SYNTHESIS OF SHAPE MEMORY EPOXYURETHANE POLYMERS WITH A WIDE RANGE OF SWITCHING TEMPERATURES

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Shape memory polymers (SMPs) have attracted increasing interest from both academia and industry. Such materials have a high innovation potential and can be formed in films for packaging, heat-shrinkable tubes, smart fabrics, intelligent medical devices, implants for minimally invasive surgery, self-deployable sun sails in spacecrafts and so on.

A typical thermoset polymer is a mixture of many long, entangled molecular chains that are connected by net points created by either chemical cross-linking or physical cross-linking. At temperatures higher than the glass transition temperature, those polymer chains are flexible and a polymer is soft and is characterized by the rubbery state. The switch temperature (T_{sw}) between permanent and temporary shape of thermoset SMPs is usually related towards the glass transition temperature (T_g), so it is a key parameter defining the temperature range of their shape deformation and recovery.

In our work we propose an approach to modify the basic epoxy resin (we used epoxyurethane resin) having high T_g value (114 °C) by poly(ethylene glycol) diglycidyl ether with low T_g value (-10 °C) in different ratios while content of curing agent was the same in all composites. We consider the compatibility of these components and a presence the sole glass transition in the range between mentioned T_g values. Such an approach allows us to create an epoxyurethane material with controlled temperature of memory shape effect in wide temperature range.

The object of the research were polymer materials synthesized from reactive mixtures of two epoxy oligomers, aromatic and aliphatic: epoxyurethane resin (EPU) taken as a basic polymer and poly(ethylene glycol) diglycidyl ether (DEG-1 trademark) serving as modifier. Also we used polyethylene polyamine (PEPA) as hardener (10 % of reactive mixture). The ratio EPU/DEG-1 in reactive mixture was in a range 100/0 – 70/30.

EPU resin was produced as a result of reaction of aromatic diglycidyl ether of bisphenol A based resin (ED-20 trademark) with urethane oligomer macrodiisocyanate (MDI) with addition of 1.4-butandiole (BD) as lengthener of molecular chains in proportion ED-20/MDI/BD = 65/33/2. MDI was previously synthesized in reaction of polypropylene glycol having MM = 1052 with toluene diisocyanate taken in stoichiometric ratio 75/25. Reaction of synthesis was maintained up to achievement of ca. 6 % of free NCO-groups in the MDI product. Afterwards these NCO-groups reacted with OH-groups of epoxy resin providing integrated chemical structure of epoxy resin. EPU contains the rigid segments remained from the molecular structure of aromatic resin ED-20, namely the pairs of benzene rings. On the other hand, it also includes the flexible groups of MDI in the EPU molecules structure.

Since the modifier DEG-1 resin includes the flexible $–CH_2–CH_2–O–$ groups the chemical structure of EPU/DEG-1 epoxy polymer contains in a mixture of rigid and flexible chains where part of rigid structure fragments of EPU is substituted by flexible DEG-1 chains. Bigger number of flexible chains with increasing of DEG-1 content in SMEPs imparts softer structure of polymer material with lower T_g value.

It was found that alteration of EPU/DEG-1 ratio from 100/0 to 70/30 leads to the change of glass transition temperature T_g from 114 to ca 45 °C. Since T_g value is identified with switching temperature T_{sw}, such an approach makes possible to obtain the materials with shape memory effect in different temperature intervals that gives them the attractiveness for use in different applications, for example, materials with T_{sw} close to temperature of human body are of interest for applications in the biomedical fields.