



Photo – Polymerizable and Injectable Polyurethanes for Biomedical Applications: *In Vivo* Tests

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Abstract – Two types of photo-polymerizable and injectable polyurethanes acrylate (PUA) based on (poly)propylene glycol (PPG) or (poly)caprolactone diol (PCL) and 2-hydroxyethyl methacrylate (HEMA), were synthesized and characterized in order to have information of their use as injectable material for biomedical applications. *In vivo* biocompatibility of PUA polymers and control (PMMA microspheres) was evaluated by surgical and injectable implants in the dorsum of rats. The response to the presence of foreign body was graded according Duranti et al. [1]. After four weeks, the synthesized materials were in the stage corresponding to grade I: light inflammatory reaction. Our study demonstrated the viability of the synthesized photo - curable polyurethanes to be used in biomedical applications. Further, injectable polymer systems have the advantage of molding *in situ* employing minimally invasive procedures.

Two types of PU acrylate (PUA) were prepared by introducing vinyl groups to the ends of the polyurethane main chains by using HEMA. A 250 mL three-neck glass flask equipped with a heating mantle, a mechanical stirrer, a thermometer and a nitrogen gas inlet system were used. Firstly PCL 1250 (PUA-PCL) or PPG 1000 (PUA-PPG) and HEMA were added to the reactor and stirred at 50°C until to reach a homogeneous mass. IPDI (isophorone diisocyanate) (NCO/OH ratio of 1.5) was then added. The mixture was heated to 60°C and maintained for two hours with stirring and then 0.01% of dibutyltin dilaurate (DBTL) was added to the system. The reaction was carried out at 60°C for 1 h and another amount of 0.01% of DBTL was added. The reaction was continued for approximately 1 h and was monitored by FT-IR measurements until the absorption peak of NCO group at 2270 cm⁻¹ disappeared.

Two different types of radiation curable polymers were prepared from PUA derived from PPG and PCL (see Table 1). (±)-Camphorquinone (CQ) was successfully incorporated in each sample. The content of the photoinitiator was fixed at 1.0% to the weight of the polymer and 2-(dimethylamino) ethyl methacrylate (DMAEM) was used as catalyst for curing. The films were prepared by casting the mixtures onto Teflon mold and allowing then to be exposed to a Degulux® soft-start Halogen lamp 12 V / 75 W for 1 minute. The completion of curing was monitored by observing decrease in C=C absorption peak intensity (cm⁻¹) using FTIR-ATR spectroscopy.

Table 1 – Composition (wt. %) of the synthesized polyurethane acrylates (PUA)

	PCL 1250	PPG 1000	HEMA	IPDI	CQ	DMAEM
PUA/PPG		68.20	8.80	22.80	0.10	0.10
PUA/PCL	72.84		7.60	19.40	0.08	0.08

1) NCO/ OH molar ratio = 1.5. (%NCO free = 4.04).

2) The amount of catalyst was 0.02% of DBTL based on IPDI and PPG or PCL.

The absence of important inflammatory responses, suggests that the polyurethane acrylates studied can be considered biocompatible and have potential for biomedical application.

Table 2 – Classification according to the inflammatory response of the implanted PUA after 4 weeks

CONTROL	III	Inflammatory reaction with presence of lymphocytes and giant cells
PUA/PPG	I	Light inflammatory reaction
PUA/PCL	I	Light inflammatory reaction

References

[1] F Duranti, G. Salti, B. Bovani, and M. Calandra, A Clinical and Histological Study, Dermatol Surg-Mass med Soc (2!998).