High Molecular Weight Soft Segment based Polyethylene Shape Memory Polymers

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Shape memory polymers (SMPs) have gained great attention owing to their peculiar ability to remember original state upon stimulation. Polyurethane based SMPs (SMPUs) are the most prominent SMPs. It is generally understood that low molecular weight, M_w, and high functionality, f, polymers are essential in producing high density cross links for better shape memory effect (SME), and high Mw and low f polyols (soft segment) can only produce low density cross links, hence weak mechanical and poor SME properties. So far, SMPUs are typically synthesized using polyols with low molecular weight ranging from a few hundred to a few thousand Daltons and high functionality, f>50 [1]. Little effort has been made to synthesize SMPs with high molecular weight and low functionality. It is scientifically interesting and important to synthesize SMPs with high M_w and low f polyols as it may lead to new phenomena and functions or provide more choices for synthesis of various SMPs.

In this study, polyethylene glycol (PEG) with Mn~6000g/mol and f~2 (called PEG-SMPU), and polycaprolactone (PLC) with Mn~2000g/mol and f~56 (PLC-SMPU) were used as the soft segment to synthesize the SMPUs. PEG-200, a combination of diisocyanate (isophorone diisocyanate (IPDI) and 4,4′-diphenylmethane diisocyanate (MDI)) were introduced as the hard segments in the synthesis. The research is to compare the properties of the high Mw and low f SMPUs with those low Mw and high f SMPUs, and to investigate the impact of the concentration of two diisocyanates on the SME and thermomechanical properties. The synthesis process can be found from our paper [2]. The results are summarized as follows;

- Both PEG and PLC-based SMPUs can be tailored with transition temperature Tg in the range of 40~60C, close to human body for medical device applications.
- PEG-SMPUs have higher heat of fusions than the PLC-SMPUs, indicating PEG PU has high crystallinity. The heat of fusion increases while Tg decreases with increase of the IPDI concentration.
- The elongation at break is high for both types of SMPUs with high MDI concentration (low IPDI). PLC-SMPUs showed a maximum elongation at break of ~980%, that of PEG-SMPUs is about half of this. But the maximum stress of PEG SMPUs increases with IPDI concentration, while that of PLC SMPs showed an opposite effect.
- PEG-SMPUs showed much better recovery rate (99%) and shape fixity (95%), much high than PLC-SMPUs (~85% and 89%), but the recovery stress produced by these SMPUs is only half of those by PLC-SMPUs.
- The most remarkable result is that PEG-SMPUs has a ***much short response time*** under thermal stimulation, in the order of a few seconds compared to 60sec~few minutes of other SMPs. The results show high molecular weight based SMPs have better properties, are suitable for MEMS fabrication, and hold more potential for applications.

1). D.W. Vilar; Chem.& Technol. Polyurethanes, Vilar Polyurethanes 2002.
2). M.Ahmad et al. Macromol. Chem. & Phys. In press.

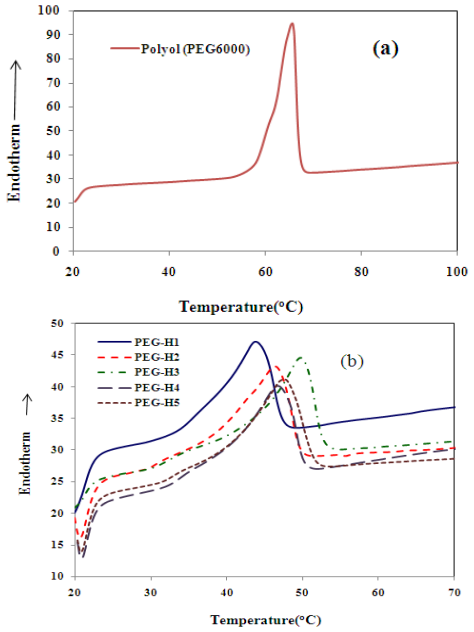

Fig.1: DSC results of the PEG-6000 polyol (a) and PEG-SMPUs (b) respectively.

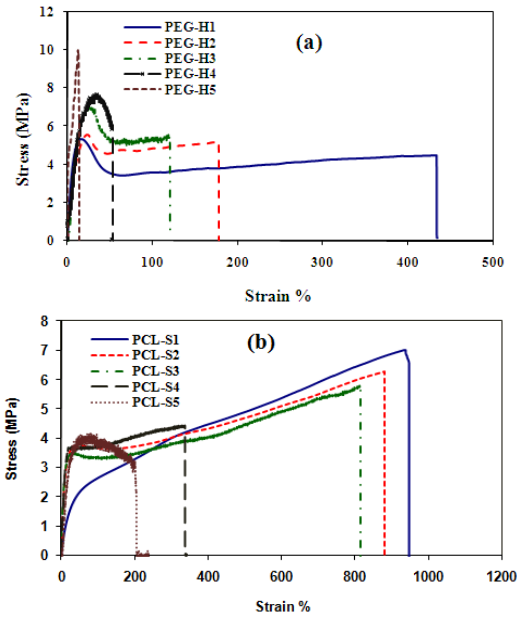

Fig.2: Stress vs. strain for PEG and PCL SMPUs series at ambient temperature.

Table I. Molar ratio of diisocyanates used for synthesis of SMPUs.

Sample	MDI	IPDI	γ
PEG-H1, PCL-S1	19.95	0	1.0
PEG-H2, PCL-S2	16.5	3.37	0.83
PEG-H3, PCL-S3	13.36	6.65	0.668
PEG-H4, PCL-S4	10.0	10.0	0.50
PEG-H5, PCL-S5	6.6	13.7	0.325

[γ = MDI / (MDI+IPDI)]

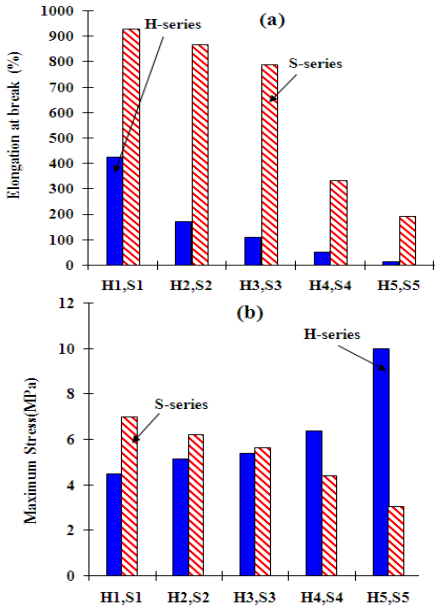

Fig.3: summaries of elongation at break (a) and maximum stress (b) for PEG and PCL SMPUs respectively at ambient temperature.

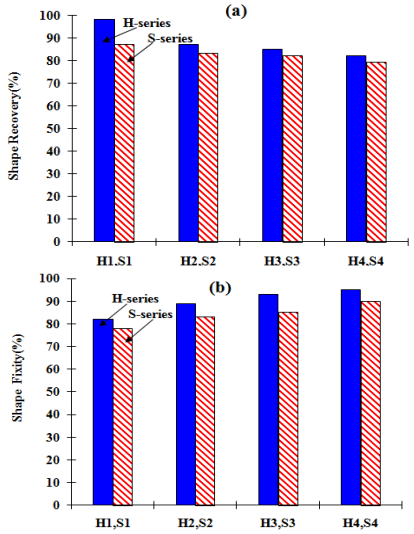

Fig.4: Shape recovery and shape fixity of the PEG (a) and PCL SMPUs (b) at 60 °C and 50% strain.

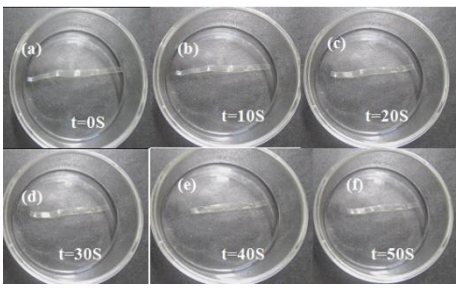

Fig.5: Shape recovery of the extended PCL-S3 sample at 60 °C. The shape recovery takes place slowly and completes only ~80% after 50 sec, a much slower rate than that recorded for PEG-SMPUs.