

Studies on polyurethane potting compound based on HDI-TMP adduct for fabrication of haemodialyzer

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Polyurethane potting compounds based on hexamethylene diisocyanate-trimethylol propane (HDI-TMP) adduct (Component "A") and polypropylene glycol, polyethylene glycol and castor oil (Component "B") were prepared as potential compounds for the fabrication of haemodialyzer. The setting characteristics of the potting compounds having isocyanate index 2.0 are better than those compounds having 1.35. The aging stability of PEG and PPG based potting compounds are poorer than those of castor oil based potting compounds. Appreciable hydrolytic, oxidative and chemical stability could be observed with castor oil based potting compounds of HDI-TMP adduct.

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1. Introduction

Aromatic polyurethanes made from methylene diisocyanate (MDI) are susceptible to degrade if processed in the presence of moisture [1] and if autoclaved in an aqueous solution [2]. γ -radiation sterilization and autoclaving are used to sterilize the polyurethane devices. Excessive and repeated sterilization are prone to cause chain scission of polyurethane and formation of low molecular weight components. It has been reported that a potential carcinogenic chemical, 4,4'-diamio diphenyl methane (MDA) is formed in thermoplastic MDI-based polyurethane during autoclave sterilization [2]. Similarly, 2,4 and 2,6 toluene diamine (TDA) have been found as hydrolytic products of toluene diisocyanate based polyurethane foam (Microthane) when it reacts with water at elevated temperature [3]. Chan *et al.* [4, 5] have detected TDA in clinical samples of urine and breast tissue of patients with 7 month old polyurethane (Polyester-TDI) foam-covered Meme breast implants (Surgitek)^R. The degradation of microthane foam cover in Meme breast implant has resulted in court litigation and the implant was withdrawn from the market. The resistance of aromatic diisocyanate (TDI, MDI, etc) based polyurethane to thermohydrolytic degradation is poor in comparison with that of polyurethane based on aliphatic diisocyanate such as dicyclohexyl methane diisocyanate (H_{12} MDI) and 1,6-hexamethylene diisocyanate (HDI). Aliphatic crosslinked polyurethanes [6–9] and low elastic modulus polyurethane-urea [10] were developed by Jayabalan *et al.* who evaluated various

characteristics for long-term medical applications. Adhesives and potting compounds were also developed for surface modification of PVC material [11] and potting of hollow fiber bundles in dialyzer housing component for the haemodialyzer [12–15]. Potting compounds used in the fabrication of haemodialyzers should have fast setting character with easy dispensability. TDI-based potting compounds are no longer in commercial use. Therefore, aliphatic diisocyanate-based potting compounds are needed. Accordingly potting compounds based on isocyanurate of hexamethylene diisocyanate were developed by the authors [16]. The present paper deals with the studies on 1,6-hexamethylene diisocyanate and trimethylol propane (HDI-TMP) adduct-based potting compounds using different polyols, for use in haemodialyzer and oxygenator.

2. Experimental

2.1. Materials

HDI (Aldrich Chemical Co., USA), polypropylene glycol (PPG) of molecular mass 400 (Fluka AG), polyethylene glycol (PEG) of molecular mass 600 (E. Merck, India Ltd), castor oil of molecular mass 932 (pharmaceutical grade), trimethylol propane (2ethyl-2 (hydroxy methyl)propane-1, 3-diol) (TMP), dibutyl tin dilaurate (DBTDL), Fluka AG) and dimethyl formamide (DMF) were used. PPG, PEG and castor oil were vacuum dried at 60 °C to ensure dryness.

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2.2. Synthesis of multifunctional HDI-TMP adduct

An adduct compound based on HDI and TMP was prepared by bulk polymerization under the inert atmosphere of nitrogen. TMP was dried in a vacuum oven at 60 °C. 4.026 g (0.03 M) of TMP was weighed in a three-necked flask. 15.138 g (0.09 M) of HDI was also added to it. It was then heated, with stirring up to 96 °C so that a viscous solution of the adduct was obtained.

2.3. Preparation of potting compounds using HDI-TMP adduct and polyols

The potting compounds based on HDI-TMP adduct are two components. The HDI-TMP adduct was used as component ‘‘A’’. The polyols PPG-400, PEG-600 and castor oil-932 were used as component ‘‘B’’. The formulations of potting compounds are given in Table I. Two potting compounds based on isocyanate index 1.35 and 2.0 were prepared. The code HDI/TMP/PPG/1.35 indicates the potting compound based on HDI-TMP adduct and PPG polyol with isocyanate index, 1.35. Similarly the code HDI/TMP/PPG/2.0 indicates the potting compound based on isocyanate index 2.0. The functionality of PPG and PEG is two whereas the functionality of castor oil (932) is 2.7. The molecular weight (calculated) of the HDI-TMP adduct is 638.78. The weight of component ‘‘B’’ was varied so that NCO/OH mole ratio of 1.35 and 2.0 was derived.

2.4. Characterization of potting compound

Doughing time and time for hardening of potting compound was determined as per ASTM standard F 451–76. About 2 g of the adduct was mixed with accurately weighed amount of polyols. DBTDL was added as catalyst. Doughing time and time for hardening were noted at room temperature. The time required for a clean glass rod to form the adhering fibers between the glass rod and the surface of the setting mass was noted as doughing time. The time required for total setting was taken as time for hardening.

2.5. Preparation and analysis of cured potting compound

Potting compounds were cured with DBTDL catalyst at 60 °C for 24 h in an air oven. Infra-red spectral analyses were carried out for cured potting compounds. The cured sample was masticated in a mortar and pestle and the fine powder was used for making KBr pellets for recording

the spectrum. A Nicolet (Impact 410) Fourier transform infra-red (FTIR) instrument was used. The cured potting materials were tested for density, crosslink density and molecular weight between crosslinks as per the method described elsewhere [17]. The relative hardness of the various cured polyurethane potting materials were determined using a Shore ‘‘A’’ durometer. The polymer blocks were piled into 6 mm thickness and pressed under the needle of the durometer. The hardness was measured directly from the instrument.

2.6. Studies on aging stability of cured potting materials

The stability of polyurethane potting materials was evaluated in various media, Ringer’s solution, phosphate buffered saline (PBS) (pH 7.4), 2% formaldehyde solution and oxidation medium, 30% hydrogen peroxide solution. The Ringer’s solution and PBS (pH 7.4) were prepared as per the standard procedure. The polymers were weighed accurately and immersed in different media and the weight loss was measured. The media were changed every week to retain the complete activity. The weight loss (%) was plotted against duration of exposure and relative aging stability was examined.

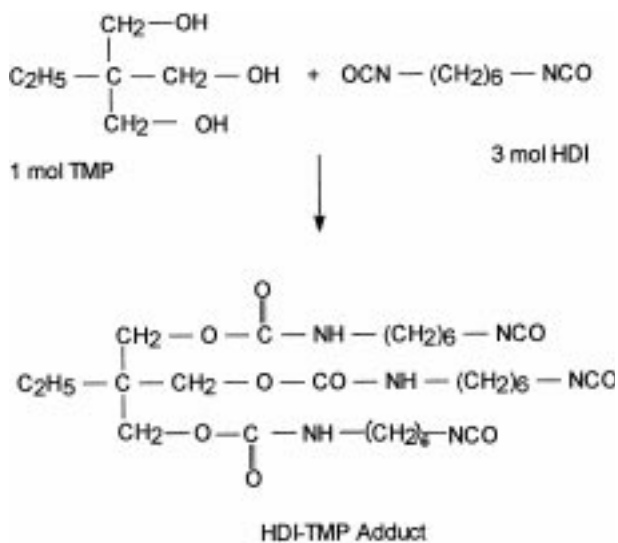
3. Results and discussion

3.1. Preparation and characterization of potting compounds

The essential properties of a potting compound are short setting time, easy dispensability, non-wicking and good aging stability. Owing to the increased stability of polyurethane materials based on aliphatic diisocyanates, aliphatic isocyanates were chosen for the present study. Isocyanate present in the multifunctional isocyanate (functionality more than two) compound are found to have lower reactivity in comparison with that of diisocyanate compound. Therefore the multifunctional isocyanate compounds are quite useful for short polyurethane processes such as foams, sealants, coatings and potting compounds. The multifunctional isocyanate compound reacts with polyol under room temperature and sets to a hard mass due to branching and crosslinking through multiple isocyanate groups. Such reactions enable slow gelation, which is helpful to get uniform product. Moreover the multifunctional isocyanate compounds have low vapor pressure at room temperature to guarantee safe handling. Due to these advantages multifunctional aliphatic isocyanate compounds were synthesized. The reaction between hexamethylene

TABLE I Formulation of potting compounds

Potting Compound	Component ‘‘A’’	Component ‘‘B’’	Isocyanate index	Weight of components (g)	
				A	B
HDI/TMP/PPG/1.35	HDI/TMP adduct	PPG ₄₀₀	1.35	1.0	0.689
HDI/TMP/PEG/1.35	HDI/TMP adduct	PEG ₆₀₀	1.35	1.0	1.033
HDI/TMP/Castor oil/1.35	HDI/TMP adduct	Castor oil	1.35	1.0	1.189
HDI/TMP/PPG/2.0	HDI/TMP adduct	PPG ₄₀₀	2.0	1.5	0.705
HDI/TMP/PEG/2.0	HDI/TMP adduct	PEG ₆₀₀	2.0	1.5	1.058
HDI/TMP/castor oil/2.0	HDI/TMP adduct	Castor oil	2.0	1.5	1.227



Scheme 1 Synthesis of potting compound component "A"-HDI-TMP adduct.

diisocyanate and trimethylol propane takes place in the absence of a catalyst under nitrogen atmosphere as shown in Scheme 1. The reaction product, adduct of hexamethylene diisocyanate-trimethylol propane is a yellowish viscous resin.

The setting characteristics of a potting compound testify the quality of the potting compound. The short duration setting enables faster processing. The doughing time and time for hardening for HDI-TMP series are given in Table II. Among the polyols the reactivity of polypropylene glycol is relatively less than that of polyethylene glycol. Accordingly with the PEG polyol based potting compounds HDI/TMP/PEG/1.35 and HDI/TMP/PEG/2.0 the doughing time and time for hardening is comparatively less than that of PPG based potting compounds. However HDI/TMP castor oil/1.35 reveals longer setting duration in comparison with PPG and PEG based potting compounds. This is due to the high molecular weight of castor oil. However with HDI/TMP/castor oil/2.0 the setting duration is relatively reduced. This is due to increased isocyanate index.

3.2. Characterization of cured potting compounds

The data on infra-red spectral analyzes of the cured potting materials based on isocyanate index 1.35 are given in Table III. The absence of a peak around 2250 cm^{-1} indicates the absence of unreacted isocyanate in the cured potting material. The spectral responses of potting compounds based on isocyanate index 2.0 are also similar to that based on isocyanate index 1.35. The PPG based potting materials show a peak around 1375 cm^{-1} for C-H bending of pendent CH_3 which was absent in PEG and castor oil based potting materials. PEG based potting materials exhibit a distinct peak around 1350 cm^{-1} for C-H stretching of $-\text{COO-CH}_2\text{-CH}_2-$ linkage. Both PPG and PEG based potting materials exhibit a peak around 1110 cm^{-1} for $-\text{C-O-C}$ ether linkage. The castor oil based potting materials show a peak around 3400 cm^{-1} for O-H stretching and around 1740 cm^{-1} for C=O stretching of

ester carbonyl. HDI/TMP based potting materials show a distinct peak around 1710 cm^{-1} for C=O stretching of urethane (hydrogen bonded).

The swelling studies of cured potting materials carried out in solvents having different solubility parameters, methanol (14.5), ethanol (12.7), dimethyl acetamide (10.8), tetrahydrofuran (9.1) and toluene (8.9) reveal that all the cured potting materials are crosslinked. The swelling coefficient (degree of swelling) of all the cured materials are low, which are characteristic of a cross-linked system. Among the solvents, dimethyl acetamide imparts a higher degree of swelling. The castor oil based potting materials HDI/TMP/castor oil/1.35 and HDI/TMP/castor oil/2.0 show a trend of low swelling coefficient in solvents except in tetrahydrofuran and toluene. However, the swelling coefficient of these potting materials in dimethyl acetamide is the highest among the solvents. Owing to the higher degree of swelling (swelling coefficient) only in dimethyl acetamide it is understood that the solubility parameter of the cured potting materials is 10.8. The density of cured potting materials is given in Table IV. The low density of the cured potting materials is due to the presence of micro-voids in the solid material. All the cured potting materials show a density less than 1. The crosslink density and molecular weight between crosslinks of cured potting materials are given in Table IV. The swelling characteristics of the potting materials reflect on the crosslink density and molecular weight between crosslinks. The higher the swelling coefficient, the lesser is the crosslink density. The lesser the crosslink density, the higher is the molecular weight between crosslinks. Among all the cured potting materials HDI/TMP/PPG/2.0 shows the highest crosslink density.

The hardness of the cured potting material is given in Table IV. The hardness is influenced by percentage of hard segment and crosslink density. The hard segment is constituted by component "A" and soft segment is component "B". The concentration of component A is kept constant in all potting compounds. However the hardness of HDI/TMP/PPG/1.35 is lower than in the HDI/TMP/castor oil/1.35. This is due to the less crosslink density of HDI/TMP/PPG/1.35 in comparison with that of HDI/TMP/castor oil/1.35. In the case of HDI/TMP/PPG/2.0 higher hardness was observed in comparison with that of HDI/TMP/castor oil/2.0 which is due to increased crosslink density.

TABLE II Setting characteristics of potting compounds

Potting compound	Doughing time (min)	Time for hardening (min)
HDI/TMP/PPG/1.35	45	55
HDI/TMP/PEG/1.35	25	35
HDI/TMP/castor oil/1.35	50	85
HDI/TMP/PPG/2.0	65	90
HDI/TMP/PEG/2.0	30	45
HDI/TMP/castor oil/2.0	35	55

TABLE III FTIR spectral responses of cured materials of the potting compound with polyols

Spectral responses	Peak position (cm ⁻¹)		
	HDI/TMP/PPG/1.35	HDI/TMP/PEG/1.35	HDI/TMP/castor oil/1.35
N—H stretching (free)	3427.76	3427.38	—
O—H stretching	—	—	3402.92
C—H stretching of —CH ₂ or alkyl	2926.25	2924.79	2929.01
	2860.42	2860.89	2858.56
C=O stretching of ester group	—	—	1741.00
C=O stretching of urethane (hydrogen bonded)	1712.78	1710.71	1706.79
N—H bending	1589.48	1576.09	1537.53
C—H bending of pendent -CH ₃	1378.23	—	—
C—H bending of —CO—O—CH ₂ —CH ₂ —	—	1352.81	—
—C—O—C of ether group of polyol	1110.88	1108.20	—

3.3. Studies on aging of cured potting materials

The data of aging stability of cured materials in hydrolytic media, Ringer's solution, PBS, oxidative medium hydrogen peroxide and sterilization medium formaldehyde are given in Table V. The potting materials based on PEG₆₀₀ and PPG₄₀₀ have higher maximum weight loss (%) in hydrogen peroxide oxidation medium. Such weight loss is greater in potting materials having isocyanate index 1.35 in comparison with the potting materials having isocyanate index 2.0. Among PEG and PPG potting materials only HDI/TMP/PPG/2.0 potting material is found to have relatively less weight loss which may be due to higher crosslink density. Comparatively the potting materials based on castor oil are relatively more stable in all the media. The weight loss (%) is significantly less for HDI/TMP/castor oil/1.35, HDI/TMP/castor oil/2.0, even in hydrolytic media. Polyurethanes synthesized using castor oil and multifunctional isocyanate have excellent hydrolytic stability due to a higher degree of crosslinking through castor oil unit [13–15]. The weight loss observed in the formaldehyde is mainly due to the leaching of unreacted low molecular weight components. The weight loss in castor oil based potting compounds in formaldehyde is significantly lower in comparison with that of PEG and PPG based potting materials. The weight loss in PPG and PEG based potting materials was observed after the duration of 1 week and reaches a steady state after 3–4 weeks duration. The weight loss of HDI/TMP/castor oil/1.35 in these media was rather slow. The steady state in

weight loss in Ringers' solution and PBS was attained after 3 weeks and in hydrogen peroxide and formaldehyde after 4 weeks. The initial weight loss is attributed to the leaching of unreacted components. The subsequent weight loss in Ringer's solution and PBS is due to hydrolytic degradation. The hydrolytic degradation in polyurethane is mediated at the urethane linkage leading to the formation of amine and hydroxyl terminated chains of low molecular weight. The weight loss in hydrogen peroxide is due to oxidative degradation as shown in Scheme 2. The oxidation of ether linkages of polyol component leads to the formation of crosslinks and generation of low molecular weight fragments.

4. Conclusion

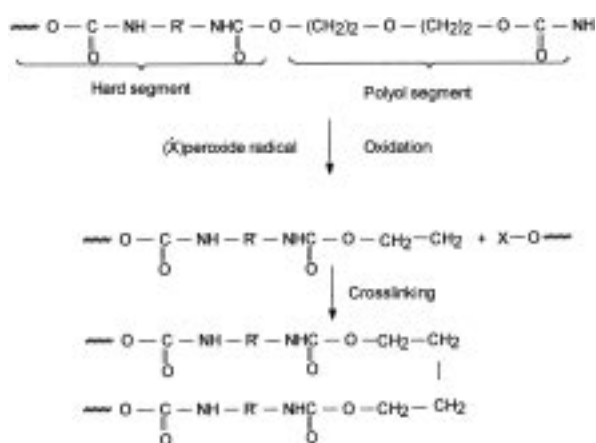
Multifunctional hexamethylene diisocyanate-tri methylol propane adduct having a functionality of 3 was prepared as component "A" for two component potting materials for use in haemodialyzer and oxygenator. The setting characteristics reveal faster setting with potting compounds having higher isocyanate index. The data on aging stability reveal degradation of PPG and PEG based potting materials in Ringer's solution, PBS, hydrogen peroxide solution and formalin. The weight loss is found to be lesser with potting compounds based on isocyanate index 2.0. However, the castor oil based potting materials reveal appreciable stability both in hydrolysis and oxidation media as well as in chemical sterilization medium, formaldehyde. Therefore the potting compounds, HDI/TMP/castor oil/1.35 and HDI/

TABLE IV Physical and mechanical properties of cured materials of the potting compound

Cured material of the potting compound	Density of polymer (g/cc)	Swelling coefficient	Crosslink density × 10 ³	Mol. wt between crosslinks (Mc)	Hardness (Shore A)
HDI/TMP/PPG/1.35	0.9035	2.4590	0.6245	1601.28	14
HDI/TMP/PEG/1.35	0.8985	2.2528	0.7302	1369.47	12
HDI/TMP/castor oil/1.35	0.9168	1.5610	1.3250	754.72	35
HDI/TMP/PPG/2.0	0.8208	2.3260	2.5292	395.38	28
HDI/TMP/PEG/2.0	0.8181	1.8696	1.0990	909.99	25
HDI/TMP/castor oil/2.0	0.8151	1.9380	1.0350	966.18	22

TABLE V Aging data of cured materials of the potting compound

Cured material of the potting compound	Maximum weight loss (%)			
	Ringer's solution	PBS	Formaldehyde solution	30% Hydrogen peroxide
HDI/TMP/PPG/1.35	29.40	26.50	27.40	31.00
HDI/TMP/PEG/1.35	47.20	45.67	46.19	48.97
HDI/TMP/castor oil/1.35	4.80	4.76	1.71	1.89
HDI/TMP/PPG/2.0	12.90	8.93	9.12	12.30
HDI/TMP/PEG/2.0	30.30	28.85	27.94	30.60
HDI/TMP/castor oil/2.0	1.37	2.68	2.03	4.81



Scheme 2 Mechanism of oxidative degradation of ether segment of polyurethane.

TMP/castor oil/2.0 are probably more suitable for potting of hollow fibers for the fabrication of hollow fiber haemodialyzers and oxygenators.

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