

# Vinyl ester matrix resins for advanced materials

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Polymer matrix composites are used in the aerospace, automotive, and infrastructure industries to reduce high weight associated with their metallic counterparts. Vinyl ester (VE) is an attractive class of matrix resins due to its high chemical and corrosion resistance, good thermal and mechanical properties. This paper is concerned with presenting a short review with some important results regarding of polyurethane (PU)-vinyl ester resins (VER).

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## 1. Introduction

Polymer matrix composites (PMC) are an emerging class of materials that are utilized in a wide variety of applications. The matrix can consist of either thermoset or thermoplastic polymers. Thermoset matrices are superior to thermoplastic matrices with respect to modulus, glass transition temperature ( $T_g$ ), and processibility (viscosity and processing temperature). PMCs can be designed to reduce weight, increase mechanical properties, reduce the number of elements in a component, obtain a unique combination of properties, and increase shaping freedom. The polymer matrix plays an important role in the ultimate performance of a composite. The potential for low viscosity (better processibility) and generally superior material properties makes thermosets an attractive class of polymers in PMCs [1].

Vinyl ester resins (VERs) are additional products of various epoxide resin and ethylenically unsaturated monocarboxylic acids. The resins have thermal reactive double bonds. Presently, there is an increasing interest in VERs, being recognized as materials with many applications in obtaining of composites for transportation, in automobile industry, in buildings construction, as component part of pipes, tanks and ducts. Other applications are in coatings, adhesives, as well as electrical and aerospace industry. The researchers in the field of VERs are today directed towards the synthesis of new resins with advanced properties, in obtaining of new information regarding the mechanism of the curing reaction and to gain better control of the materials synthesized on the basis of VERs [2].

Epoxy-acrylic resins found a variety of uses, as matrices in the composite aeronautic industry, in optical fiber coatings, as structural adhesives, UV curing inks, coupling agents, as well as printed circuit boards and paints [3]. Therefore, the chemical modification with

polyisocyanates was employed to increase of the epoxy-acrylate resin elasticity.

Crosslinked VERs is used as the matrix polymer of high performance composite materials because of their stiffness, chemical resistance and relatively high thermal stability [4].

Interpenetrating polymer networks (IPNs) are a special kind of multicomponent polymeric materials, having the advantage of crosslinking, which allows exceptional control of morphology [5]. The study of IPNs has aroused great interest because most IPNs exhibit better mechanical properties than their individual networks due to a synergistic effect induced by forced compatibility of the components [6].

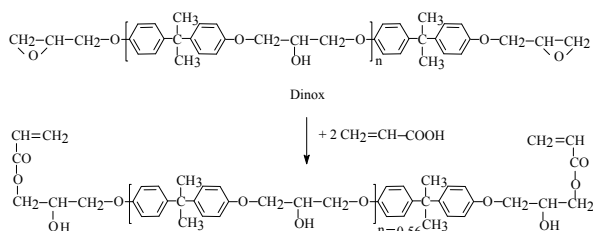
## 2. Experimental

### 2.1. Preparation of poly-HABA resin

Generally, VERs is prepared by addition of ethylenically unsaturated monocarboxylic acids to an epoxy backbone, in presence of a basic catalyst. The VER, that is the cross-linked polyhydroxy-acrylate of bisphenol A (poly-HABA), was synthesized starting from the Dinox epoxy resin, the latter being obtained from Bisphenol A and acrylic acid, in presence of triethylbenzylammonium chloride, used as catalyst, and hydroquinone, as thermal polymerization inhibitor.

The obtained solution was washed many times with sodium bicarbonate (30 wt.% aqueous solution) in order to remove the traces of unreacted acrylic acid. It was then dried on anhydrous calcium chloride and distilled under vacuum [7].

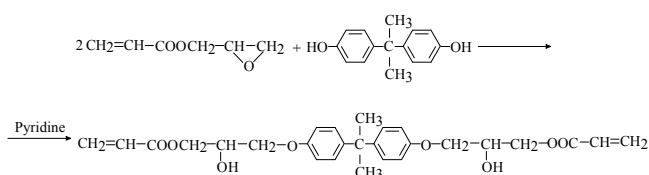
The general reaction yielding the poly-HABA resin in given in scheme 1.



Scheme 1. Synthesis of poly-HABA resin.

## 2.2. Preparation of DHABA

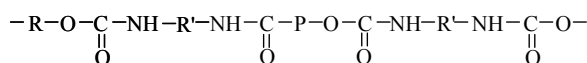
Dyhydroxyacrylate of bisphenol A (DHABA) resin was obtained by an addition reaction of glycidyl acrylate to Bisphenol A, in presence of pyridine. The synthesis was carried out in a 500 ml round-bottom flask, fitted with a stirrer, reflux condenser, heating system, thermometer and oil bath, starting from 114 g Bisphenol A, 128.13 g glycidyl acrylate, 6.3 g pyridine, used as catalyst, and 0.74 g hydroquinone, used as thermal polymerization inhibitor. The mixture was stirred at 100°C for 24 h, and the obtained product was washed several times with distilled water, filtered off and dried in vacuum at 60°C for 10 h. The yield varied between 80 and 85% by weight. The reactions used for the synthesis of DHABA are shown in Scheme 2.



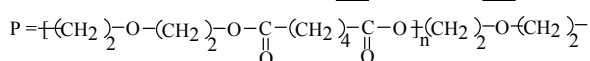
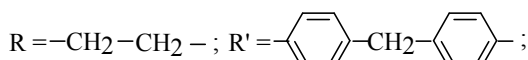
Scheme 2. Synthesis of DHABA

## 2.3. Synthesis of PU

PU was synthesized using a copolyester obtained by fusion condensation of adipic acid, ethylene glycol, diethylene glycol (1:0.5:0.6 molar ratio) with 4,4'-diphenyl-methane diisocyanate (MDI), as was previously reported [8]. The copolyester used for PU synthesis had a number-average molecular weight of 2000, and an acidity index of 0.2 mg KOH/g.



where:



Scheme 3. Structure of PU

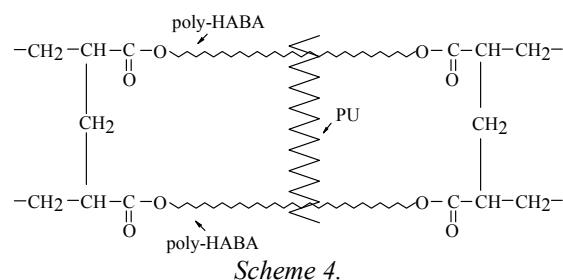
## 2.4. Preparation of PU-poly-HABA SIPNs

SIPNs of PU-poly-HABA resin were carried out after a sequential procedure by mixing the PU solution in dimethylformamide (DMF) with variable amounts of poly-HABA resin, as is shown in Table 1.

Table 1. Composition of S-IPNs synthesized from PU and poly-HABA.

Sample	PU (%)	Poly-HABA (%)
PU	100	-
S-1	90	10
S-2	80	20
S-3	70	30
S-4	60	40
Poly-HABA	-	100

The PU chains interpenetrate the cross-linked poly-HABA resin leading to a SIPNs material, as is figuratively shown in Scheme 4.



Scheme 4.

## 2.5. Synthesis of PU-DHABA graft copolymer

PU-DHABA graft copolymer was synthesized in basic medium, starting from 30 g PU dissolute in 125 ml fresh distilled DMF. The obtained solution was treated with 9 g DHABA, in presence of pyridine (pyridine/DHABA molar ratio between 0.678 and 3.402), and hydroquinone (0.1% by weight against DHABA). The mixture was stirred at 60°C for 4 h and continued at 80°C for 1h, to complete the grafting process. The crude final product was purified by successive precipitations from DMF solutions, with distilled water, filtered off several times, washed with acetone, and dried in vacuum at 80°C for 2 h.

## 2.6. Preparation of PU-DHABA crosslinked graft copolymer

The synthesized PU-DHABA graft copolymer was dissolute in DMF. The obtained solution was cast as a film on a glass slides by means of a doctor-bleading. The slides were heated in an oven at 140°C for 3 h. The traces of solvent were completely removed, and the films, cooled at room temperature, were detached from the glass slides as



thermal stability of PU is lower as that evaluated for poly-HABA resin.

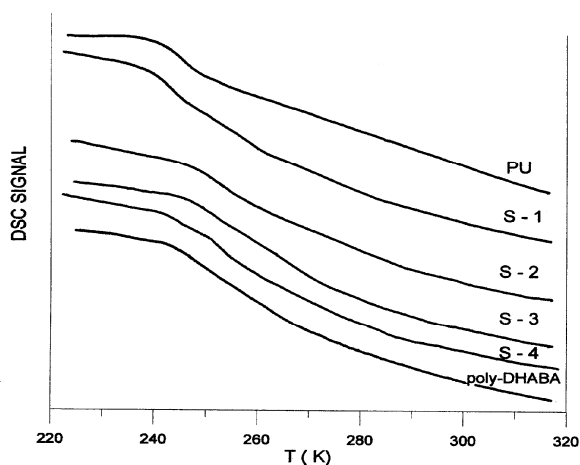


Fig.3. DSC curves of PU-poly-HABA SIPNs, PU and poly-HABA resin at a heating rate of 12°C/min.

Generally, the thermal degradation of the synthesized SIPNs in dynamic condition and in presence of oxygen shows three to five decomposition stages. The SIPNs degrades starting with 200°C, an increasing decomposition rate being observed in the 250-500°C temperature range (the second and third stage), where the weight loss reaches about 70-80 wt %. The curves in Fig. 3 show that the synthesized SIPNs present an apparent thermal stability placed between that of PU and of poly-HABA resin, at temperatures higher than 300°C.

Table 2. Some mechanical properties of PU and of synthesized SIPNs, respectively

Sample	Stiffness (MPa·10 <sup>-3</sup> )	Modulus of elasticity (MPa)	Resilience (MPa)
PU	2.957	1.149	19.543
S-1	3.162	1.488	22.950
S-2	3.560	2.585	20.984
S-3	3.940	3.312	16.302
S-4	6.606	5.401	18.543

The synthesized SIPNs exhibit excellent mechanical properties. The values obtained using this procedure is listed in Table 2.

It can be remarked that with increase of the poly-HABA amount the stress used for the strain of the same unit of length increases too. This behaviour is quantitatively described taking into consideration the stiffness of the each sample analyzed to a certain extent.

Generally, the stiffness of the SIPNs increases with increase of poly-HABA resin amount, being much higher in comparison with the stiffness determined for PU. The elastic resistance of the studied SIPNs to deformation is characterized by both modulus of elasticity and resilience.

These two mechanical properties were measured and the values obtained are summarized in the same Table 2.

### 3.2. Characterization of PU-DHABA crosslinked graft copolymer

The value of  $T_g$  evaluated for PU-DHABA crosslinked graft copolymer was -18°C, lower as  $T_g$  of PU (-15°C).

The TG and DTG experiments show important differences in the thermal behavior of the synthesized PU-DHABA graft copolymers in comparison with the thermal decomposition of PU and of DHABA resin. The first stage in the range between 100-250°C corresponds only to DHABA resin, and it is probably due to volatilization of undesirable components present in the starting resin and release of some small molecules. The PU-DHABA copolymers decompose starting with about 250°C. A high rate of decomposition is recorded in the range between 280-450°C, with important weight losses (around 60-70%).

The PU-DHABA crosslinked graft copolymer was analyzed regarding the physico-mechanical properties.

The curve stress - strain, recorded for PU - DHABA crosslinked graft copolymer, shows a special behaviour as against the curves recorded for PU, as well as for PU - DHABA mixture. Moreover, the crosslinked graft copolymer shows, as compared to PU, a high increase of the initial elasticity modulus (57 times), of the elongation at break (about 3 times), the elastic resilience (2 times) and of the resistance to the limit of elasticity (4 times). Simultaneously, the elongation at break decreases (2 times). These data proved that the synthesized crosslinked graft copolymer was crosslinked by means of the chemical bonds, as well as by the hydrogen bonds.

### 4. Conclusions

VERs is additional products of various epoxide resins and ethylenically unsaturated monocarboxylic acids. The synthesized poly-HABA resin was characterized by IR and <sup>1</sup>H-NMR spectroscopy. It was used to prepare a series of S-IPNs in presence of polyurethane.

PU-VER S-IPNs were synthesized and characterized regarding the method of synthesis, their morphology and the mechanical properties. By incorporation of the VERs in the linear PU the synthesized S-IPNs show an improvement in the mechanical properties.

The DSC measurements show a high degree of miscibility of crude polymers in the SIPNs. By incorporation of the poly-HABA resin in the linear PU, the synthesized SIPNs show an improvement in the mechanical properties. The thermal stability of the synthesized SIPNs is placed between that of PU and poly-HABA resin for temperatures higher than 300°C.

The incorporation of VER in PU by grafting process leads to increase of the mechanical properties of PU, as well as of the thermal stability.

Grafting results in an increase in the initial elasticity modulus, in the break resistance, in the elastic resilience, as well as in the resistance to the limit of elasticity. An improvement of the thermal stability was remarked by grafting process.

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