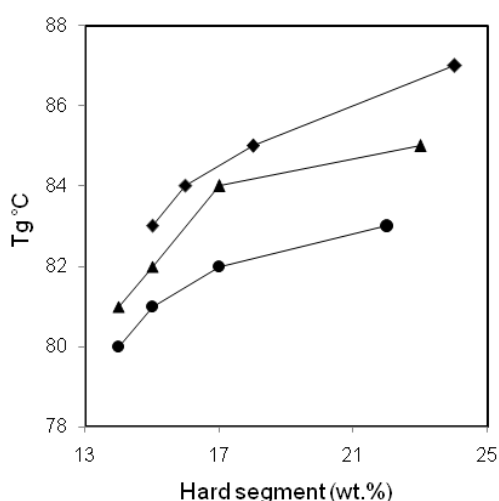

Figure 6. Effect of hard segment concentration on the Tg of the soft phase. (● ;,1a, ▲ ;,2a ♦;,3a)

3.7 TGA

The decomposition temperatures (Td) of the synthesized poly(urethane-urea) are observed between 410 and 418°C (Table 3). The longer chain length of HMDA used in polymerization leads to an increasing of the decomposition temperature of poly(urethane-urea). The increase of the decomposition temperature of poly(urethane-
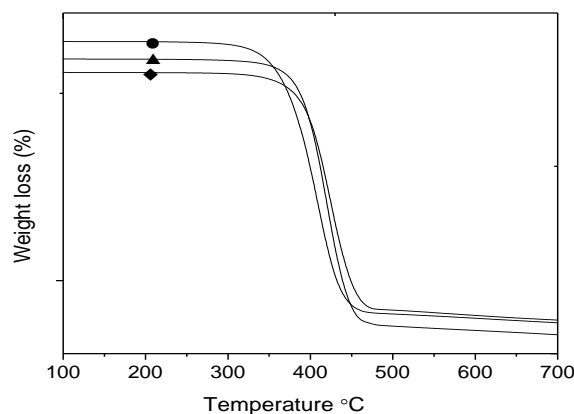
Figure 7.TGA thermo grams of three copolymer (● ;,1a, ▲ ;,2a ♦;,3a)

urea) could be associated with the increase of soft segment part interaction of polymers and also cross-link formed in polymers. The longer chain length of HMDA used in preparation of poly(urethane-urea) leads to increase the interaction of poly(urethane-urea) chains. Synthesized copolymer did not show any thermal degradation upto 414°C. It is shown in Fig.7. It reveals that the formation of PUU is stable in mentioned temperature.

From the table 3, one observes that, as the HS content increases, the thermal stability increases, which is due to the increasing toughness of the system.

3.8 Swelling Ratio of Polymer

The hydrophobic characters of the soft segment prevent the entry of water molecules, resulting in a greater hydrolytic stability of the polyurethane. The hard segment content is the main factor that controls the amount of absorbed water. In general, as the hard segment content increases, a more hydrophilic character is introduced in the network structure and thus we expect increase in the water uptake. But, PUU is semi-crystalline materials and therefore physical crosslink's between the chains is possible. The density of physical cross linking depends on the hard segment content. The physical cross linking point opposes the water molecule to penetrate through the soft matrix. Therefore upon increasing the hard segment content, the swelling ratio decreases in the tested samples.
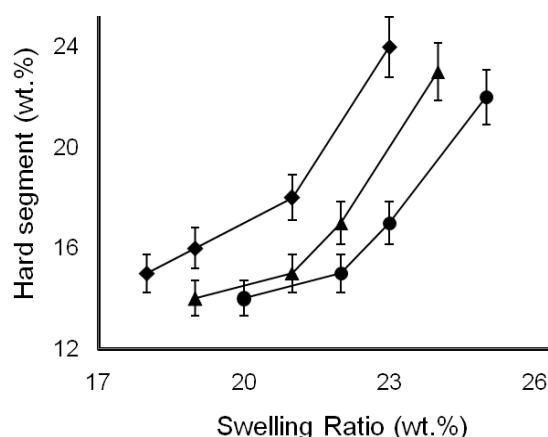
Figure 8. Swelling Ratio of the three copolymer with respect to HS concentration. (● ;,1a, ▲ ;,2a ♦;,3a)

The swelling ratio of the series1,2 and 3 is 20- 25wt. %, 19-24 wt. %and 18-23 wt. % respectively. In all compositions, the swelling ratio decreases in the order of 1<2<3 series due to difference in packing between soft and hard segments. The correlation between hard segment content to that of water absorption is presented in the Fig.8 and it reveals that the water absorption increases with decrease in the hard segment content on the copolymer.The water absorption dataare presented in the table 3.

3.9 Solvent Resistivity

Amorphous polymer like polystyrenes can very easily attacked by solvents, but the solvent resistance of semi-crystalline polymer is better. Solvent resistance behaviour of multi-block copolymer is studied by suspending injection moulded bars in chloroform and other organic solvents at room temperature for 1h. After drying the samples, the weight loss is determined. The PSt dissolve completely in chloroform with in 1hr as shown in Table 3. The multi block copolymer had dramatic lower weight losses in chloroform and in other organic solvents. Although solubility decreases with increasing hard segment content, the absorbed high values of solubility is due to the highly
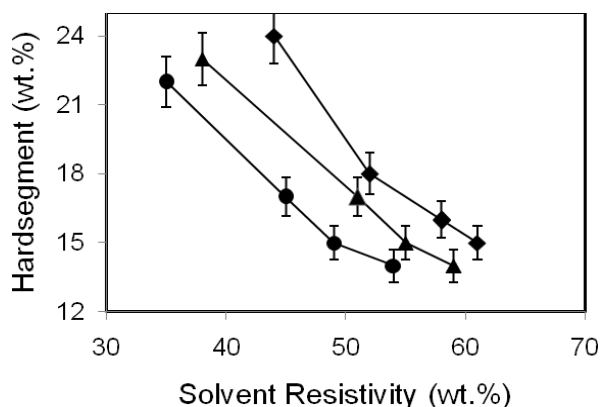

Figure 9. Solvent resistivity of the three copolymer with respect to HS concentration. (● ;, 1a, ▲ ;,2a ♦;,3a)

polar nature of the urethane –urea linkage present in the polymer chain. The weight losses after 1h in chloroform and other organic solvents increase strongly with decreasing HS concentration. The solvent resistivity of the series 1, 2 and 3 is 35- 54wt. %, 38-59 wt. % and 44-61 wt. % respectively. The solubility increases in the order of 3>2>1 series due to difference in the chain flexibility which inturn increases in the order of HMDA>BDA>EDA. Fig. 9 shows the relationship between the hard segment content to that of solubility in chloroform clearly shows that the solubility increases with decrease in hard segment content. Aromatic diisocyanate (MDI) has showed better solvent resistivity compare to aliphatic diisocyanate (HMDI) [19].

IV. Conclusion

The polystyrene having weight average molecular weight of around 2000 g/mol is used for the synthesis of PUU. Three series of polyurethane-urea (with EDA, BDA and HMDA chain extender) are synthesized via conventional two-step melt polymerization method. The low molecular weight of the polystyrene is modified from low to high using MDI as chain extender and (2310 to 9366 g/mol) thereby changing the hard segment concentration from 24 to 14 wt.%. From the FT-IR study it was concluded that the crystalline increases with the decreasing chain length of the extenders. From the DSC curves, it can be seen that, upon increasing the chain length of the extender from EDA to HMDA shifts the Tg value from low to higher temperatures. PUU(HMDA) has higher *Tg* value due to the higher hard segment contents and low crystallinity. Similarly, Tm value is in the order of PUU(EDA)>PUU(BDA)>PUU(HMDA).From the temperature dependent FTIR, it was concluded that the crystallinity of the hard segment is very high (85%). DSC data confirm the melting temperature of the polymer is varies from 237°C to 263°C. Thermal stability of these materials is very high (around 414°C). The solvent resistivity and the swelling ratio of the copolymer depend on the extender type and the hard segment content. Overall, the synthesized segmented copolymer is transparent, high molecular weight and semi crystalline.

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