Study on the Structure and Properties of a Hybrid Resins

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Abstract

Polysilicate modified polyurea/vinyl ester hybrid resins were produced by dispersing water glass (WG) in a mixture of vinyl ester (VE) and polyisocyanate in presence of a liquid phosphate as emulsifier. As styrene-crosslinkable VE resins bisphenol A (BA) and novolac types (N), whereas as polyisocyanate a polymeric methylene diphenyl isocyanate (PMDI) were used. The structure and selected properties of the hybrid resins were determined and compared to those of the neat VEs and polysilicate filled polyurea (denoted as 3P resin). Using VE for resin hybridization, which worked as an additional emulsifier for the WG/PMDI/phosphate system, resulted in a fine particle dispersion of the polysilicate. It was found that the type of VE affected not only the dispersion of WG (and thus of the polysilicate) but also the network formation of the polyurea/VE hybrids and their properties. Information about the structure of the polysilicate filled hybrid resins was gained from dynamic-mechanical thermal analysis (DMTA), scanning electron and atomic force microscopic measurements. It was argued that the resin hybridization yielded a conetwork instead of an interpenetrating one. The properties of the hybrid systems were determined by DMTA, fracture mechanical tests, thermogravimetric analysis and flammability measurements. It was established that the stiffness and resistance to thermal degradation of the initial 3P resin was strongly improved by hybridization with VEs. The fracture toughness (Kc) proved to be less sensitive to the formulation of the hybrid resins. On the other hand, the fracture energy (Gc) and limiting oxygen index experienced a positive deviation from the additivity as a function of the 3P/VE composition, at least in a given range.

Keywords: Fracture mechanics, Morphology, Network formation, Polyisocyanate, Polyurea, Vinyl esterresin, Water glass, Polysilicate

1. Introduction

Inorganic-organic hybrid materials became under spot of interest due to the beneficial combination of properties of polymers and ceramics. Nowadays considerable efforts are dedicated to produce composites in which the fillers of different aspect ratios are nano-scaled dispersed in the polymer matrix. This problem has been studied previously(Nalwa,2003, and Utracki,2004). For the in situ production of the inorganic phase usually different routes of the sol–gel chemistry are followed. This problem has been studied previously(Nalwa,2003,and Kickelbick,2003,pp.83-114). The related precursor compounds are mostly alkoxysilanes-titanates and the like, which all are rather expensive. Water glass (WG) can be considered as a cheap alternative precursor. Note that the sol-gel transition of WG (termed also to hardening, silicification) is known from ancient times. This problem has been studied

previously(Stoye,1993, p.94-96). The basic reaction of the silicification when induced by atmospheric CO_2 is given by:

$$mNa_2O \text{ -}nSiO_2 \cdot xH_2O + mCO_2 \rightarrow nSiO_2 \cdot (x\text{-}y) \; H_2O + mNa_2CO_3 + yH_2O \qquad (1)$$

Silica gel (Hydro- or xerogel)

The above reaction can be reproduced when dispersing WG in polymeric isocyanates. In the corresponding water (WG)-in-oil (polyisocyanate) type emulsion (W/O) the isocyanate groups react first with water via releasing CO2:

$$R\text{-}NCO + H_2O \rightarrow R\text{-}NH_2 + CO_2 \uparrow \qquad (2)$$

The primary amine group reacts with the isocyanate whereby a polyurea chain forms:

$$R\text{-}NH2 + OCN\text{-}R \rightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R \qquad (3)$$

The CO_2 formed (cf. Eq. (2)) induces the silicification of WG (cf. Eq. (1)) resulting in polysilicate particles in the polyurea matrix. In order to control the course of reactions 1-3 an emulsifier is needed for which liquid phosphates proved to be the most suitable? This problem has been studied previously(US Patent 5 622 999,1997). The emulsifier is responsible for controlling the W/O-emulsion and slowing down the reaction of the polyurea formation (cf. Eq. (3)). In the final crosslinked product it works as plasticizer. Using polymeric isocyanates with a functionality of >2 crosslinked polyurea based composites can be produced. Recall that they contain polysilicate particles derived from the WG. This proprietary system marketed by Polinvent Ltd. (Budapest, Hungary) is denoted 3P resin (from polyisocyanate, phosphate, polysilicate). These resins possess some remarkable properties, such as curing under water which allows us the repair of leaking or corroded buried pipes without their digging. On the other hand, the mechanical properties and the resistance to thermal degradation of the 3P resins are modest. This is due to the complex chemistry of the related systems. Note that Eqs. (2) and (3) represent the major reactions apart from which several by-side reactions, such as di- and trimerisation of the isocyanates, biuret formation between the urea and isocyanates, etc. take place. It has to be mentioned here that the crosslinking chemistry of the 3P resin and its hybrids was not addressed in this work.This work was aimed at improving the mechanical and thermal properties of 3P a resin by hybridization with styrene-crosslinkable vinyl ester resins (VE). This patented hybridization strategy considers three major aspects. This problem has been studied previously(Hungarian Patent Application P04 01799,2004). First, VE resins can be additionally crosslinked by adding polyisocyanates. In the corresponding vinyl ester-urethane hybrids, marketed by DSM Composite Resins (Zwolle, The Netherlands), additional crosslinks form between the secondary -OH groups of VE and -NCO groups of the polyisocyanate. The crosslinking, properties and property modifications of such vinyl ester-urethane hybrids are well reported in the literature. This problem has been studiedpreviously(Jost, 2002, p.1383-9; Gryshchuk, 2002, p.4763-8; Gryshchuk, 2002, p.672-80 and Gawdzik, 2001, p.2062-7). Second, VEs are known as chemically resistant and thus able to withstand strong alkali media such as WG. Third, the VE itself may act as an additional emulsifier for the dispersion of WG (W/O emulsion) and thus may also influence the WG-induced reactions. So, VE is expected to reduce the mean particle size of the in situ formed polysilicate phase and to form a conetwork with the polyisocyanate/polyurea through urethane formation. This occurs between the -NCO of the polyisocyanate and the -OH groups of the VE. Both above mentioned changes should be associated with an improvement of the properties according to our working hypothesis. The novel hybrid resins are foreseen as matrix materials for traditional composites which are produced by resin transfer molding and wet filament winding techniques.

2. Experimental

2.1 Formulations

Polymeric methylene diphenyl isocyanate (PMDI), Ongronat CR-30-60 was purchased from Borsodchem Rt (Kazincbarcika, Hungary) and exhibited the following characteristics: NCO content30-31.5 wt%, viscosity: 520–680 mPa s. WG (Sodium silicate type, Betol 3P) was purchased from Woellner Silikat GmbH (Ludwigshafen, Deutschland). This WG had a modulus $SiO_2/Na_2O = 2.0 \pm 0.05$, and viscosity: 600 ± 100 mPa. As primary emulsifier for the PMDI/WG system tris(1-chloro-2-propyl)phosphate (Fyrol PCF, Akzo Nobel, Duren, Germany) was used. The base 3P resin contained 42 wt% PMDI, 18 wt% phosphate and 40 wt% WG. For the hybridization of the above 3P resin a styrene diluted (_30 wt%) bisphenol-A type VE (Daron-XP-45-A2) and novolac type VE (Atlac590 HV) of DSM Composite Resins (Zwolle, The Netherlands) were chosen.Their chemical build-upis given in Ref. For their crosslinking 1.5 phr(parts per 100 g of resin) dibenzoyl peroxide (peroxide content 50 wt%; Lucidol CH-50 L of Akzo Nobel, Duren, Germany) and 1.5 phr N,N-diethylaniline (active component content: 10 wt%; NL-64-10 of Akzo Nobel) served. The above VE resins are referred further on as VE (BA) and VE (N), respectively. In order to study the effect of resin hybridization, the formulations listed in Table 1 were prepared.

2.2 Preparation of the hybrid resins

The reference 3P resin was produced by homogenizing the phosphate with the PMDI with a propeller mixer (1 min,

2000 rpm). Then WG was introduced and dispersed to receive a stable W/O emulsion (1 min, 800 rpm). In case of the VE/3P hybrids first the peroxide was introduced in the VE and homogenized. Afterwards WG was added to this composition (denoted as A component) and mixed (1 min, 2000 rpm). In another beaker the component B was prepared. This contained the necessary amount of PMDI, phosphate and activator (the latter was used only for the neat VE resins) which were homogenized accordingly. The A and B components were then unified and homogenized again (1 min, 800 rpm).

All resulting mixtures were degassed in vacuo prior to pouring them into the moulds. Plates (170×10×4 mm) and compact tension (CT) specimens were produced by pouring the homogenized and degassed resins in PTFE moulds. Crosslinking of the resins occurred according to the following regime: room temperature for 20 h and 100 °C for4 h.

2.3 Tests

The phase structure of the samples was characterized by dynamic-mechanical thermal analysis (DMTA). DMTA spectra were taken on rectangular specimens (50×10× 4length×width ×thickness) in flexural mode at 10 Hz using an Eplexor 150 N device of Gabo Qualimeter (Ahlden,Germany). The static and cyclic (sinusoidal) loading components were set for 10 N and 5 N, respectively. DMTA spectra, viz. complex modulus (E*) and its constituents (storage and loss moduli, $E^{/}$ and $E^{//}$, respectively), mechanical loss factor (tan d) as a function of temperature (T), were measured in the interval T =-100 . . . + 200 °C at a heating rate of 1°C/min.

To determine the mean particle size and particle size distribution of the silicate phase the fracture surfaces of the CT specimens were inspected in a scanning electron microscope (SEM; JSM 5400 device of Jeol, Tokyo, Japan). The surfaces were coated with an Au/Pd alloy prior to SEM investigations. SEM pictures of minimum 3 showing more than 100 particles were taken into consideration when determining the particle size distribution. It is noteworthy that the related SEM pictures served also to deduce the major failure mechanisms.

For the thermogravimetric analysis (TGA) of the hybrids a TG50 device of Mettler Toledo (Giessen, Germany) was used. The TGA experiments were conducted in air in the temperature range T =25 . . . + 630°C with heating rate 10 °C/min.

To determine the flammability of the resins the limiting oxygen index (LOI) test according to ISO 4589-2 was performed. LOI means the minimum concentration of oxygen in a nitrogen/oxygen mixture which is required just to support the combustion of a test sample under specified test conditions. A material has fire retardant performance if its LOI value is higher than 21 vol% which is the concentration of oxygen in the air. The higher this value is, the better the flame resistance of the material is.

The fracture toughness (Kc) and fracture energy (Gc) were according to ISO 13586-1 standard. The tests were done with a Zwick universal testing machine type 1445 (Ulm, Germany) at room temperature (RT) with a crosshead speed of v =1 mm/min. The CT-specimens (dimension: 35×35×4/thickness/mm3) were notched before loading by sawing. The sawn notch of the CT specimens was sharpened by producing a sharp crack with a razor blade that was placed on the notch root before hitting it in a fixing rig with a hammer.

3. Results and discussion

3.1 Phase structure

Fig. 1a displays the E0 vs. T and tanδ vs. T traces for the 3P, VE (BA) and their hybrid resins. One can recognize that combining 3P with VE (BA) the stiffness ($E^{/}$) is increased considerably at least below a given threshold temperature. The latter depends on the actual 3P/VE (BA) composition and lies between ca. 100 and 150°C. One can also see that the E0 values of the hybrids do not follow the trend with the compositional ratio in the whole temperature range (cf. Fig. 1a). The glass transition temperature (Tg), when assigned to the peak temperature of the tanδ (cf. Fig. 1b), is increasing above a 3P/VE (BA) ratio of 75/25. It is noteworthy that the Tg of the heat 3P resin could not be determined due to premature failure of the tested specimen. Nevertheless, the related tanδ vs. T trace suggests that it is at T > 200°C. Note that the intensity of the tanδ peak of VE (BA) is reduced owing to the hybridization with 3P and also broadened at the same time (cf. Fig. 1b).

The DMTA behavior of the hybrids 3P/VE (N) is similar to that of the 3P/VE (BA) variants. However, when comparing the E0 vs. T traces in Figs. 1a and 2a, one can see that the stiffness is dominated by the VE (N) below T≈50°C irrespective to its actual amount in the hybrids. Again the intensity of the Tg-relaxation of VE (N) is reduced through hybridization with the 3P resin. Moreover, the Tg-relaxation became broader and the Tg was shifted to higher values for composition 3P/VE (N)≥75/25(cf. Fig.2b).

The DMTA behavior of the hybrids suggests the formation of a heterogeneously crosslinked network. This may be a conetwork or a grafted interpenetrating one (g/IPN). As a g/IPN should be phase-segregated while a conetwork not, attempt was made to shed light on this issue by AFM.

Completely different, but still nanostructured morphology can be concluded for the 3P resin. The related heterogeneity

is likely the outcome of the various chemical reactions involved in the crosslinking of this 3P resin. Note that the related crosslinking pathway is not yet known.

The morphology of the hybrids 3P/VE (BA) =75/25 and = 50/50 resembles to that of the neat 3P. One can claim that in these hybrids a conetwork has been formed. So, the styrene crosslinkable VE has been built in the polyurea-based network mostly through the reactions between the -NCO groups of PMDI and -OH groups of the VE. Effects of the compositional ratio in the hybrids should appear-among others- in their mechanical behavior at higher temperatures. This expectation is based on the DMTA behavior of the hybrids as shown before (cf. corresponding $E^/$ vs. T traces in Fig. 1a).

The structure of the 3P/VE (BA) = 25/75 differed markedly from that of the neat 3P and its hybrids at high 3P contents .In this system, a phase-segregated nanogel structure is present showing clear similarities with that of the crosslinked VE (BA)

It is worth of noting that the phase structure of the 3P/VE (N) hybrids was similar to the 3P/VE (BA) formulations (and thus not shown here). The only exception was noticed for the 3P/ VE (N) = 25/75 hybrid for which the g/IPN structure (if any) was poorly resolved. This finding is, however, in concert with the DMTA behavior – cf. corresponding $E^/$ vs. T trace in Fig. 2a.

3.2 Polysilicate dispersion

Characteristic SEM pictures taken from the fracture surfaces of the 3P/VE hybrids are depicted in Fig.3.

One can observe that the VE worked as additional emulsifier for the initial W/O-type emulsion (i.e. WG dispersed in PMDI and phosphate) as expected. This corroborates our earlier results achieved however on a different VE (BA)/3P system.The hybrid system reported in Ref. differed from the present one not only in the base 3P resin composition but also in the WG and phosphate used. The main particle size of the polysilicate was reduced owing to the emulsifying action of the VE. Parallel to that the distribution of the polysilicate particles became narrower. The latter was characterized by the ratio of the weight (dw) to number–average mean particle size (dn) – cf. Table2.

SEM pictures in Fig.3 and the data in Table 2 indicate that VE (N) is a slightly better emulsifier than VE (BA). It is noteworthy that a finer and more uniformly dispersed silicate phase should be associated with improvements in the mechanical performance. This expectation is based on the fact that in such systems the stress concentration field induced by the particles is leveled off which depresses premature failure of the specimens.

3.3 Thermal and flame resistance behavior

The first indication that the hybridization followed might have affected the thermal resistance was delivered. Recall that the ablation induced by Ar^+ ion bombardment is basically a thermal degradation process. The TGA curves (mass loss vs. T) for the 3P and its hybrids with VE (BA) and VE (N) are shown in Figs. 4 and 5. Note that the 3P resins starts to degrade at rather low temperature (T≈150°C), however, becomes markedly stable to thermal degradation at higher temperatures (T > 400°C) – cf. Figs.4 and 5. On the other hand, both VEs are quite stable initially (up to ca.350°C), but degrade very fast and almost without residue afterwards. It has to be mentioned that no attempt was made to determine the degradation kinetics and trace the related products in this work. The TGA traces in Figs.4 and 5 suggest that the change in the thermal resistance as a function of the VE/3P composition follows in the first approximation the additivity rule (rule of mixture), at least for selected temperature intervals. A similar statement holds for the LOI results, However, The results indicate for the presence of some synergistic effect in the VE/3P range 50/50. . .75/25. It has to be mentioned that outstanding flame resistance of the 3P resin is owing to the chlorine-containing phosphate which was used as primary emulsifier in our case. The positive effect of this chlorine-containing phosphate is well resolved for the VE/3P hybrids, as well. The observed synergism in LOI can likely be assigned to the morphology development discussed before.

3.4 Fracture mechanical response

Effects of the compositional changes for the fracture toughness (Kc) and fracture energy (Gc) are depicted. It is interesting to note that the fracture toughness (Kc) does not change markedly as a function of the composition and VE type. Clear improvement in Kc can be noticed only for the VE (N)/3P systems. The fracture energy (Gc) is far more sensitive to the formulation of modified resins including hybrid ones. It was shown that the fracture energy of VE (BA) and VE (N) can be strongly enhanced by incorporating functional star-shaped polymers. These compounds influenced the crosslinking process and created a nanoheterogenous morphology, which favored the targeted shear deformation. Note that Gc experiences a positive deviation from the additivity (synergism) for the hybrids with both VEs . The only difference is related with the compositional range where synergism occurs (this is the whole composition range for VE(N), whereas for VE(BA) synergism in Gc can be concluded for the VE(BA) rich hybrids). The high Kc and Gc values of the neat 3P resins are due to its complex crosslinking which affects the morphology development. The resulting heterogeneous morphology is linked with low stiffness as already shown in the DMTA traces. Note that the

stiffness (E or Young's modulus) can be estimated by considering the above fracture mechanical data via $E \approx K^2/Gc$ (which strictly holds for plane strain conditions). The so calculated E-moduli lay somewhat below those derived at ambient temperature from the DMTA test (cf. Figs. 1a and 2a). Recall that the latter was measured in flexure mode. On the other hand, tensile E-moduli can be estimated from the CT tests which were used to determine the Kc and Gc values. The flexural and tensile moduli may differ from one to another, especially for such complex systems as these hybrid resins.

3.5 Failure behavior

The SEM pictures in Fig. 3 demonstrate that the silicate particles are involved in crack pinning and crack bifurcation events. Crack pinning is obvious by the merging sections of the running crack front behind the particles in form of "tails".

Crack bifurcation means deviation from the planar crack surface, the characteristic features of which are ridges, steps on the fracture surface. Crack bifurcation and pinning are dominant in the 3P and VE/3P hybrids albeit the polysilicate particles are not covalently bonded to the matrix. This problem has been studied previously(Karger-Kocsis,2007,p.853-9 and Erdelyi,2007,p.21-31).The particles are partly or fully debonded from the matrix as the hydrogel/xerogel transition of WG is accompanied with pronounced volume shrinkage. Anyhow, the related "partly filled holes" still act as stress concentrators and trigger the stress release mostly via bifurcation. The shear deformation of the matrix is hindered in the hybrids, especially at high 3P contents. On the other hand, shear deformation (being a very efficient energy absorbing mechanism) is well resolved for the system VE/3P = 75/25. This is the reason why for these systems higher Gc values were found than the expected ones according to the additivity.

It is the right place to mention that for these systems a g/IPN structure was proposed. IPN structured systems are, on the other hand, predestined for shear deformation as discussed in the literature. This problem has been studied previously(Sperling LH,1981).

Finally, a basic question has to be posed: was the property improvement achieved by changes the silicate dispersion or matrix morphology? The results, presented above, suggest that the network hybridization is a more efficient tool for property upgrade than the creation of a fine and uniform dispersion of the silicate particles.

4. Conclusions

This work was devoted to study the effects of resin hybridization on the structure, thermal and fracture mechanical properties of thermosets produced from polyisocyanate, water glass (WG) and vinyl ester resins (VE), whereby the type and amount of the VE were varied. It was established that VE acts as an additional emulsifier for the 3P resin being initially a water-in-oil type emulsion (i.e. WG dispersed in a phosphate containing polymeric isocyanate). The size of the in situ formed polysilicate particles was reduced by VE hybridization. Based on DMTA and AFM investigations the formation of a conetwork was concluded, at least for the hybrid systems with high 3P resin contents (P50%). Hybridization with VE resins improved the stiffness and resistance to thermal degradation of the 3P resin. With respect to the flame resistance (LOI) and fracture energy (Gc) synergistic effects were found for the hybrid resins at least in a given composition range. The latter depended on the type of the VE. The novel hybrid resins proved to be suited to produce composite parts using wet filament winding.

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Table 1. Composition and designation of the VE/3P hybrids studied

Material code	VE content(%)	3P content(%)	PMDI content(%)	WG content(%)	Phosphate content(%)
3P	0	100	42	40	18
VE(BA)	100	0	0	0	0
VE(BA)/3P 75/25	75	25	10.5	10	4.5
VE(BA)/3P 50/50	50	50	21	20	9
VE(BA)/3P 25/75	25	75	31.5	30	13.5
VE(N)	100	0	0	0	0
VE(N)/3P 75/25	75	25	10.5	10	4.5
VE(N)/3P 50/50	50	50	21	20	9
VE(N)/3P 25/75	25	75	31.5	30	13.5

Table 2. Number (dn) and weight-average diameter (dw) of the polysilicate particles in the VE/3P hybrids

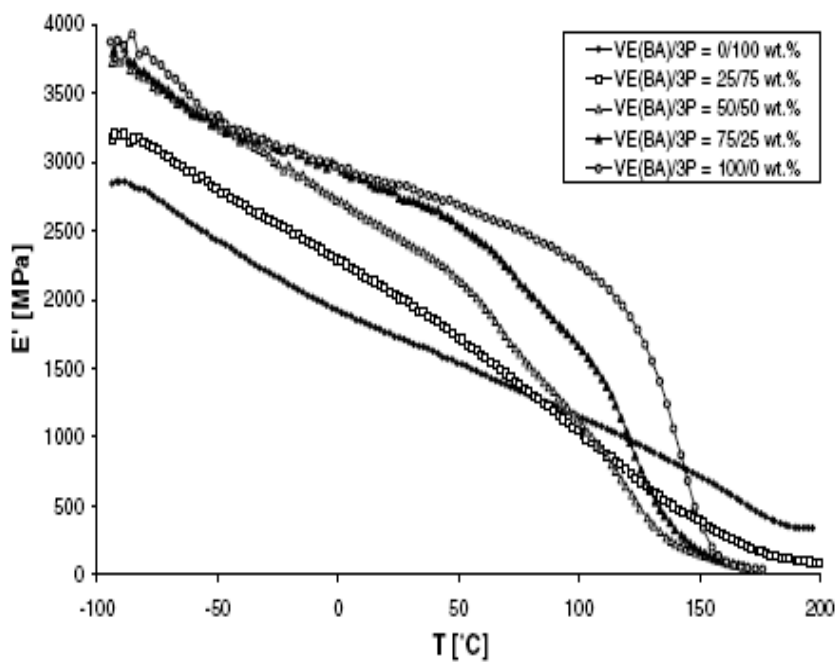| Composition	dn(μm)	dw(μm)	dw/dn
VE(BA)/3P=75/25	2.57	7.01	2.72
VE(N)/3P=75/25	1.21	2.30	1.88
VE(BA)/3P=50/50	4.13	8.12	1.97
VE(N)/3P=50/50	3.11	4.48	1.44
VE(BA)/3P=25/75	8.58	21.45	2.50
VE(N)/3P=25/75	4.00	5.96	1.49
VE/3P=0/100	7.81	22.05	2.82

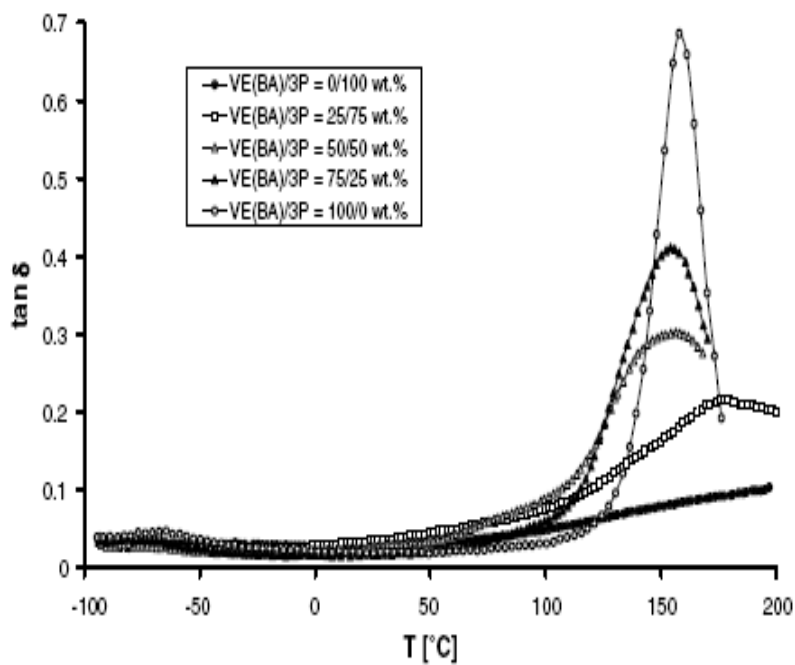Figure 1a. E0 vs T traces for the 3P, VE(BA) and their hybrid systems

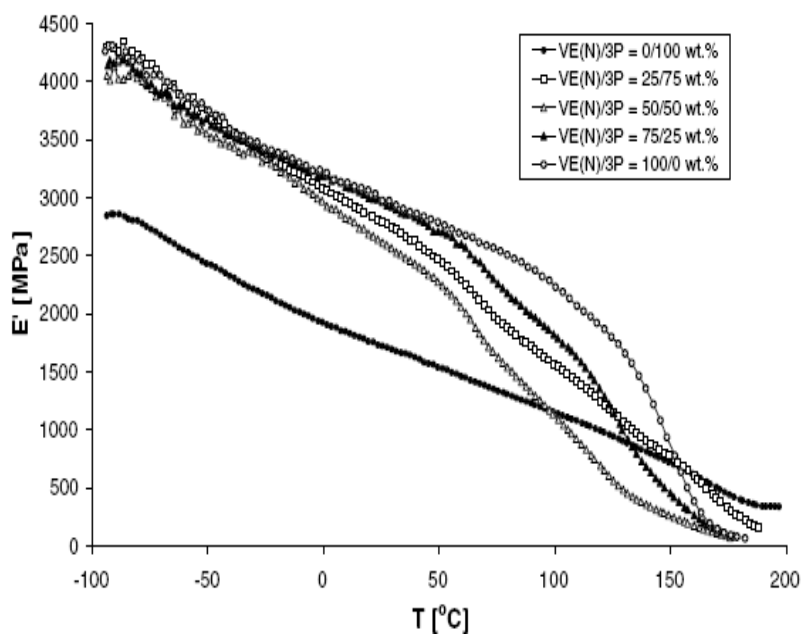Figure 1b. tanδ vs T traces for 3P, VE(BA) and their hybrid systems

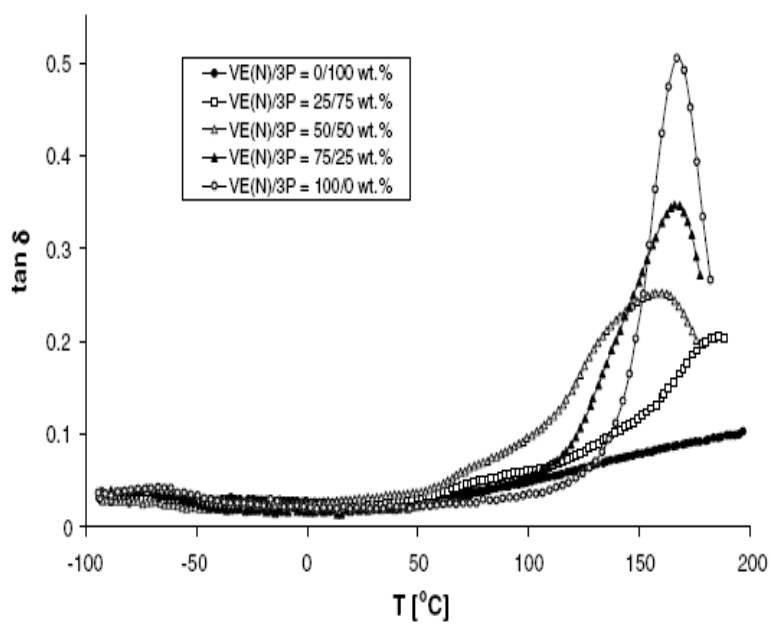Figure 2a. E′ vs T traces for the 3P, VE(N) and their hybrid systems

Figure 2b. tan δ vs.T traces for 3P, VE(N) and their hybrid systems
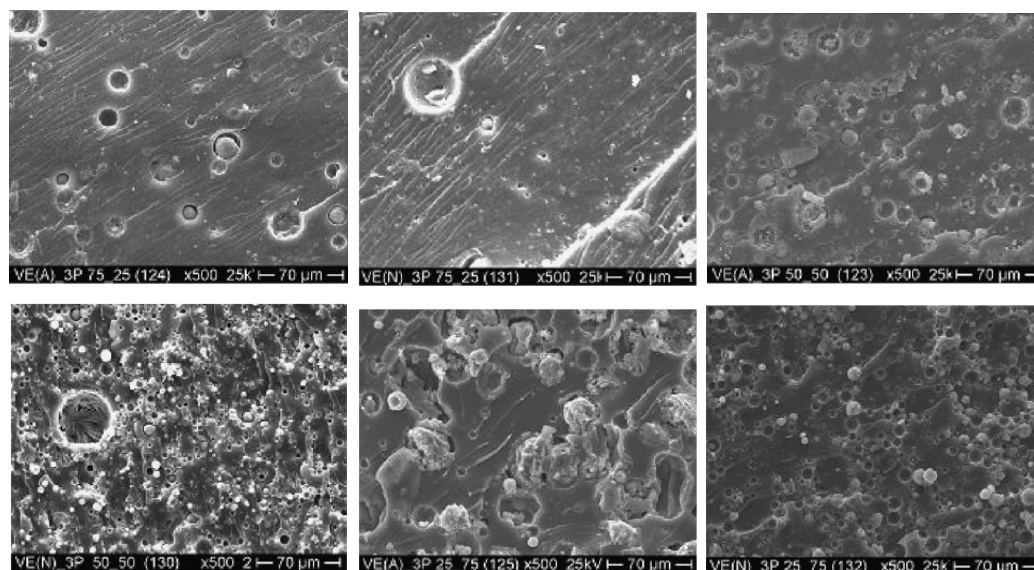
Figure 3. SEM pictures showing the difference in the silicate dispersion as functions of VE resin type and VE/3P composition. Designations: hybridized with VE (BA) – left; hybridized with VE (N) – right. From top to bottom: VE/3P = 75/25, =50/50, 25/75
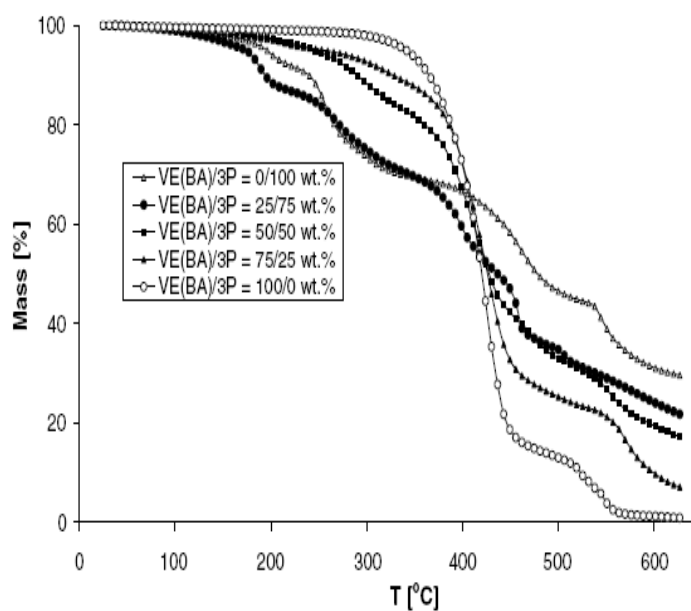

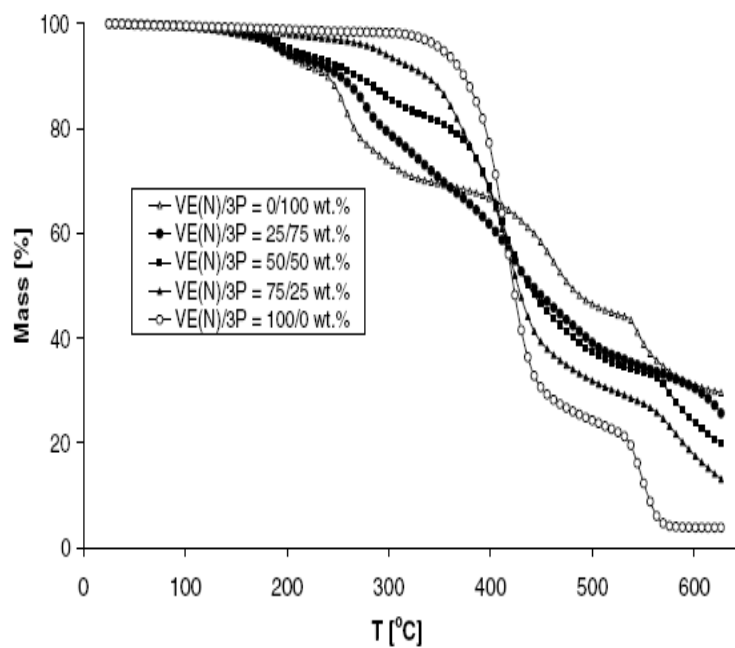Figure 4. TGA traces of the 3P resin and its hybrids of VE (BA)

Figure 5. TGA traces of the 3P resin and its hybrids of VE (N)