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Impact Resistance of Unsaturated Polyester Resins Modified by Organosiloxanes Compounds

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Introduction

Unsaturated polyester resins (UP) are formed from carboxylic acids and polyfunctional alcohols and they are cured by radicalar copolymerization with vinvlic or acrylic monomers. Styrene is the most useful due to its low cost and high efficiency.

The UP resins properties can be enhanced by proper choice of raw materials, as well as the monomer and the conditions of cure. However, impact resistance of UP is low, limiting some applications. Several works have studied adhesion between resin and modifiers in a way of improving impact resistance with no adverse effect on flexural strength, heat distortion temperature and so on.

This work was aimed to modify UP resins with poly (organosiloxanes). These are constituted by flexible and nonpolar backbones, with low solubility parameter and surface tension and, therefore, low miscibility with organic polymers (Yilgor et all, 1989).

For this reason, blends or copolymers of organic polymers with poly(organosiloxanes) are imiscible mixtures with low adhesion among the differents phases and consequently weak mechanical properties.

In order to minimize low adhesion between resin and modifier we proposed the formattion of grafting copolymers. Hence, glycidyl methacrylate (GMA) was added to the resin network by radicalar reaction, as well as aminopropyltriethoxysilane (APTS), which amino group reacts with GMA. The addition of 1.1.3.3 tetrametil 1.3 diethoxydisiloxane (chain extender) allowed poly(organosiloxane) network to grow up and the addition of water guaranteed hydrolisis and polycondensation during the cure. By this way it is possible to graft a long siloxane chain on the UP resin. increasing its flexibility and probably its impact resistance.

The gafting reactions are presented below:

CH₂ (UP modified by GMA)
$$CH_{3} - C$$

$$CH_{3} - C$$

$$CH_{3} - C$$

$$CH_{2} - CH_{2} - CH_{2}$$

Experimental

Orthophthalic resin, trade name RESAPOL 10-230 and isophthalic resin, trade name RESAPOL 10-169 supplied by Resana S/A were used in this work. Both are pre-accelerated by cobalt octoate (0.5 wt%t) and methylethylketone peroxide were used as initiator (1 wt%)

Modified ortho and iso resins were prepared with 2.5 and 5.0% by weight of aminopropyltriethoxysilanc (Aldrich) and equimolar quantities of glycidyl methacrylate (Aldrich), 1.1.3.3 tetrametil 1.3 diethoxy-362 disiloxane (Hüls) and water. After addition of the

initiator the samples were cured at room temperature for 24 hours, post-cured at 65 °C for 24 hours and vacuum dried at 75 °C for 3 hours to eliminate residual monomers

Impact resistance were evaluated according to Cantilever Beam (Izod type) test (ASTM D 256-79), in the TMI testing machine. At least 12 samples (2.5 mm x 0.5 mm x thickness) of each composition were tested

The dynamic-mechanical behaviour and dependence of Tg on additives were evaluated in the DMA 938 - TA Instruments. Samples were heated at 5 °C/ min. in a range of -150 - +150°C, under oscillatory

deformation amplitude of 0.2 mm and frequency of 1 Hz. Samples were made into polyethylene molds with about 2 mm diameter. For comparison, the pure resins were submitted to both tests.

Results and discussion

Figure 1 shows the loss modulus (E") curves of the pure and modified UP resins. We can see the incorporation of additives lowered values of Tg of both resins, indicating network flexibility. In a previous work (Rosa et all. 1995), dynamic mechanical analysis suggested grafting copolymerization. That work also showed a plasticization effect due to incorporation of silane and acrylic components. So, the dangling segments increased the free volume of the resin network.

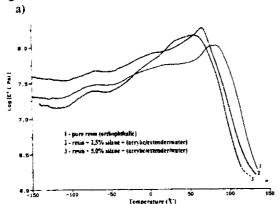


Figure 1. Loss modulus x Temperature of pure and modified UP resins: a) orthophthalic resin; b) isophthalic resin.

Recently, some works (Pandit and Nadkarni, 1994; Tieghi et all. 1992) studied miscible and imiscible adducts incorporation on the UP matrix and a better impact resistance have been obtained to both adducts. The miscible adducts created flexible dangling segments. The imiscible adducts created a second phase in the matrix. Despite of this, there was some interfacial chemical compatibility between the adduct and the

allowing a more intense energy dissipation and probably a greater impact resistance.

Table 1 exhibits the impact resistance (σ_{imp}) as well as the standard deviation (σ_{n-1}) for the resin modified by 2,5 and 5 wt% of silane and equimolar quantities of acrylic, extender and water. Small amounts of additives improved impact resistance. However, the resin modified by larger amounts of additive presented values close to the pure resin. This fact was due to the phase separation between the matrix and the poly (organosiloxane) homopolymer. The broadening of loss modulus peak of the resin modified by 5% of silane and stoichiometric quantities of the other compounds indicated the phase segregation.

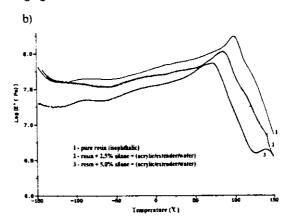


TABLE 1: IMPACT RESISTANCE OF PURE AND MODIFIED UP RESINS

	Orthophthalic resin		
	Purc	2.5% silane	5.0% silanc
σ _{mp} (J/m)	15.1	17.0	15,1
σ_{n-1}	1.65	1.84	1,96

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References

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matrix. The resulted multiphase structure was resistante to impact like the HIPS structure.

Phase segregation that occurs when greater amounts of acrylic and silicon compounds was added to the resin created incompatible domains with the resin. Therefore, only small amounts of additives is efficient to improve impact resistance because it creates flexible segments without phase separation.

	Pure	2.5% silane	5.0% silane
σ _{unp} (J/m)	13,3	14,9	13.3
σ_{n-1}	1.52	1.70	1,10

Isophthalic resin

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