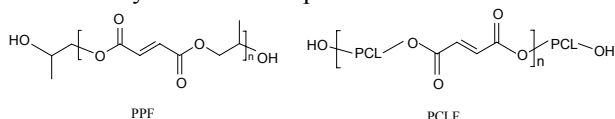


# Controllable Properties of Photocrosslinked Blends of Poly(propylene fumarate) and Poly(caprolactone fumarate)

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**Introduction:** Poly(propylene fumarate) (PPF) is one of the most promising candidate materials with satisfactory properties in biocompatibility, mechanical properties, osteoconductivity, sterilizability, and handling characteristics to substitute autologous or allograft bone (Scheme 1).<sup>1</sup> PPF can be crosslinked via radical polymerization with monomers of methylmethacrylate or *N*-vinyl pyrrolidinone (NVP).<sup>1</sup> Previously we have developed polycaprolactone fumarate (PCLF) (Scheme 1) based on polycaprolactone (PCL) and fumarate segments. Due to the presence of PCL unit, the PCLF chain is much more flexible than the PPF chain. In this work, we report the physical and photocrosslinking properties of the blends of PPF and PCLF. We have reported some preliminary results on the chemical crosslinking between PPF and PCLF. Here we want to show that PCLF can be photocrosslinked with PPF without the addition of crosslinkers to minimize potential cytotoxicity. Furthermore, the network properties can be well modulated by the blend composition.



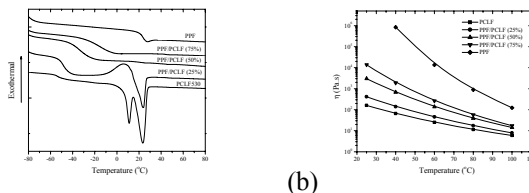
**Scheme 1**

**Methods:** PPF with  $M_n=3460$  g/mol and one PCLF sample with  $M_n=2520$  g/mol were used to make PPF/PCLF blends. Three blends with a PPF content of 25%, 50%, and 75% were prepared by first dissolving PPF and PCLF in a co-solvent methylene chloride and then evaporating the solvent in a vacuum oven. DSC was measured at a heating rate of 10 °C/min in a nitrogen atmosphere. To keep the same thermal history, each sample was preheated from room temperature to 100 °C and cooled to -90 °C at a cooling rate of 5 °C/min. Photocrosslinking were initiated with ultraviolet (UV) ( $\lambda=315-380$  nm) using a photoinitiator bisacylphosphine oxide (BAPO, Ciba Geigy). About 15 mg of BAPO was added into 1.5 g P(PF-co-CL) solution in 500  $\mu$ L of methylene chloride and mixed thoroughly. The polymerizing mixture was transferred into various Teflon and glass molds, such as multi-channel tube mold. The mold was placed under UV light for 30 min to perform crosslinking. After crosslinking, films or tubes were removed from the mold after the mold was cooled to ambient temperature. The dynamic frequency sweep measurements of the blends as well as PPF and PCLF have been performed on a TA AR2000 rheometer and viscosities have been obtained. Mechanical properties of crosslinked multi-channel tubes were tested on DMA. Contact angles were measured on a home-made detector. Bone marrow stromal cell viability, attachment, and

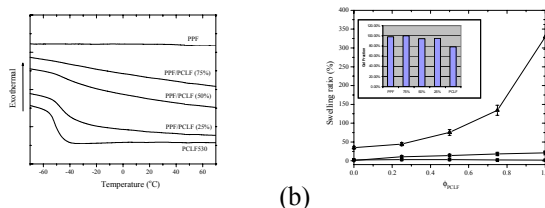
proliferation have been performed to show the effect of blend composition.

**Results/Discussion:** DSC curves in Fig.1 show there is a single broad glass transition for the blends and the glass transition temperature increases with increasing PPF content in the blends, which indicate the miscibility of PPF and PCLF. Meanwhile, the viscosity increases with adding PPF and the temperature dependence becomes stronger as shown in Fig. 1b. The crystallinity of PCLF was significantly suppressed by adding PPF in the blends. When the PPF content is higher than 50%, there is no visible crystalline peak in DSC curves.

All the PPF/PCLF blends have been tested to show they are self-crosslinkable without adding additional crosslinkers. All the crosslinked products are amorphous and no glass transition was found when the PPF composition is higher than 75% as shown in Fig. 2a. It is interesting to note that the gel fraction was efficiently increased from 78 to >95% after adding PPF components since PPF has higher double bond density. All the crosslinked products are hydrophobic with the contact angles of >90°. The swelling ratio in methylene chloride increases from 35% to 330% with PCLF composition while it is negligibly low in water or ethanol.



**Fig. 1:** (a) DSC curves and (b) viscosities at different temperatures of PCLF, PPF, and their blends.



**Fig. 2:** (a) DSC curves and (b) swelling ratios (Inset of (b): gel fraction) of crosslinked products.

**Conclusions:** The miscible blends of PPF/PCLF have been photo-crosslinked and characterized. The composition can be used to efficiently modulate the physical properties of the crosslinked products.

## References:

1. Peter SJ et al. In *Handbook of Biodegradable Polymers*; Domb AJ et al; Eds; Harwood Academic Publishers: Amsterdam, 1997 and references therein.

## Acknowledgments

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