PREPARATION OF INTERPENETRATING POLYMER NETWORKS OF 2-HYDROXYETHYL METHACRYLATES AND POLY(DIMETHYL SILOXANE) IN SUPERCRITICAL CARBON DIOXIDE

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Introduction

In the last few decades extensive interest has been given to the development of silicone hydrogel contact lenses - a soft contact lens type with high oxygen-permeability as well as hydrophilic properties.[1] This paper states the approach to produce an interpenetrating polymer network (IPN).[2] In this cross-linked silicone is swollen with a mixture of a hydrophilic monomer and liquid or supercritical carbon dioxide ($scCO_2$), and then the monomer is polymerized and cross-linked. The silicone network will ensure a high oxygen-permeability, whereas the polymer network will ensure the hydrophilic properties.

Materials and Methods

98% 2-hydroxyethyl methacrylate (HEMA) with 200 ppm monomethyl ether hydroquinone as inhibitor supplied by Acros Organics (Germany) was purified by distillation at reduced pressure, and the fraction at 67°C and 3.5 mbar was collected and stored at 5°C. Diethyl peroxydicarbonate (DEPDC) was synthesized and stored in hexane at -18°C.[3] 5.5 LabLine CO_2 was supplied by Svanemøllen Industries A/S (Denmark) and was used as received.

In a typical experiment all chemicals and a contact lens are placed in a stainless steel reactor. Then the reactor is closed, placed in an oil bath at 25°C and pressurized with CO_2 to 100 bar under stirring. After an impregnation time the oil bath is heated to 75°C, which increases the pressure. After the polymerization the reactor is removed from the oil bath, and when the temperature returns to ambient temperature the pressure is slowly released.

Results and Discussion

$scCO_2$ is a suitable solvent for producing IPNs in which silicone is the substrate material, because Hansen's solubility parameters (HSP) of $scCO_2$ and silicone are quite similar. This means that $scCO_2$ is a good solvent to swell silicone, which in turn enhances the impregnation of monomer. It is a common perception that small organic molecules are soluble in $scCO_2$ whereas larger molecules are not. This means that when a polymer-chain grows too long it will precipitate.

The polymers produced by polymerizing HEMA with DEPDC as initiator in $scCO_2$, are not soluble in any known solvents for PHEMA, e.g. MeOH, and EtOH, even after soaked for over a year. This strongly indicates that the produced PHEMA is cross-linked. One possible explanation is that when PHEMA precipitates during the polymerization an auto-acceleration known as the Trommsdorff effect may occur.[4,5] Since free radical polymerization is an exothermic process, enough energy may be produced during this auto-acceleration to initiate a chain transfer reaction to monomer,[6] which in turn leads to cross-linking of PHEMA. This is an issue regarding the production of contact lenses since particles scatter light, and hence the IPNs become opaque. It should be noted that it is not the cross-linking itself that is the problem, but that the polymers first precipitate and then cross-link.

Cross-linking can be avoided if the Trommsdorff effect does not occur. Since the Trommsdorff effect arises from the precipitation, it is necessary to make a homogeneous polymerization instead of a precipitation polymerization (avoid precipitation during the polymerization). To examine this hypothesis, a conventional free radical polymerization of HEMA in EtOH was carried out. This resulted in a viscous mixture of PHEMA and EtOH. PHEMA was precipitated in diethyl ether and could be dissolved in known solvents for PHEMA. This indicates that the produced PHEMA was not cross-linked. This knowledge can be transferred to the IPN system. HSP has been applied to determine the amount of EtOH to be added to avoid a precipitation of PHEMA. Experiments have shown that cross-linking of PHEMA under free radical polymerization of HEMA in $scCO_2$ can be avoided if EtOH is applied as co-solvent.

Conclusion

It is found that when HEMA is polymerized in $scCO_2$, the polymer precipitates and subsequently begins to cross-link due to a chain transfer side reaction. This results in an insoluble white precipitate. If EtOH is added as co-solvent the precipitation and hence cross-linking can be avoided. This discovery makes it possible to produce a silicone hydrogel, which is suitable as contact lens material.

References:

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