Bull. Mater. Sci., Vol. 20, No. 5, August 1997, pp. 727–735. © Printed in India.

Effect of γ-radiation sterilization on the stability of polyurethane potting compounds based on castor oil/SMDI and caprolactone polyol/SMDI, used for hollow fibre haemodialyzer

M JAYABALAN* and P P LIZYMOL
Polymer Division, Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram 695 012, India

MS received 30 August 1996; revised 31 May 1997

Abstract. Stability of polyurethane potting compounds based on castor oil/SMDI and caprolactone polyol/SMDI in repeated gamma radiation sterilization was studied. Radiation-induced degradation and leaching of low molecular weight fragments are higher in castor oil based polyurethane than in caprolactone polyol based polyurethane. For castor oil and caprolactone polyol based polyurethanes degradation increases up to 5 Mrad dose of sterilization. Further increase of dose of sterilization decreases leaching in caprolactone polyol based polyurethane which has resulted from secondary reactions leading to crosslinking. In the case of castor oil based polyurethane such crosslinks undergo cleavage at 10 Mrad dose of sterilization.

Keywords. γ-Radiation sterilization; hollow fibre; haemodialyzer; potting compound castor oil; caprolactone polyol; SMDI; polyurethane.

1. Introduction

Polyurethane is one of the widely used polymers in various biomedical applications such as artificial heart diaphrams, ventricular assist bladders, vascular grafts, mammery prostheses, pace maker lead insulators due to its excellent biocompatibility and wide range of physical and mechanical properties. Among all polyurethanes, linear segmented polyurethane based on diphenyl methane diisocyanate (MDI) is considered as more promising owing to the microphase segregation of soft and hard segments. However, degradation during processing and long-term implantation has been noticed by many investigators (Szycher *et al* 1983; Mazzu and Smith 1984). γ-Radiation sterilization and autoclaving are used to sterilize the polyurethane devices. Excessive and repeated sterilization will result in chain scission and formation of low molecular weight components such as methylene dianiline (MDA) (Mazzu and Smith 1984). Comparatively aliphatic polyurethanes are more stable under thermal conditions than aromatic polyurethanes. Therefore, polyurethanes based on dicyclohexyl methane diisocyanate (SMDI) were developed for various biomedical applications (Jayabalan *et al* 1991; Jayabalan and Rathinam 1992; Jayabalan and Shunmugakumar 1994; Shunmugakumar and Jayabalan 1992). In our previous study (Jayabalan and Lizymol 1995), SMDI based polyurethanes were developed as potential potting compound for the development of hollow fibre haemodialyzer. Effect of autoclaving sterilization on the stability of potting compound was studied. It was found that in the case of caprolactone polyol based polyurethane, autoclave sterilization with one cycle

* For correspondence

may induce leaching of polyurethane fragments. It was found that up to 2nd cycle sterilization, the decomposition of allophanate linkage leading to formation of urea linkage is increased for caprolactone polyol based polyurethane. Further increase in sterilization decreases the amount of urea formation which may be due to the non availability of allophanate group for further degradation (Jayabalan and Lizymol 1997). In the case of castor oil based polyurethane, the possibility of thermohydrolytic attack by autoclaving producing methanol-soluble and methanol-insoluble fragments in higher cycles of sterilization (Jayabalan and Lizymol 1995) is increased.

The present paper deals with the stability of the cured potting compound based on both castor oil/SMDI and caprolactone polyol/SMDI in repeated γ-radiation sterilization.

2. Materials and methods

Two polyurethane prepolymers were prepared using dicyclohexyl methane diisocyanate (SMDI) and castor oil and SMDI and polycaprolactone polyol with different NCO/OH ratio. The prepolymers were analysed by UV spectrophotometry using a UV-160A Shimadzu Spectrophotometer. The setting time of the prepolymers was investigated using excess diisocyanate. The setting time was determined as per ASTM standard F 451–76. The composition which gives lowest setting time was used as potting compound. These prepolymers were cured using SMDI and the cured materials were characterized for thermal stability using a Dupont 990 Thermal Analyser by heating from ambient to 500°C at a rate of 10°C/min. Presence of residual isocyanate content was identified by infrared spectroscopy using a Perkin Elmer 597 IR Spectrophotometer. Spectrum was recorded using polyurethane film.

The stability of cured potting compound in γ-radiation sterilization was investigated by subjecting 1 g of the sample to repeated sterilization. Radiation dose of 2·5, 5·0, 7·5 and 10·0 Mrads were used. The sterilized samples were immersed in 20ml methanol and kept at 40 ± 2°C for a duration of 30 days. The methanol extract was subjected to vacuum evaporation using a rotary evaporater at 60°C. The residue was redissolved in methanol using a definite quantity. The methanol solution was used for determination of low molecular weight compounds using the UV spectrophotometer. The stability of cured potting compound in hot methanol treatment was also investigated as control experiment.

3. Results and discussion

3.1 *Castor oil based polyurethane (SD/02)*

Infrared spectrum of cured SD/02 (figure 1a) shows the responses 3300 cm^{-1} (N–H stretching hydrogen bonded), 1500 cm^{-1} (N–H bending) and 1710 cm^{-1} (C = O stretching hydrogen bonded) indicating the formation of polyurethane. The absence of peak at around 2250 cm^{-1} indicate the absence of unreacted isocyanate in the cured polyurethane. The absence of peaks at around 1732 cm^{-1} for free C = O stretching and at around 3450 cm^{-1} for free N–H stretching indicate the formation of hydrogen bonding in the cured polyurethane (David and Stakey 1969). The formation of

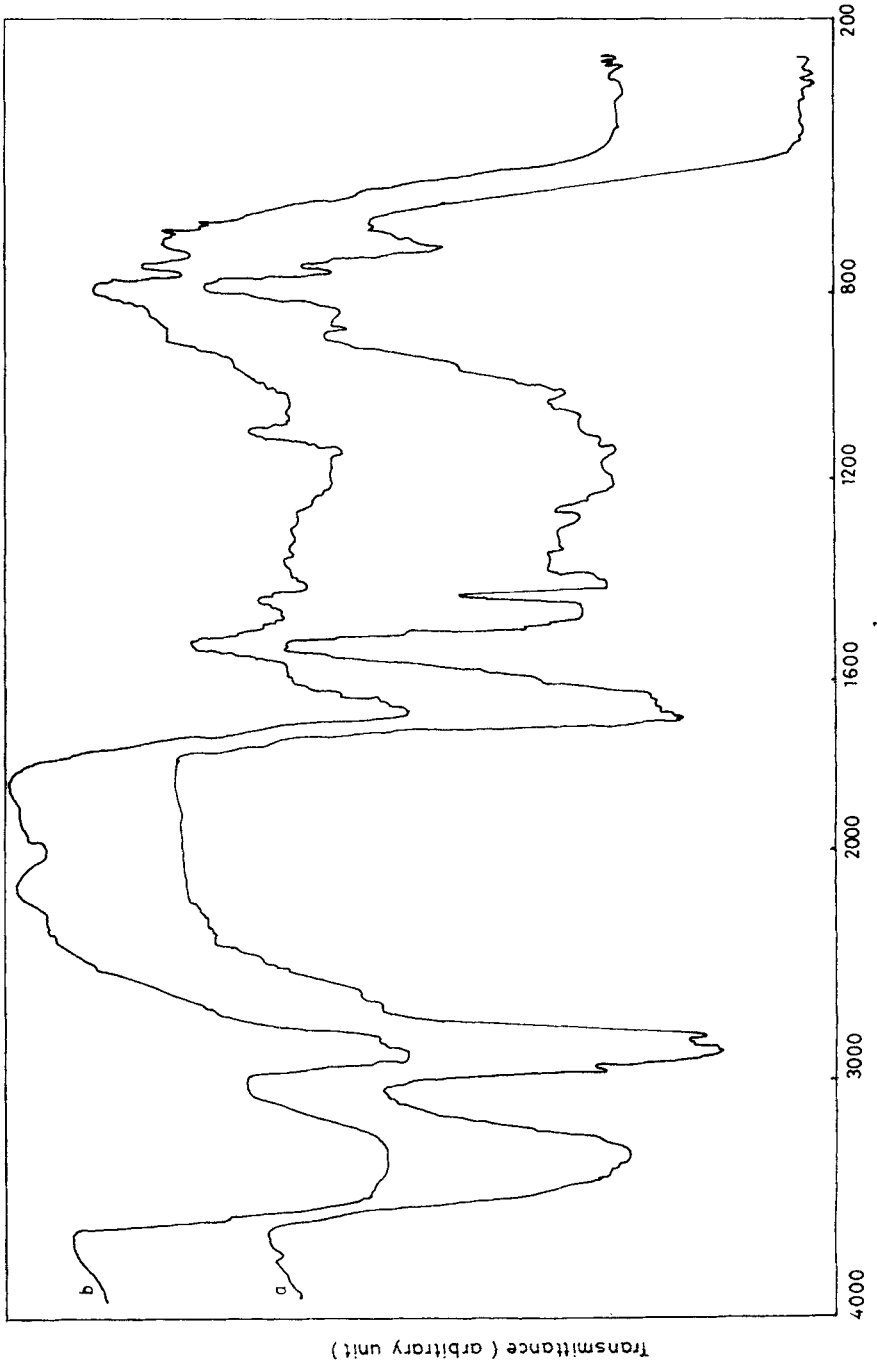

Figure 1. IR spectra of cured polyurethane potting compound **a**. SD/02 and **b**. AD/06.

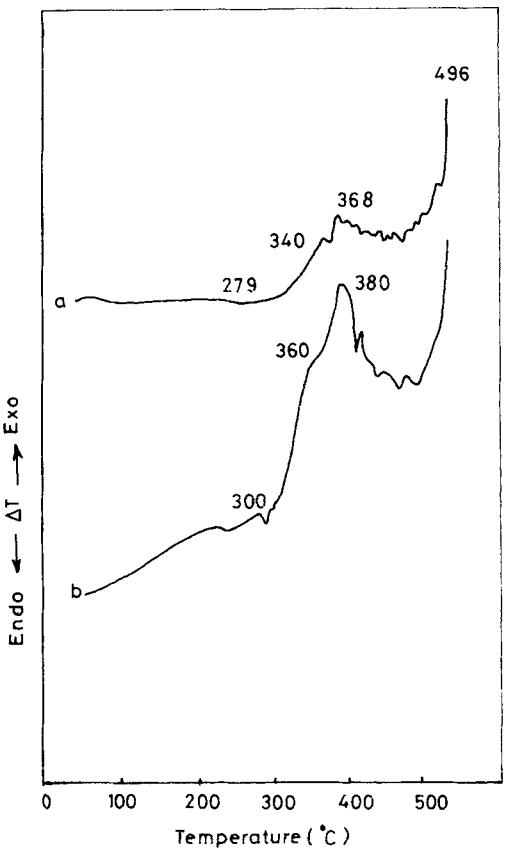

Figure 2. DTA thermogram of cured and untreated polyurethane **a**. AD/06 and **b**. SD/02.

hydrogen bonds is ascertained with the appearance of a band centred at 3300 cm^{-1} for hydrogen bonded N–H stretching and multiple peaks around 1680 cm^{-1} for bonded C = O stretching. The shift of N–H stretching peak for 150 cm^{-1} indicated moderate degree of hydrogen bonding as reported by Kontou *et al* (1990).

The differential thermogram of cured SD/02 (figure 2a) showed a weak endotherm at 300°C which may possibly be due to softening by weakening of feeble physical crosslinks such as hydrogen bonds (a virtually crosslinked structure) in some domains. The weak endotherm at 360°C is probably due to chain scission at chain ends. The exotherm at 380°C is due to condensation through newly formed chain ends.

Figure 3a is the UV spectrum of prepolymer (component A) of SD/02. The major absorption peak is at about 246 nm.

The extent of radiation-induced degradation and leaching of low molecular weight fractions could be gauged from the absorbance data (table 1 and figure 4) observed for the single major peak at around 226 nm. Comparison of figures 3a and 4 reveals that the component leached in methanol from sterilized samples is not the prepolymer (component 1), but some other degraded methanol–soluble fragment. With increase of radiation dose up to 5 Mrad and then from 7·5 to 10 Mrad the polyurethane undergoes degradation when compared with control methanol treatment alone. From table 1 and

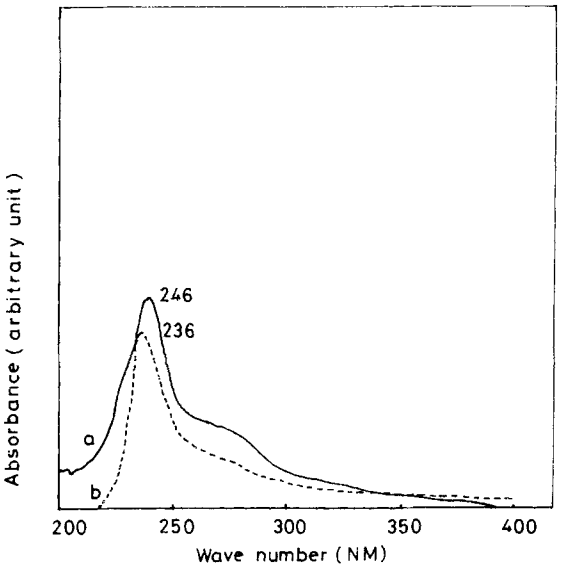

Figure 3. UV spectra of prepolymers (component I) **a.** SD/02 and **b.** AD/06.

Table 1. Absorbance of methanol extract from 1 g of the cured SD/02 sample after γ-radiation sterilization.

Sample	Dose (Mrad)	Absorbance for methanol-soluble fraction from 1 g of the sample at about 226 nm
Control SD/02	0	80·35
Test SD/02	2·5	449·09
SD/02	5	542·54
SD/02	7·5	452·215
SD/02	10	647·98

figure 4 it is observed that methanol induces degradation during extraction. Methanol induces hydrolytic degradation at urethane linkage and also leaching of low molecular weight components (Bruck 1980). The increased leaching in radiation-sterilized polyurethane samples up to 5 Mrad may be due to the enhancement in degradation of urethane linkage by radiation. Further increase of radiation dose results in secondary reactions resulting in the formation of allophanate linkage. The degradation of urethane linkage may lead to formation of methylene dicyclohexylamine. The possibility of simultaneous cleavage at two successive urethane linkages to form amine is rare (Shintani and Nakamura 1991). Abundant terminal amino groups in the potting materials compared with thermoplastic polyurethane may be available (Shintani and Nakamura 1989) due to insufficient curing. Therefore, these polyurethane chain ends are more prone to formation of amine upon radiation as shown in figure 5. However the amine was not detected with the present samples. This is because isocyanate reacts

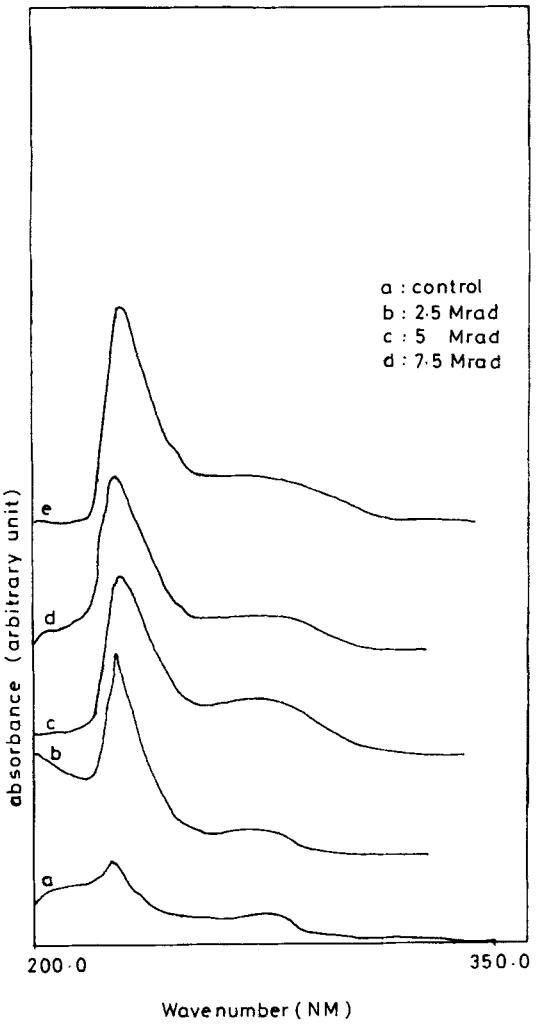

Figure 4. UV spectrum of methanol extract of SD/02 potting compound.

to form allophanate instead of forming just amine. The formation of allophanate linkage may be the reason for the comparatively less intensity of absorption at 7·5 Mrad. On further increase of radiation dose up to 10 Mrad, allophanate linkage undergoes breaking down resulting in a higher intensity of absorption than the preceding one. From the observations it can be concluded that radiation sterilization of castor oil based polyurethane potting compound induces degradation and leaching of low molecular weight components other than diamines.

3.2 *Caprolactone polyol based polyurethane (AD/06)*

Figure 1b shows the infrared spectrum of cured and control AD/06 (1·15) from which we can find the absence of unreacted isocyanate with the absence of peak at 2250 cm^{-1}. The presence of peak at 3300 cm^{-1} (N–H stretching H–bonded) and 1710 cm^{-1}

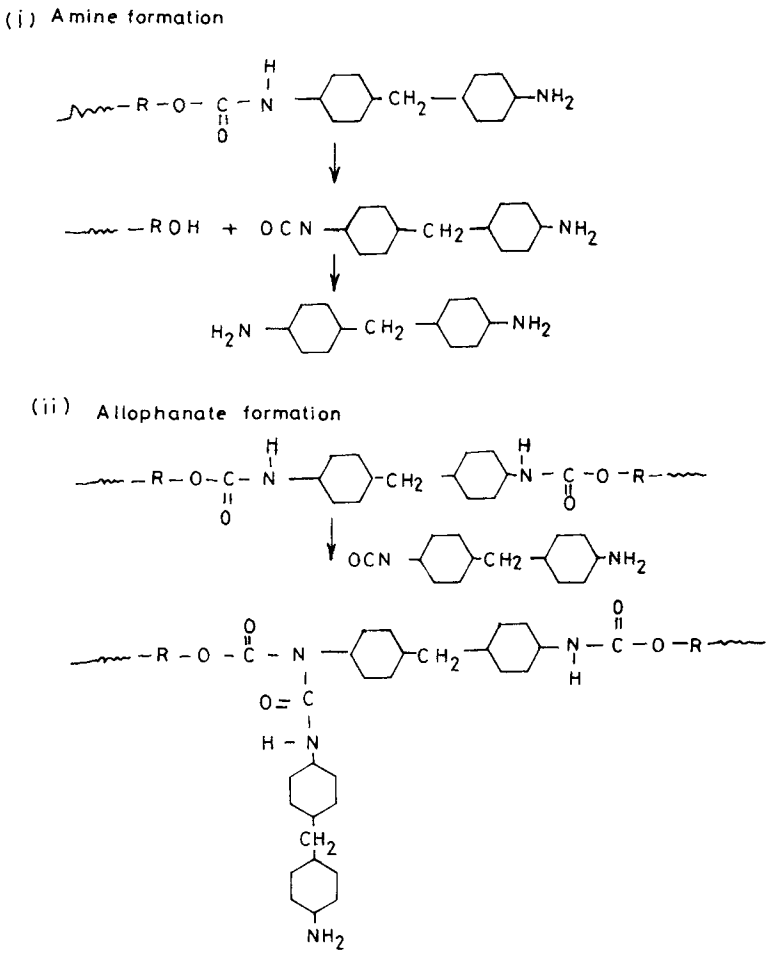

Figure 5. Formation of diamine and allophanate linkages.

Table 2. Absorbance of methanol extract of 1 g of the cured Ad/06 sample after γ-radiation sterilization.

Sample	Dose	Absorbance for methanol-soluble fraction from 1 g of the sample at about 226 nm
AD/06 Control Test	0	80·975
AD/06	2·5	223·58
AD/06	5	273·57
AD/06	7·5	269·82
AD/06	10	100·29

(C = O stretching H-bonded) indicates the formation of polyurethane. Absence of peak at 1732 cm^{-1} for the C = O stretching and at around 3450 cm^{-1} for free N–H stretching indicate the formation of hydrogen bond in the cured polyurethane (David and Stakey 1969). The formation of hydrogen bonds is ascertained with appearance of broad band centring at 3300 cm^{-1} for bonded N–H stretching and shoulder at

1660 cm^{-1} for bonded C = O stretching 1710 cm^{-1} as in the case of SD/02 system indicating moderate degree of hydrogen bonding.

The differential thermogram (figure 2b) of the potting compound showed a weak endotherm at 279°C which may possibly be due to softening by cleavage of feeble physical crosslinks such as hydrogen bonds (a virtually crosslinked structure) in some domain. Two exotherms are visible at 340°C and 368°C. They may be due to condensation through newly formed chain ends. Figure 3b is the UV spectrum of prepolymer (component A) of AD/06. The spectrum shows a prominent absorption peak at 236 nm. Comparison of tables 1 and 2 shows that the effect of radiation on degradation is less in the case of caprolactone polyol based polyurethane compared to castor oil based polyurethane. The degradation on polyurethane linkage of both castor oil based polyurethane and caprolactone based polyurethane by methanol are almost same. Moreover, the intensity of absorption in sterilized samples (figure 6) increases up to 5 Mrad and then decreases with further increase in radiation dose. UV spectra of methanol extract of sterilized samples (figure 6) and prepolymer (figure 3b) gives absorbance at two different wave numbers. This shows that component leached from cured polyurethane is not the prepolymer but some other fragment as in the case of SD/02. Up to 5 Mrad sterilization may induce degradation of urethane linkage and leaching of low molecular weight fractions as in the case of castor oil based

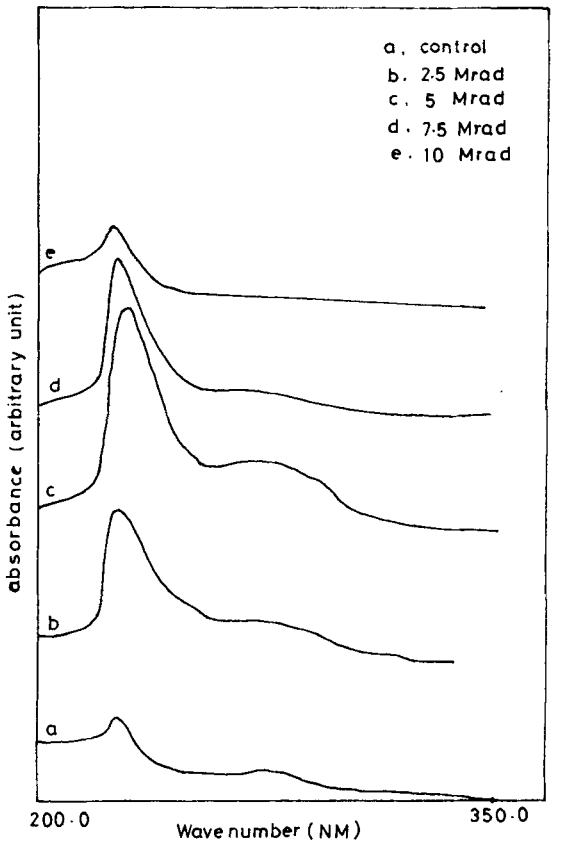

Figure 6. UV spectrum of methanol extract of sterilized AD/06 potting compound.

polyurethane but to a lesser extent. On further increasing the radiation dose the intensity of absorption decreases. At higher radiation doses secondary reactions may occur resulting in crosslinking and formation of allophanate linkage (as shown in figure 5) thereby decreasing the extent of leaching.

In the case of both castor oil and caprolactone based polyurethane, radiation sterilization induces degradation and crosslinking though no amine product was detected in sterilized samples. Degradation is more for castor oil based polyurethane with increased dose of radiation. On the other hand degradation is getting reduced with increased dose of radiation in the case of caprolactone polyol based polyurethane.

Acknowledgements

The authors acknowledge Director, SCTIMST, Thiruvananthapuram and Head, B.M.T. Wing, SCTIMST for supporting Haemodialyzer programme under which this work was carried out. The analytical help provided by Dr K Sreenivasan and Mr Willey Paul is also acknowledged.

References

Bruck S D 1980 *Properties of biomaterials in physiological environment* (Boca Raton, Florida: C.R.C. Press) p. 76

David D J and Stakey B B 1969 *Analytical chemistry of polyurethane* (New York: Wiley Interscience)

Jayabalan M and Rathinam K 1992 *Clinical Mater.* **11** 179

Jayabalan M and Shunmugakumar N 1994 *Med. Prog. Through Tech.* **20** 201

Jayabalan M and Lizymol P P 1995 *Macromolecules–Current trends* (ed.) S Venkatachalam (New Delhi: Allied Pub.) **2** 1136

Jayabalan M and Lizymol P P 1997 *J. Polym. Mater.* **14** 49

Jayabalan M, Shunmugakumar N, Rathinam K and Kumari T V 1991 *J. Biomed. Mater. Res.* **25** 1431

Kontou E, Spathis G, Niaounakis M and Kefalas V 1990 *Colloid. Polym. Sci.* **268** 639

Mazzu A and Smith C P 1984 *J. Biomed. Mater.* **18** 961

Shunmugakumar N and Jayabalan M 1992 *Artif. Organs* **16** 256

Shintani H and Nakamura A 1989 *J. Anal. Toxicol.* **13** 354

Shintani H and Nakamura A 1991 *J. Appl. Polym. Sci.* **42** 1979

Szycher M, Poirier V C and Demsey D T 1983 *J. Elastomer Plast.* **15** 81