

Interconnected Silsesquioxane–Organic Networks in Porous Nanocomposites Synthesized within High Internal Phase Emulsions

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Novel porous nanocomposites with uniquely interconnected silsesquioxane (SSQ)–organic networks were synthesized within high internal phase emulsions (HIPE). These nanocomposite polyHIPE, with densities of around 0.13 g/cm³, were synthesized from 2-ethylhexyl acrylate (EHA), divinylbenzene (DVB, organic cross-linker), and either methylsilsesquioxane (MSQ) or vinylsilsesquioxane (VSQ, SSQ cross-linker). The porous structure, thermal properties, and mechanical properties were investigated. The $\tan \delta$ peak temperature and the room temperature modulus increased in a linear fashion with increasing DVB content, reflecting the increase in cross-link density and in backbone rigidity. These properties were significantly larger for polyHIPE with VSQ than for polyHIPE with MSQ. A comparison based on the cross-linking group content demonstrated that adding DVB produced more significant increases in thermal and mechanical stability than adding VSQ. The interconnected SSQ–organic networks, from combined VSQ and DVB cross-linking, produced the most thermally stable nanocomposite polyHIPE.

Introduction

A high internal phase emulsion (HIPE) has been defined as an emulsion in which the discrete internal phase occupies more than 74% of the volume. “PolyHIPE” are porous cross-linked polymers based on HIPE and result from the polymerization of monomers and cross-linking comonomers in the HIPE’s continuous phase.^{1,2} Holes that develop within the continuous envelope surrounding the discrete droplets during polymerization yield continuity of both phases.³ A wide variety of monomers and cross-linking comonomers have been used for polyHIPE synthesis, and many variations on the synthesis procedures have been investigated.^{1,2,4–14} The high porosities, high degrees of interconnectivity, and unique micrometer-to-nanometer-scale open-pore structures of poly-

HIPE are of interest for such applications as filtration media, supports for heterogenic catalytic reactions, absorbents, ion exchange systems, and heat resistant structural foams.^{1,2,15–21} The thermal and mechanical properties for such applications could be enhanced through the synthesis of nanocomposites.

Silsesquioxanes (SSQ), with the empirical formula $\text{RSiO}_{1.5}$, include random structures, ladder structures, cage structures, and networks.²² The modification of polymers with SSQ has been used to enhance such properties as use temperature, oxidation resistance, surface hardening, mechanical properties, and flammability resistance.^{23–27} Methylsilsesquioxane (MSQ) and vinyl silsesquioxane (VSQ) have pre-existing network structures that include cage-like structures, as seen in Figure 1, where R is CH_3 for MSQ and R is $\text{CH}=\text{CH}_2$ for VSQ.

There are several routes available for incorporating SSQ into a polyHIPE and forming a nanocomposite. One route would be to add trialkoxysilanes to the monomers in the HIPE and form an SSQ network through alkoxysilane

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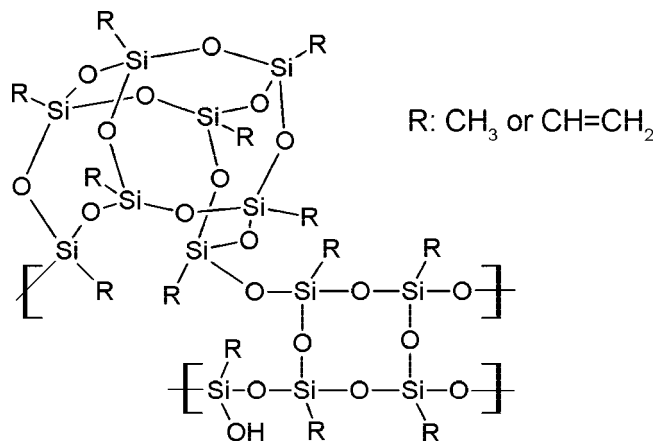


Figure 1. Structure of MSQ (R is CH₃) and VSQ (R is CH=CH₂).

hydrolysis and condensation (HC) reactions. Adding a trialkoxysilane bearing a vinyl group to the HIPE can be used to synthesize an SSQ network that is interwoven with the polymer network and grafted to the polymer backbone.^{7,28–30} Adding a trialkoxysilane that does not bear a reactive group would yield an SSQ network that is interwoven with the polymer network but not grafted to the polymer backbone. The structure of the network formed by alkoxy silane HC reactions will depend on the synthesis conditions. A second route for SSQ incorporation would be to add preformed SSQ structures directly to the monomers in the HIPE. Such structures would include those similar to MSQ (preformed networks and cages, Figure 1) as well as polyhedral oligomeric silsesquioxane (POSS) cages. If the SSQ unit does not bear any reactive groups (such as MSQ) then a blend would be formed. If the SSQ unit bears only one reactive group then the SSQ units would be grafted to the polymer backbone.³¹ If the SSQ unit bears multiple reactive groups (such as VSQ) then the SSQ would cross-link the polyHIPE.³² The pre-existing SSQ network structure in MSQ and VSQ can be extended further through curing, condensation of the Si–OH groups seen in Figure 1.³³

This manuscript describes the synthesis of novel nanocomposite polyHIPE with uniquely interconnected SSQ–organic networks. These nanocomposite polyHIPE are based on 2-ethylhexyl acrylate (EHA), divinylbenzene (DVB) as a cross-linking comonomer, and either MSQ or VSQ. The combination of an organic network with an SSQ network is illustrated schematically in Figure 2 for MSQ (the networks are not interconnected) and for VSQ (the networks are interconnected). This combination of SSQ–organic networks can be used to produce polyHIPE with superior thermal and mechanical stability.

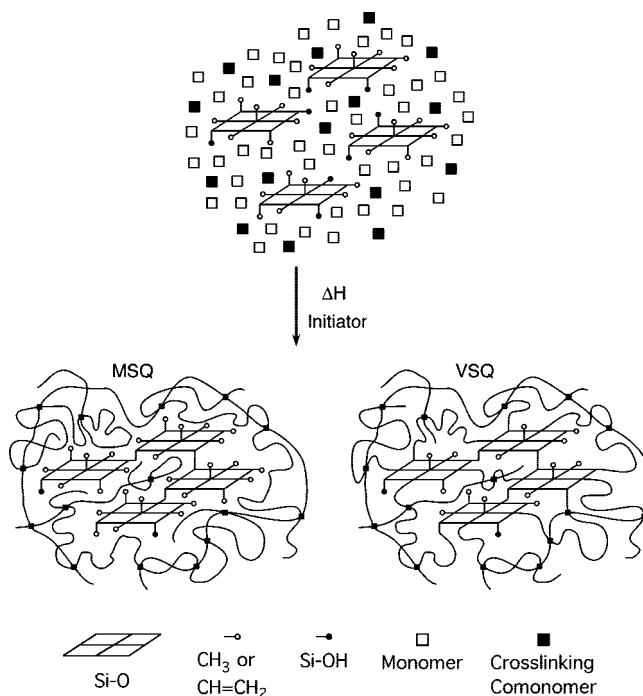


Figure 2. Schematic illustration of the SSQ and organic networks within the nanocomposite polyHIPE with either MSQ or VSQ.

Table 1. HIPE Compositions and PolyHIPE Densities

polyHIPE	EHA/DVB/SSQ, wt %	EHA/DVB/SSQ, mol %	ρ , g/cm ³
D26	80/20/0	74/26/0	0.13
D16-V	62/16/22	46/16/38	0.12
D8-V	70/8/22	53/8/39	0.13
D4-V	74/4/22	57/4/39	0.14
D0-V	78/0/22	60/0/40	0.16
D15-M	62/16/22	43/15/42	0.10
D8-M	70/8/22	49/8/43	0.14

Experimental Section

Materials. The monomer used for polyHIPE synthesis was EHA (Aldrich). The cross-linking comonomer was DVB (which contains 40% ethylstyrene (ES), Riedel-de-Haen). EHA and DVB were washed to remove the inhibitor (once with 5 wt % sodium hydroxide (NaOH) solution and then three times with deionized water). The emulsifier was sorbitan monooleate (SMO, Span 80, Fluka Chemie). The water-soluble initiator was potassium persulfate (K₂S₂O₈, Riedel-de-Haen). The HIPE stabilizer was potassium sulfate (K₂SO₄, Frutarom, Israel). The SSQ component was either MSQ or VSQ (Hybrid Plastics). The basic structural units of MSQ and VSQ, used to calculate representative molar quantities, were CH₃–SiO_{1.5} and CH₂=CH–SiO_{1.5}, respectively.

PolyHIPE Synthesis. The organic phase of the HIPE contained various amounts of EHA, DVB, VSQ, MSQ, and emulsifier (Table 1). The aqueous phase consisted of deionized water containing initiator and stabilizer (K₂SO₄ and K₂S₂O₈, respectively). The volume ratio of organic phase to aqueous phase was approximately 1/6. The recipe for a representative synthesis (a EHA/DVB/VSQ mole ratio of 62/16/22) is given in Table 2. The (EHA + DVB)/VSQ and (EHA + DVB)/MSQ mole ratios were held constant at 78/22 except for the reference polyHIPE that did not contain SSQ (D26 with a EHA/DVB molar ratio of 74/26). The EHA/DVB molar ratio in the nanocomposite polyHIPE was varied from 100/0 to 74/26. The polyHIPE are named “Dx-y”, where x indicates the molar percentage of DVB and y is either V for VSQ or M for MSQ.

The polyHIPE synthesis procedure was described in detail elsewhere and is unchanged for the synthesis of the polyHIPE

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Table 2. Typical PolyHIPE Recipe (D16-V)

	component	amount, wt %
organic phase	EHA	7.58
	DVB	1.90
	VSQ	2.67
	SMO	1.90
	total	14.05
aqueous phase	H ₂ O	85.29
	K ₂ S ₂ O ₈	0.19
	K ₂ SO ₄	0.47
	total	85.95

nanocomposites.²⁸ Briefly, the aqueous phase was added slowly to the organic phase with continuous stirring. Polymerization took place in a convection oven at 65 °C for 24 h. The polyHIPE was dried in a vacuum oven at 60 °C for about 48 h. The emulsifier, initiator, and stabilizer were removed by Soxhlet extraction in deionized water for 24 h and in methanol for 24 h. The polyHIPE was then dried in a convection oven at 60 °C for 12 h.

Characterization. The densities, ρ , of the polyHIPE were determined from gravimetric analysis. The porous structure was characterized using high resolution scanning electron microscopy (SEM) with uncoated specimens and accelerating voltages of 2.5–5 kV (HRSEM, LEO 982, Zeiss). The thermal properties were characterized using dynamic mechanical thermal analysis (DMTA) temperature sweeps at 3 °C/min at a frequency of 1 Hz on $7 \times 7 \times 7$ mm³ cubes in compression (MK III DMTA, Rheometrics). The mechanical properties were characterized using compressive stress–strain measurements on $5 \times 5 \times 5$ mm³ cubes at 25 °C (MK III DMTA, Rheometrics). The measurements were carried out until an equipment-related force limitation was reached. The modulus, E , was calculated from the slope of the stress–strain curves at low strains. Thermogravimetric analysis (TGA) was conducted in air from 25 to 1000 at 20 °C/min (2050 TGA, TA Instruments). The differential thermogravimetry (DTG) curves, derivatives of the TGA thermograms, were calculated using the supplied software.

Results and Discussion

Structure. Minimal shrinkage of the polyHIPE was observed during polymerization and drying. The density of D26 is 0.13 g/cm³, and the porosity, estimated by assuming a polymer density of 1 g/cm³, is 87% (Table 1). The densities of the nanocomposite polyHIPE varied between 0.10 and 0.16 g/cm³, corresponding to porosities between 90 and 84%. The density decreases with increasing DVB content for both the Dx-V and Dx-M series of nanocomposite polyHIPE. This decrease in density with DVB content indicates that increasing the DVB content enhances the polyHIPE resistance to shrinkage. An EHA-based HIPE with no VSQ and with less than 26 mol % DVB collapsed during polymerization and drying, indicating insufficient cross-linking.⁵ An EHA-based HIPE with no DVB and with less than 40 mol % VSQ collapsed during polymerization and drying, indicating insufficient cross-linking.³² A VSQ content of 40 mol %, however, provided enough cross-linking to stabilize the polyHIPE, in spite of the absence of DVB. A HIPE with no DVB and with 40 mol % MSQ collapsed since MSQ does not cross-link the polyHIPE.

The porous structure typically found in polyHIPE consists of “voids”, the volume vacated by the droplets of the dispersed phase, and “holes”, the openings through the walls surrounding the voids. The combination of voids and holes create the polyHIPE’s open-pore structure. The structures

in Figure 3, however, are similar to those from polyHIPE that have undergone some degree of destabilization. D16-V (Figure 3a) exhibits large spherical voids on the order of 50–300 μ m, which result from water droplets that merge during the Ostwald ripening that is part of the destabilization process.^{34,35} The walls of these large voids consist of a porous nodular structure (Figure 3b). The walls between the large voids consist of voids on the order of 5–30 μ m that are typical of polyHIPE structures (Figure 3a). These smaller voids are connected by holes of around 0.5–2 μ m in diameter (Figure 3c). D15-M (Figure 3d,e) and the other nanocomposite polyHIPE in the Dx-V and Dx-M series exhibit similar porous structures.

Properties. The variation of $\tan \delta$ with temperature for the Dx-V series is seen in Figure 4. The variation of $\tan \delta$ with temperature for the Dx-M series (not shown) is quite similar. The $\tan \delta$ peak temperature and the breadth of the $\tan \delta$ peak in Figure 4 both increase with increasing DVB content. The $\tan \delta$ peak height in Figure 4 decreases with increasing DVB content. Previous work on polyHIPE and interpenetrating polymer networks (IPN) has shown that increasing the amount of cross-linking comonomer yields an increase in the $\tan \delta$ peak temperature and in the breadth of the $\tan \delta$ peak and yields a reduction in the $\tan \delta$ peak height.^{5,28,31} Increasing the DVB content produces both an increase in the amount of cross-linking and an increase in the amount of relatively stiff monomer units incorporated into the polymer backbone.

The $\tan \delta$ peak temperature increases in a linear fashion with the DVB content, with similar slopes for VSQ and MSQ (Figure 5). These changes in the $\tan \delta$ peak reflect the restrictions on the segmental mobility imposed both by cross-linking and by incorporating relatively rigid monomer units into the polymer backbone. The difference between VSQ and MSQ is also clear from Figure 5. D16-V and D15-M have similar DVB contents and similar SSQ contents, but the $\tan \delta$ peak temperature of D16-V is 30 °C higher than that of D15-M. The higher $\tan \delta$ peak temperature for the polyHIPE containing VSQ reflects the restrictions on segmental mobility imposed by cross-linking through an SSQ network.

The increase in the $\tan \delta$ peak temperature on cross-linking with DVB can be compared with the increase in the $\tan \delta$ peak temperature on cross-linking with VSQ by defining a cross-linking group content. The cross-linking group content is the percentage of the total number of groups that can, potentially, provide cross-linking sites. Each EHA molecule contributes one non-cross-linking group. Each CH₂=CH–SiO_{1.5} unit and each DVB molecule contribute one cross-linking group. The ES molecules are considered to be part of the DVB cross-linking groups, providing an additional contribution to the backbone stiffening that occurs on copolymerization of a less rigid molecule (EHA) with more rigid molecules (DVB and ES). There are three nanocomposite polyHIPE series that can be compared on this basis. The first is the Dx-V series, where the DVB content is varied and the VSQ content is around 40 mol %. The second is the

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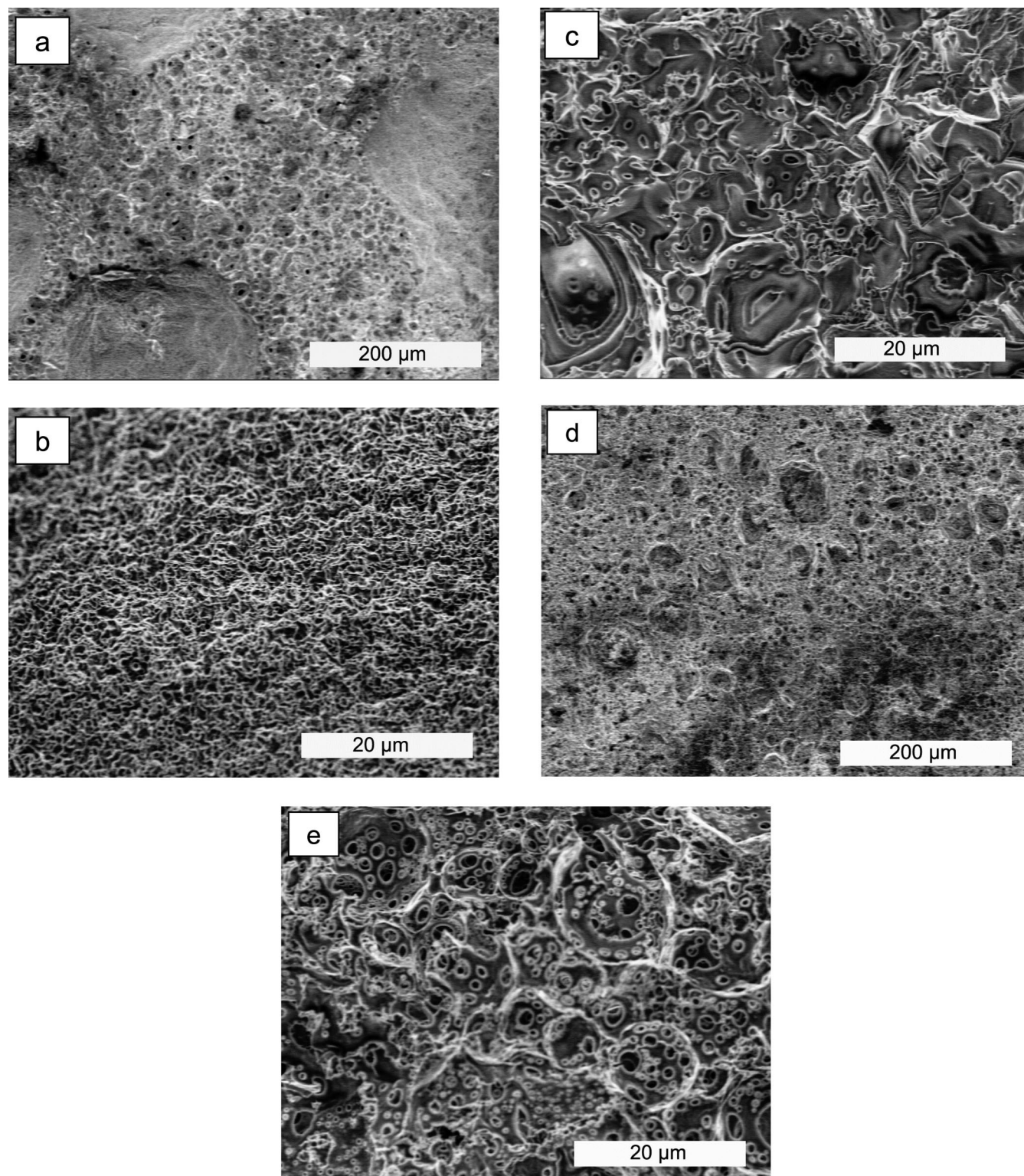


Figure 3. SEM micrographs of nanocomposite polyHIPE: (a, b, c) D16-V; (d, e) D15-M.

Dx-Vz series where the EHA/DVB molar ratio is maintained at 74/26 and the VSQ content is varied. The third is D0-Vz, where there is no DVB and the VSQ content is varied (as described in detail elsewhere).³²

The variation of the $\tan \delta$ peak temperature for these series as a function of the cross-linking group content is seen in Figure 6. The $\tan \delta$ peak temperature increases in a linear fashion with the cross-linking group content (Figure 6). Interestingly, the slopes of the lines describing the D0-Vz

and Dx-Vz series are quite similar. The variation in the cross-linking group content for both of these series is due to the variation in the VSQ content. The changes in the $\tan \delta$ peak temperature reflect the restrictions on segmental mobility imposed both by cross-linking and by reinforcement with SSQ. The slope of the line describing the Dx-V series is significantly greater than those of the D0-Vz and Dx-Vz series. The variation in the cross-linking group content for the Dx-V series is due to the variation in the DVB content.

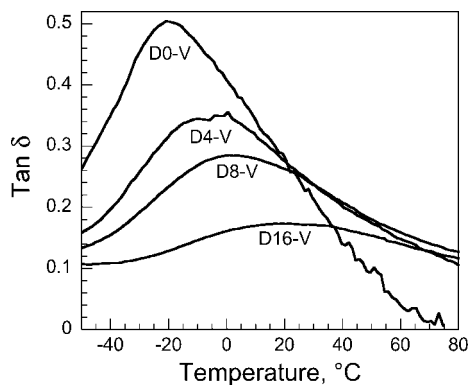


Figure 4. Variation of $\tan \delta$ with temperature for the Dx-V series.

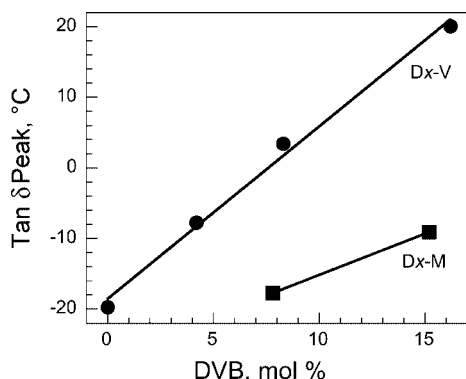


Figure 5. Variation of the $\tan \delta$ peak temperature with the DVB content.

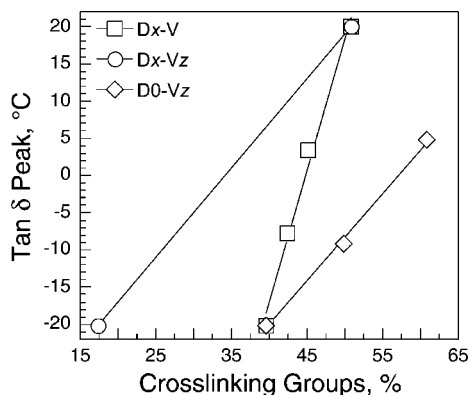


Figure 6. Variation of the $\tan \delta$ peak temperature with the cross-linking group content.

In this case, the restrictions on segmental mobility are imposed both by cross-linking and by copolymerization with more rigid monomers.

Room temperature compressive stress–strain curves for the Dx-V series are seen in Figure 7. The compressive stress–strain curves for the Dx-M series (not shown) are quite similar. The stress–strain curves are typical of polyHIPE: a linear stress–strain region, a stress plateau region, and a densification region with a steep increase in stress. Both the modulus and the plateau stress increase with increasing DVB content. The length of the stress plateau (its strain range) and the strain at which densification begins both decrease with increasing DVB content. The modulus increases in a linear fashion with DVB content, with similar slopes for VSQ

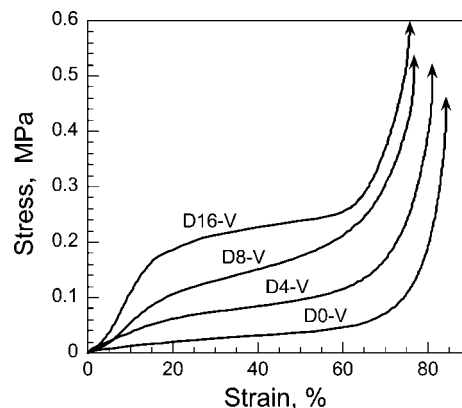


Figure 7. Compressive stress–strain curves for the Dx-V series.

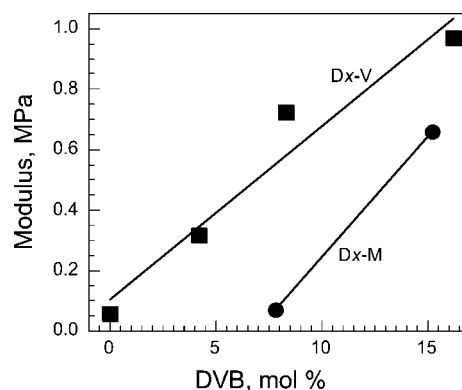


Figure 8. Variation of the compressive modulus with the DVB content.

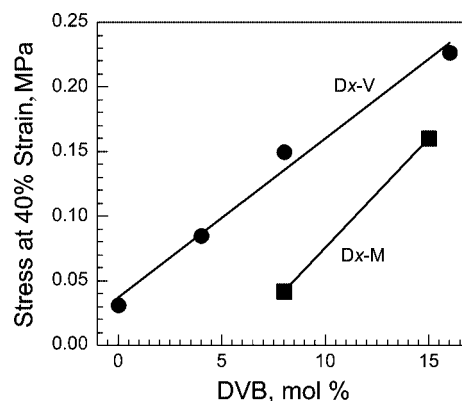


Figure 9. Variation of the compressive stress at 40% strain with the DVB content.

and MSQ (Figure 8). The relatively low modulus of D0-V, 0.06 MPa, reflects its relatively low degree of cross-linking. Increasing the DVB content enhances the modulus yielding a modulus of 0.96 MPa for D16-V. PolyHIPE with VSQ have higher moduli than polyHIPE with similar amounts of MSQ. The plateau stress can be compared at a particular strain which is within the stress plateau for each polyHIPE. The stress at 40% strain varies in a linear fashion with the DVB content, with similar slopes for VSQ and MSQ (Figure 9). As seen for the modulus, polyHIPE with VSQ have higher stresses at 40% strain than polyHIPE with similar amounts of MSQ.

Cross-linking with DVB can be compared to cross-linking with VSQ by plotting the modulus (Figure 10) and the stress

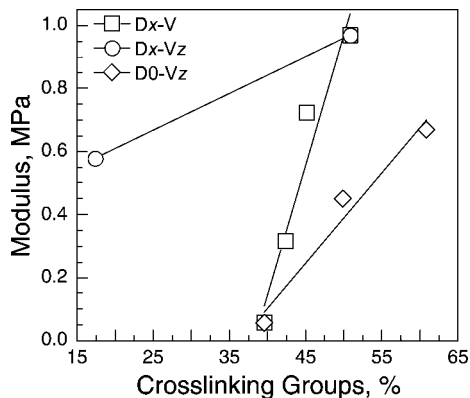


Figure 10. Variation of the compressive modulus with the cross-linking group content.

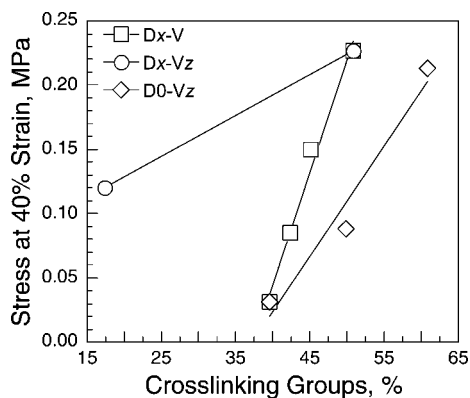


Figure 11. Variation of the compressive stress at 40% strain with the cross-linking group content.

at 40% strain (Figure 11) as functions of the cross-linking group content. The trends exhibited by the variation of the $\tan \delta$ peak temperature with the cross-linking group content in Figure 6 are also seen for the variation of the modulus and of the stress at 40% strain with the cross-linking group content in Figures 10 and 11, respectively. The modulus and stress at 40% strain increase in a linear fashion with the cross-linking group content. The slopes of the lines describing the D0-Vz and Dx-Vz series are quite similar, reflecting their origin in the variation of the VSQ content. The slopes of the lines describing the Dx-V series are significantly higher than those of the D0-Vz and Dx-Vz series, reflecting their origin in the variation of the DVB content. It is clear from the $\tan \delta$ data and the mechanical property data that DVB is much more effective in reinforcing the polyHIPE than VSQ and that VSQ is much more effective than MSQ.

Thermal Stability. The thermal degradations of D26, D16-V, and D0-V are described by the TGA and DTG thermograms in Figures 12 and 13, respectively. The degradation results are summarized in Table 3. D26 has a T_d (temperature at which the mass loss is 10%) at 281 °C and exhibits two narrow DTG peaks (285 and 344 °C) and a DTG shoulder at 360 °C. Surprisingly, T_d is lower for the Dx-V polyHIPE, 245 and 236 °C for D16-V and D0-V, respectively. The first degradation stage for the Dx-V polyHIPE is similar to that for D26 but occurs at a lower temperature. D16-V and D0-V exhibit narrow DTG peaks at 238 and 241 °C, respectively. The interconnected SSQ–organic networks in D16-V yield a significantly lower

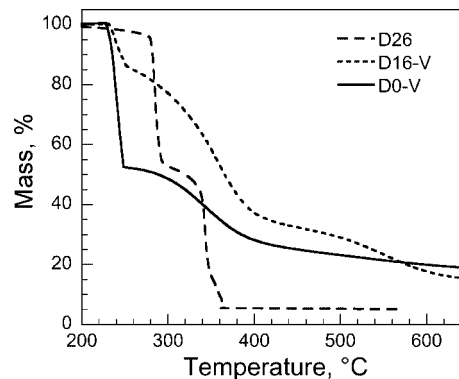


Figure 12. TGA thermograms from D26, D16-V, and D0-V.

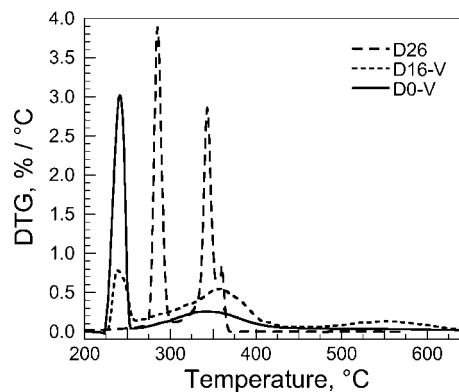


Figure 13. DTG thermograms from D26, D16-V, and D0-V.

Table 3. Thermal Degradation for D26, D16-V, and D0-V

	D26	D16-V	D0-V
T_d , °C	281	245	236
DTG peaks, °C	285 344 (360)	238 359 548	241 342
m_R , %	5.1	14.9	18.3

mass loss and a significantly smaller DTG peak during the first degradation stage. The second degradation stage for the Dx-V polyHIPE is quite different than that for D26, although it occurs at a similar temperature. D16-V and D0-V exhibit low, broad DTG peaks at 359 and 342 °C, respectively, as opposed to the high, narrow DTG peak for D26. These low, broad DTG peaks correspond to significantly smaller and more gradual mass losses, reflecting the presence of interconnected SSQ–organic networks. In general, D16-V exhibits a smaller mass loss than D0-V. However, D16-V undergoes an additional degradation stage with a DTG peak at 548 °C. At 600 °C D16-V and D0-V have similar residual masses, m_R .

Conclusions

Novel porous nanocomposites with interconnected SSQ–organic networks were successfully synthesized within a HIPE. The porous structures of these polyHIPE were similar with no discernible dependence on the DVB content or on the type of SSQ. The densities, between 0.10 to 0.16 g/cm³, decreased with increasing DVB content, reflecting the stiffening effect of DVB that enhances the resistance to shrinkage. The addition of DVB has a significant effect on

the polyHIPE properties. The $\tan \delta$ peak temperature and the room temperature modulus and stress at 40% strain all increased in a linear fashion with increasing DVB content. The increase in these properties reflects both the increase in cross-link density and the increase in backbone rigidity. These properties were all significantly greater on addition of VSQ (interconnected SSQ–organic networks were formed) than on addition of MSQ (interconnected networks were not formed). A comparison based on the cross-linking group

content demonstrated that DVB cross-linking enhanced these properties more significantly than VSQ cross-linking. The formation of interconnected SSQ–organic networks produced the most thermally stable nanocomposite polyHIPE.

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