

TOUGHENING OF UNSATURATED POLYESTER RESINS BY REACTING ADDITIVES

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Thermosetting materials based on Unsaturated Polyesters (UPR) are known to possess very low ductility. This means external energy applied on UPR (e.g. impact) has low chance to be dissipated as it occurs in rubbery materials, but is consumed on formation of cracks propagating fast from impact point to surrounding regions. Thus many attempts to apply reactive elastomers like CTBN did not lead to appropriate toughness of UPR resins. The same results were obtained for core-shell systems (Albidurs by Nanoresin) or nano-structured block-copolymers Arkema. The presence of reactive groups to link toughening agents to UPR structure did not show any visible effect on toughening of UPR used. On the other hand all above toughening agents showed good enough toughening effect in case we applied them in epoxy resin based composites. Low ductility means matrix of very low viscous properties and very low relaxation time. Within relaxation time period excitation is able to propagate to some distance from point of excitation to form crack or to be retarded by toughener. Basing on above approach we can consider polymer matrix as divided in elementary unit volumes. Each volume unit has to contain toughening element which is responsible for toughening of UPR matrix located in vicinity. The idea can be realized by using toughening additives of very low size to endeavor to fight with low relaxation time of extremely low ductile UPR matrix. In this regard the less is the toughening unit the better is toughening capacity. Toughening is only possible in case toughening additive exists as separated phase in solid UPR matrix. In case single phase solution of toughening additive in rigid matrix never toughening effect was observed. The main target of the work was to follow influence of epoxy toughener on properties of UPR. In contrast to classical toughening agents toughening effect of thermosets shows maximum upon concentration close to 0.1mol/kg of additive. Concentration of epoxy groups in toughening additive must be close to concentration of –OH and COOH end groups in UPR. In case of lower concentration it is not enough epoxy

groups to link all UPR end groups. In case of higher concentration of epoxy groups not all epoxy groups are reacted or polymerization of epoxy groups can take place. Reaction of epoxy with Unsaturated Polyester end groups can decrease entropy change of solution of epoxy in UPR before and after reaction of epoxy groups with UPR ending groups. The number of possible states of linked epoxy is much less than numbers of possible states which in free epoxy can exist. It means:

$$\Delta G_l = \Delta H_l - T\Delta S_l \text{ (liquid phase)} \quad (1)$$

$$\Delta G_s = \Delta H_s - T\Delta S_s \text{ (solid phase)} \quad (2)$$

$$\Delta S_s < \Delta S_l \quad (3)$$

The main target to obtain toughened system is:

$$\Delta G_l < 0 \text{ and } \Delta G_s > 0 \quad (4)$$

In general terms epoxy structure interior UPR matrix can be related to interpenetrated network (IPN). Such toughening effect is related not to particular epoxy resin application but to formation of toughening IPN in UPR matrix by monomer of higher ductility. As mentioned above toughened polymer can be divided in elementary volumes each containing one toughening phase separated unit. Dimensions of elementary volume for regular rubbery toughening agents (about 0.5mcm) is likely large to provide effective transfer of exciting energy from UPR matrix to elastic polymer. Molecular level distances in IPR provide good toughening effect by very short time of energy transfer compared to relaxation time in UPR. Below are a few results of application of epoxy resin as toughening agent compared to regular toughening system in highly filled (87%w/w quartz) UPR composite.

Toughening effect of different additives on filled (87% quartz) UPR

Epoxy toughener, 0.1mol/kg, 3-functional	Albidur, Core-Shell, toughener, 12%	Unmodified UPR composite	
82.0	52.0	78.0	Ultimate Strength
2.2	1.0	1.0	Impact Strength, AU
91.4	81.0	9230	Tg, C