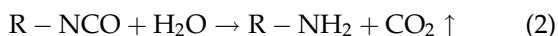


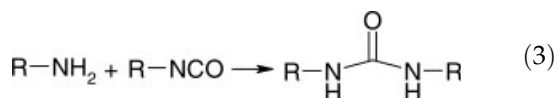
The silica gel formed is a hydrogel, more exactly a hydro/xerogel depending on its actual water content.

Exactly the earlier reaction is exploited when combining polyisocyanates with WG. Recall that the latter contains two "active" components, viz. water and alkalisilicate.

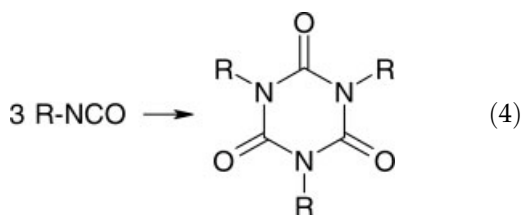
Dispersing the WG in polyisocyanates first the following overall reaction takes place:



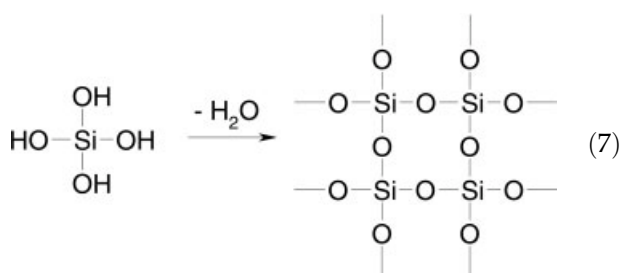
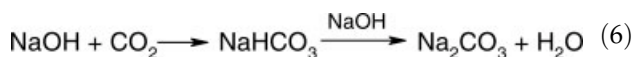
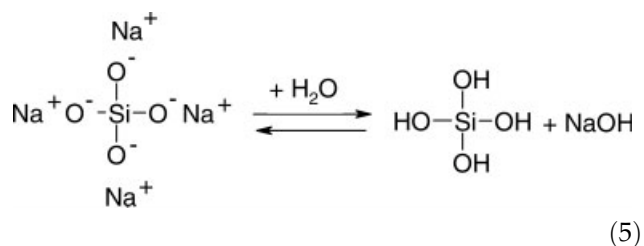
The amine groups react with the isocyanates, whereby a polyurea chain forms:



There is a possibility for trimerization of the isocyanate groups especially in the presence of suitable catalysts, as well:



From the viewpoint of WG the initial equilibrium reaction [eq. (5)] is shifted towards formation of polysilicic acid as NaOH is neutralized by CO_2 [eq. (6)]. This ends up in an *in situ* formed polysilicate framework owing to polycondensation reaction [eq. (7)].



The reaction between the $-NCO$ and $-NH_2$ groups is very fast and highly exothermic. Therefore, it is necessary to use suitable phase transfer catalysts, which control the development of $-NH_2$ [eq. (2)], and thus the polyurea/polyisocyanurate [eqs. (3) and (4)] formation. This issue was addressed by an US patent.⁴

The basic idea of this research work was to use a further thermosetting resin which acts as emulsifier to stabilize the W/O emulsion, influences the polyurea formation (as "phase transfer catalyst"), and at the same time, it is coreactive with products of the above reaction pathway. Coreactivity means that a suitable resin should react with the isocyanate groups of the polyisocyanate apart of its own crosslinking. Recall that the emulsifier effect should be accompanied with a size reduction of silicate particles in the crosslinked resin. This should have some favorable effect on the mechanical performance.

Considering the commercial success of unsaturated polyester and vinylester "hybrid resin" with polyisocyanates (Refs. ⁵⁻⁸ and references therein) VE resin was selected as "coagent" for the polyisocyanate/WG system. Note that VE crosslinks via free radical induced copolymerization with styrene. On the other hand, the secondary $-OH$ groups of VE may react with the isocyanate groups of polyisocyanate yielding a more tightly crosslinked network structure. The outcome of this reaction along with further approaches to improve the toughness of the so-called vinylester-urethane hybrids were already subjects of investigations.^{5,7-9}

EXPERIMENTAL

Polyisocyanate (polymeric MDI, Ongronat CR-30-60), purchased from Borsodchem Rt (Kazincbarcika, Hungary), showed the following characteristics: NCO content 30–31.5 wt %, viscosity: 520–680 mPa s.

WG (Sodium silicate, Inosil Na-5120) was purchased from van Baerle AG (Münchenstein, Switzerland). This WG had a modulus $SiO_2/Na_2O = 2.0$, and viscosity: 600 ± 100 mPa s.

As a primary phase catalyst for the polyisocyanate/WG system tricresylphosphate (Disflamoll TKP, Lanxess Deutschland GmbH, Leverkusen, Germany) was used. This proprietary system yielding mostly thermoset polyurea is termed as 3P resin (3P derives from polyisocyanate, polyphosphate, and polysilicates). For the hybridization of the above 3P resin a bisphenol-A type, styrene diluted (30 wt %) VE (Daron-XP-45-A2) of DSM Composite Resin AG (Zwollen, The Netherlands) was chosen. Note that this is the VE component of the corresponding vinylester-urethane hybrids offered by DSM. For its crosslinking, 1.5 phr (parts per hundred parts VE) dibenzoyl peroxide (peroxide content 50 wt %; Lucidol CH-50 L of Akzo Nobel, Düren, Germany) and 1.5 phr *N,N*-diethylaniline (active com-

TABLE I
Composition and Designation of the VE/3P Hybrids

Material code	VE content (%)	3P content (%)
VE	100	0
VE/3P 75/25	75	25
VE/3P 50/50	50	50
VE/3P 25/75	25	75
3P	0	100

ponent content: 10 wt %; NL-64-10 of Akzo Nobel) served. The base 3P resin contained 50 wt % polyisocyanate, 17 wt % tricresylphosphate, and 33 wt % WG.

To study the effect of composition the VE/3P ratio has been varied as indicated in Table I.

The hybrid resins were prepared as described below. First, the peroxide was added to VE in a beaker and homogenized. To this composition "A," the necessary amount of WG was introduced and dispersed

by a propeller mixer (1 min, 800 rpm). The "B" component contained the polyisocyanate, the tricresylphosphate, and the diethylaniline activator of VE. After mixing of this composition "B," the "A" component was introduced and homogenized (1 min, 800 rpm). The resulting mixture was degassed in vacuum before pouring into the molds.

Plates ($160 \times 80 \times 10 \text{ mm}^3$) and compact tension (CT) specimens were produced by pouring the homogenized and degassed resin in open steel and poly (tetrafluoro ethylene) (PTFE) molds. Crosslinking of the resin occurred by the following regime: room temperature for 20 h and 100°C for 4 h.

Tests

To determine the mean particle size and size distribution of the silicate phase, the fracture surface of the CT specimens were inspected in a scanning electron

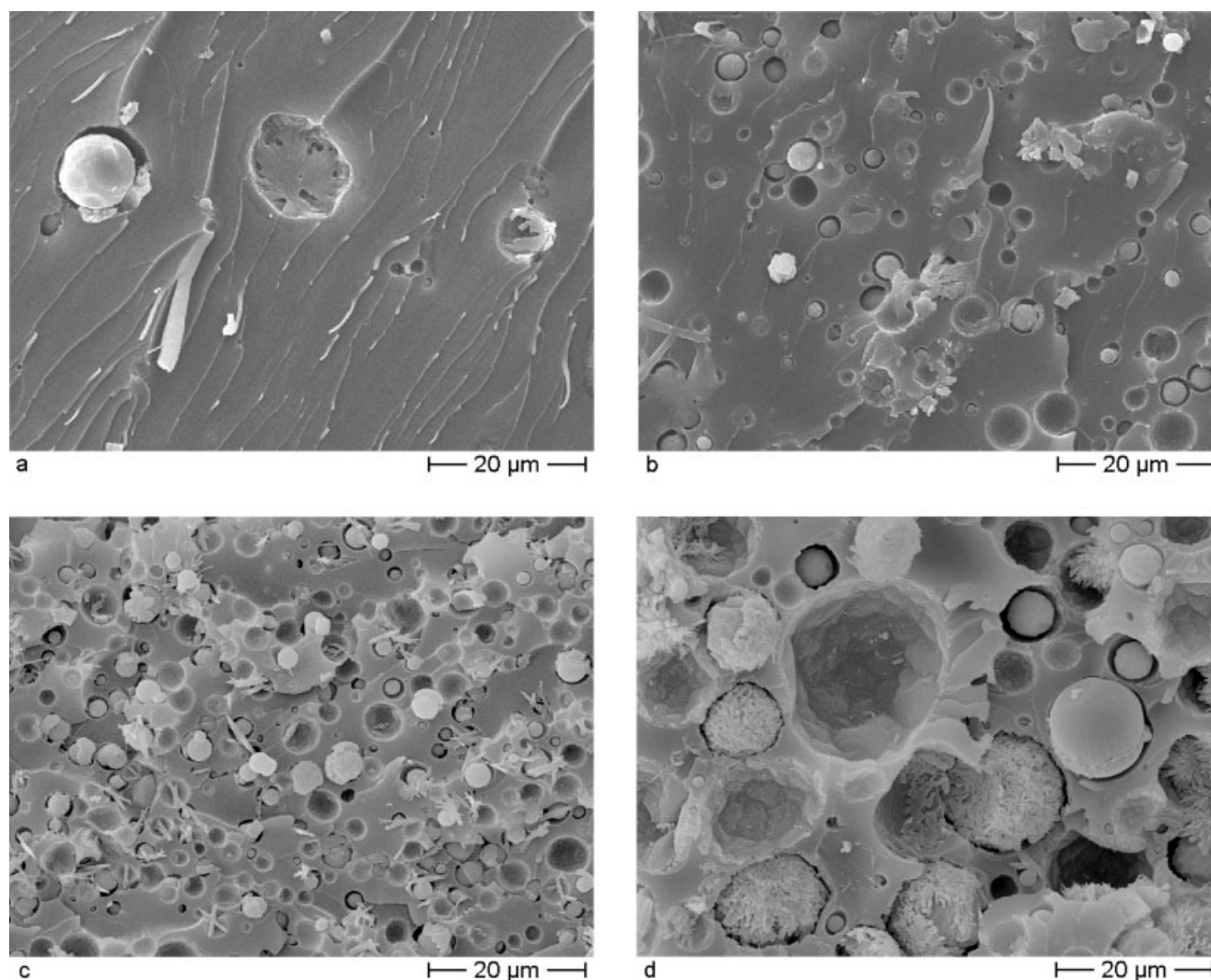


Figure 1 SEM pictures showing differences in the silicate dispersion as a function of the resin hybridization. Designations: a – VE/3P 75/25; b – VE/3P 50/50; c – VE/3P 25/75; d – 3P resin (VE/3P 0/100).

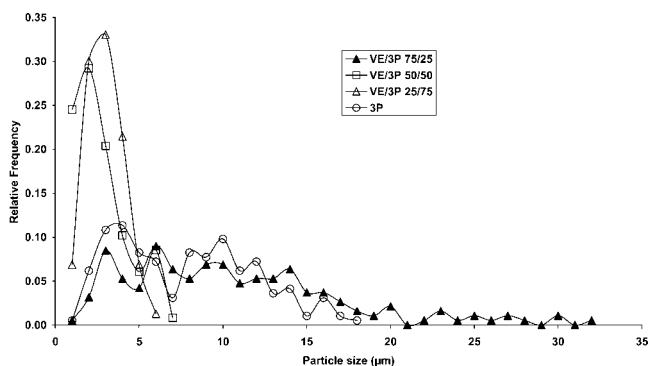


Figure 2 Particle size distribution of the silicate in the 3P and VE/3P hybrid resins.

microscope (SEM; JSM 5400 device of Jeol, Tokyo, Japan). The surface was coated with an Au/Pd alloy before SEM investigation. SEM pictures of minimum three showing more than 100 particles were taken into consideration when determining the particle size distribution.

To get information on the phase structure and thermodynamical properties, dynamic mechanical thermal analysis (DMTA) was performed. DMTA were taken on rectangular specimens ($50 \times 10 \times 3 \text{ mm}^3$; length \times width \times thickness) in 3-point bending configuration at 1 Hz using a DMA Q8000 of TA Instruments (New Castle, DE). These were performed under displacement control using sinusoidal oscillation. DMTA spectra informing us about the change in the complex modulus (E^*) its constituents (storage E' and loss moduli E'') and mechanical loss factor ($\tan \delta$) as a function of temperature (T) were measured in the interval $T = 10^\circ\text{C} \dots +200^\circ\text{C}$ at a heating rate of $1^\circ\text{C}/\text{min}$.

The flexural properties viz. modulus and strength of the hybrid resins were determined on rectangular specimens ($60 \times 10 \times 3 \text{ mm}^3$; length \times width \times thickness) in 3-point bending according to EN 63. The span

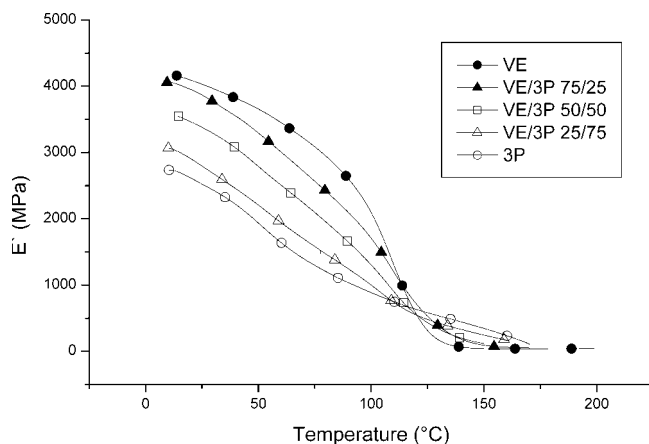


Figure 3 E' versus T traces for the 3P, VE, and their hybrids.

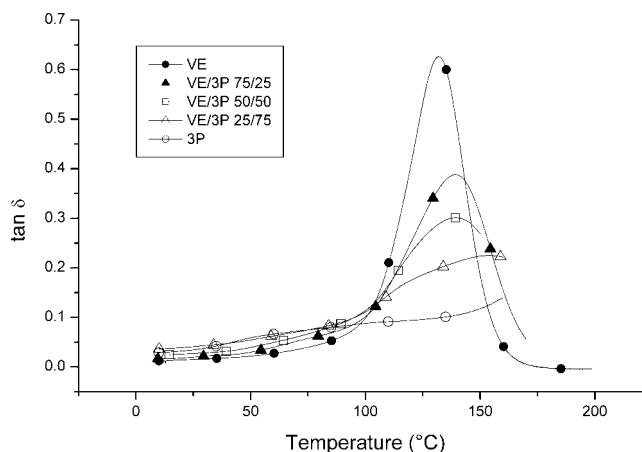


Figure 4 $\tan \delta$ versus T traces for the 3P, VE, and their hybrid systems.

length of the specimens was 50 mm and their loading occurred with $v = 1 \text{ mm}/\text{min}$ deformation rate.

The fracture toughness (K_{Ic}) and energy (G_c) were determined on compact tension (CT) specimens according to ISO 13586-1. Loading of the CT specimens (dimension: $35 \times 35 \times 4 \text{ mm}^3$) occurred on a Zwick 1445 (Ulm, Germany) universal testing machine at ambient temperature with crosshead speed of $v = 1 \text{ mm}/\text{min}$. 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. The failure mode of the hybrid resin was studied on broken CT specimens using SEM (cf. description above).

RESULTS AND DISCUSSION

Dispersion of the silicate particles

Figure 1 shows selected SEM pictures from the fracture surface of the hybrids used to determine the dispersion state of the polysilicate.

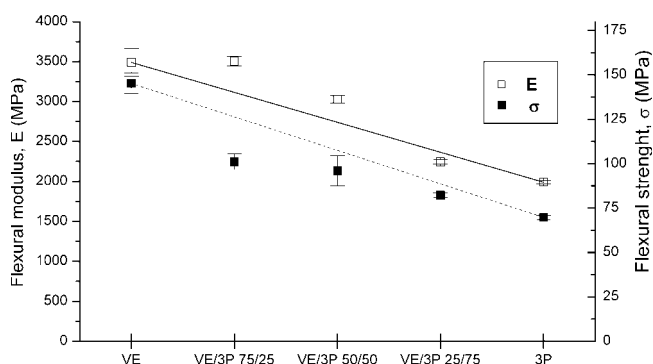


Figure 5 Changes in the flexural modulus and strength data as a function of the hybrid resin composition. Note: lines represent the additive rule.

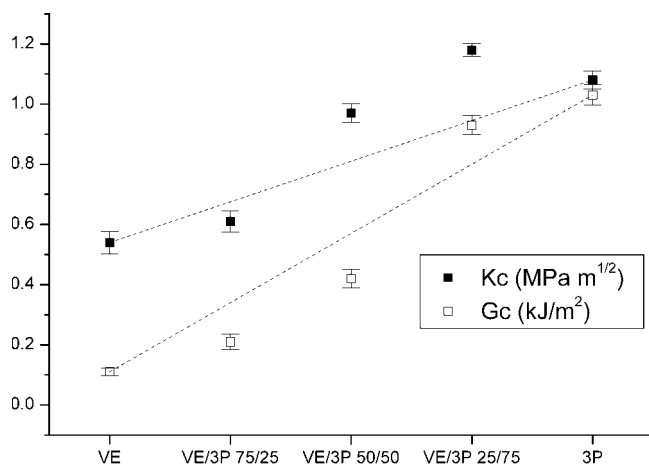


Figure 6 Changes in the K_C and G_C data as a function of the composition of the hybrid resins. Note: broken lines indicate the additivity.

The particle size distribution, along with the number-average diameter (D_n) values, are given in Figure 2. One can see that the silicate particles are present in a broad distribution and show a rather high number-average diameter (D_n) in the 3P ($D_n = 7.5 \mu\text{m}$) and VE/3P 75/25 ($D_n = 10.1 \mu\text{m}$) systems. The distribution becomes markedly narrower and D_n is substantially reduced for the VE/3P 50/50 ($D_n = 2.0 \mu\text{m}$) and VE/3P 25/75 ($D_n = 2.3 \mu\text{m}$). These findings indicate that the VE worked as emulsifier for the initial W/O-type polyisocyanate/WG emulsion, as expected.

DMTA response

The E' versus T trace display that the resin hybridization improved the stiffness in the studied temperature

range (cf. Fig. 3). One can also recognize that the stiffness upgrade follows the “rule of mixture” (additivity), at least for the composition ratios VE/3P > 25/75. The major relaxation peak, assigned to the glass transition, T_g , is shifted toward lower temperatures (cf. Fig. 4). Note that the T_g should be influenced by the cure cycle, which was, however, not studied in this case. The DMTA response suggests the formation of a conetwork or grafted interpenetrating network (IPN). The basic difference between the latter two structures is that IPN is phase-separated whereas the conetwork is not. This aspect, along with the related chemistry, is topic of ongoing investigations. Recall that coreactive sites are first of all the secondary —OH groups of the VE and the —NCO groups of the initial polyisocyanate. One may conclude that the onset of a conetwork is based on the observed T_g shift, its broadening and reduced intensity when VE contains more and more 3P resin. On the other hand, the T_g of 3P is not easy to detect and an inward shift in the T_g values of the base resin (i.e., VE and 3P) would mean the appearance of IPN. So, this option cannot be excluded either.

Anyway the broad T_g peaks signalize the development of an inhomogeneous crosslinked network. It is noteworthy, that network inhomogeneity usually enhances the toughness of the related resin (see Refs. 8, 9 and references therein).

Mechanical properties

Plotting the flexural stiffness and strength as a function of the hybrid resin composition only small deviation from the additivity can be noticed (cf. Fig. 5). The scenario is somewhat similar when considering the compositional changes of the K_C and G_C (cf. Fig. 6).

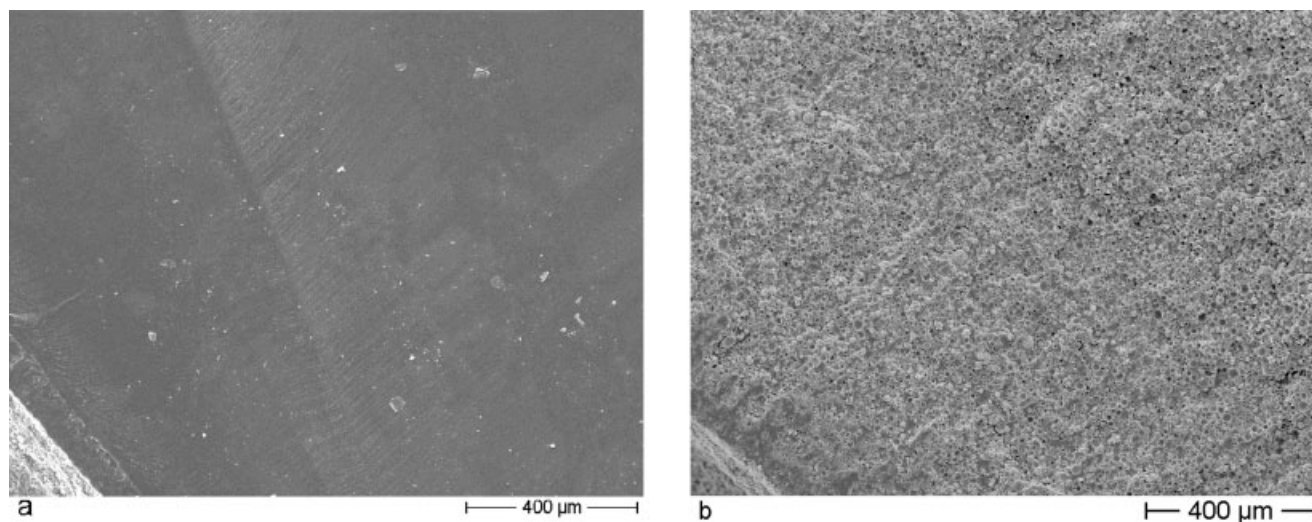


Figure 7 Fracture surfaces of the base resins. Designation: a – VE; b – 3P resin.

The high K_C and G_C data of the base 3P resin reflect its inhomogeneous crosslinking. This is due to the various chemical reactions involved in this crosslinking and their relative occurrence and rate. Nevertheless, considering the results in Figures 5 and 6, one can conclude that the static mechanical properties as a function of the resin composition obey the "rule of mixture" approach. This finding is in contrast with the large and sudden change observed in respect with the silicate dispersion (cf. Fig. 2). As a consequence, the mechanical performance of the hybrids is likely controlled by the coreactions, cocrosslinking phenomena. If this assumption holds then the failure mechanism linked with the silicate particles should not change compared with that of matrix. Increasing hybridization of VE with 3P should yield a network of enhanced shear deformation ability. This, triggered by

the formation of an inhomogeneous conetwork, was the subject of the fractographic works.

Failure behavior

Figure 7 compares the fracture surface of the base resins. Note how rugged the surface of 3P is compared to the smooth mirror-like of VE. This difference is in harmony with the toughness values of the corresponding resins (i.e., 3P: high, VE: low). High magnification SEM pictures taken from the fracture surface of the hybrid resins are given in Figure 8. One can recognize that the silicate particles are involved in crack bifurcation and crack pinning mechanisms. This particle-related failure mode is present for all hybrids irrespective to the large difference in the related particle size distributions. The fact that the effect of the mean

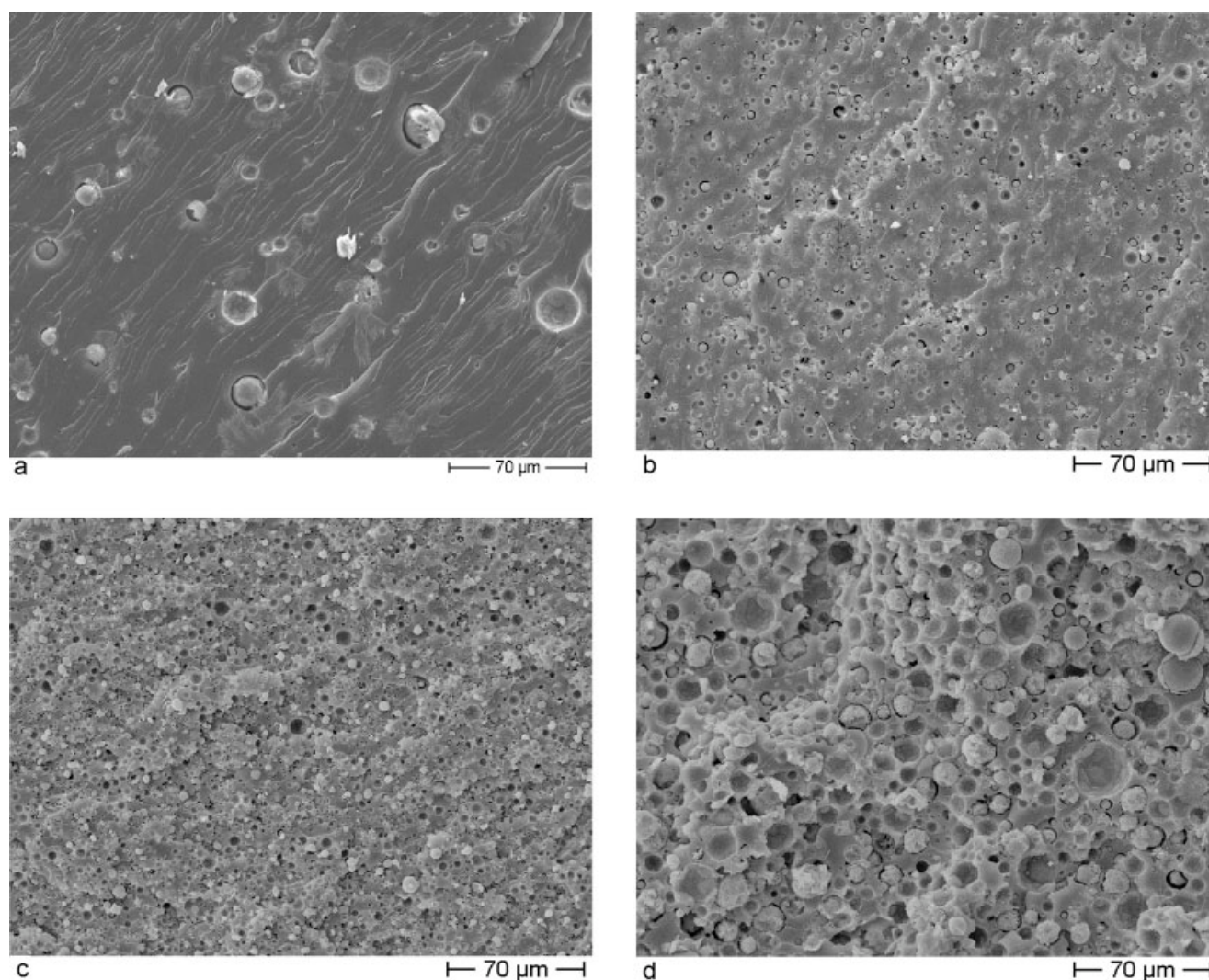


Figure 8 Fracture surfaces of the VE/3P hybrid resins. Designations: a – VE/3P 75/25; b – VE/3P 50/50; c – VE/3P 25/75; d – 3P resin (VE/3P 0/100).

particle size is marginal is not very surprising. Thermosetting resins are often toughened with modifiers the size of which lay between one and some tens of micrometers. A surprising aspect is, however, the silicate particles produced in this case are not covalently bonded to the matrix. Moreover, these particles are debonded from the polyurea matrix through the hydrogel–xerogel transition of the polysilicate as mentioned in the introduction. This is well resolved in the SEM frames in Figure 1. On the other hand, debonded particles, which may be considered as “partly filled holes,” may have toughening effect in thermosets¹⁰ as they control the crack growth/bifurcation through stress concentration/release mechanisms. In respect with the SEM pictures in Figures 1 and 8, attention should be paid on the matrix failure. Shear steps, ribs are clear identifications of the matrix ductility. Note that the shear deformability of the matrix increases with increasing 3P amount in the hybrids. Recall that this was explained by the formation of a hybrid conetwork, which has been quoted to be the major effect behind the toughness improvement. It is worth noting that the toughness (Fig. 6) changes adversely with the stiffness and strength (Fig. 5). This is a usual relationship that was often demonstrated for various polymeric systems.

CONCLUSIONS

Based on this work addressed to study the effect of resin hybridization on the morphology and static mechanical properties of a thermoset system produced from polyisocyanate, peroxide crosslinkable vinyl-ester (VE), water glass (WG), and a polyphosphate.

The following conclusions can be drawn:

- VE acts as emulsifier reducing the mean particle size of the *in situ* formed silicate in the resulting polyurea/VE system
- Hybridization of VE with the polyisocyanat/WG polyphosphate system (denoted as 3P resin) reduces its flexural stiffness and strength and enhances the fracture toughness (K_C) and energy (G_C). This was attributed to the formation of a cocrosslinked highly inhomogeneous network structure.

The authors thank Ms. N. Castellà Maymo for her help in the experimental work.

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