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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/9783527654505.ch4>

Characterization Techniques for Polymer Nanocomposites, Polymer Nano-, Micro- and Macrocomposites Series; no. 3, pp. 75-109, 2012-08-24

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***PVT* Characterization of polymeric nanocomposites**

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Montreal, March – June 2011

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1 Introduction

Two principal components of polymeric nanocomposites (PNC) are polymeric matrix and dispersed in it nano-particles, *e.g.*, natural or synthetic clays. In the IUPAC nomenclature, the nano-particles must have at least one dimension in the nano-meter range, ≤ 2 nm. The particles may be platy (only thickness being nano-sized), two-dimensional (*i.e.*, fibers, nanotubes or whiskers), or three dimensional (*e.g.*, spherical metal or metal oxide atom clusters).

Depending on the volume and applications PNCs are classified as structural (large volume) or functional (small volume for specialty applications). For the industrial production of structural PNC only layered nanoparticles are of interest. They are mainly crystalline natural clays with platelets *ca.* 0.7 to 1.7 nm thick, and the cation exchange capacity CEC = 0.8 – 1.2 meq/g.¹

Natural clays originate from the hydrothermal alteration of alkaline, 85 – 125 million years old volcanic ashes, deposited by winds in seas and lakes.^{2,3} As a consequence, chemical composition of even the same type of clay (for example, montmorillonite, MMT) changes with geographical location and open mine strata. These clays contain impurities: (1) adsorbed organic compounds (*e.g.*, humic substances, HS), (2) non-expandable clays (*e.g.*, amorphous clays, vermiculite, kaolin) and (3) diverse particulate minerals (*e.g.*, quartz, sand, silt, feldspar, gypsum, orthoclase, apatite, halite, calcite, dolomite, quartz, biotite, muscovite, chlorite, opal, volcanic dust, fossil fragments, heavy minerals, sulfates, sulfides, carbonates, zeolites, hematite, etc.).^{1,4}

Originally, the resin manufacturers reactively produced PNCs, *i.e.*, polymerizing monomer(s) in the presence of pre-intercalated clay.⁵ However, development of the melt compounding technology for PNC is more economic and it shifts their production to compounders and fabricators, adding flexibility and accelerating market penetration by PNC. In 2010 the PNC market reached 500 kton with the cost differential between the neat polymer and its PNC of about 10%.⁶ Due to superior thermal and electrical conductivity as well as other properties, the demand for PNCs is escalating for packaging, automotive, electrical and coating applications.

2 Components of polymeric nanocomposites

In structural PNC *ca.* 2 – 5 wt% clay is dispersed in polymer matrix: thermoplastic, thermoset or elastomeric. However, since most clay/polymer systems are antagonistically immiscible, in analogy to immiscible polymer blends, compatibilization is required. The process comprises two steps: 1. Conversion of clay into organoclay by intercalation with low molecular weight onium salts, and 2. Addition of functional compatibilizer(s). The amount of intercalant in organoclays is about 30 – 50 wt%, *i.e.*, 50 – 70 vol%. The amount of compatibilizer ranges from about 5 to 100 wt% of the polymeric phase.

Three types of clays are being used in industrial PNC: the natural, semi-synthetic and synthetic. Their characteristic feature is the ability to peel-off individual layers, *i.e.*, to exfoliate. This ability is related to the imbalance of electronic charges in crystalline cells that must be compensated by hydrated ions in the interlayer galleries. Of prime interest are smectite clays of the general formula: $(\text{Ca}, \text{Na}, \text{H})(\text{Al}, \text{Mg}, \text{Fe}, \text{Zn})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2(x\text{H}_2\text{O})$. The most important members of this group are MMT, hectorite (HT), saponite (ST), nontronite (NT) and beidellite (BT). These clays have three-layer structure of octahedral (Oc) sandwiched between two tetrahedral layers (Tc), *viz.* MMT: $[\text{Al}_{1.67}\text{Mg}_{0.33}(\text{Na}_{0.33})]\text{Si}_4\text{O}_{10}(\text{OH})_2$, or HT: $[\text{Mg}_{2.67}\text{Li}_{0.33}(\text{Na}_{0.33})]\text{Si}_4\text{O}_{10}(\text{OH}/\text{F})_2$. Owing to substitution in Oc of Al^{+3} atoms by Mg^{+2} the MMT platelet has 0.25 to 1.2 negative charges per unit cell, *i.e.*, $\text{CEC} \approx 0.5$ to 2 meq/g. In HT the charge imbalance is caused by replacing Mg^{+2} atoms in Oc by Li^{+} , while in saponite (ST) replacement in Tc layers of Si^{+4} by Al^{+3} atoms, engender the $\text{CEC} \approx 1.3$ meq/g.⁷

The clays may be natural, semi-synthetic or synthetic. Thus, natural MMT from Wyoming has the aspect ratio $p = d/t \approx 280$, where d is the diameter, and t is the clay platelet thickness. Its nominal orthogonal dimensions are: thickness $t \approx 1$ nm, width $W \approx 200$ nm, length $L \approx 300$ nm, with the ratio being nearly universal: $L/W \approx 1.5 \pm 0.1$. These dimensions follow Gaussian distribution with the mean value $L_{\text{av}} \approx 280$ nm. The synthetic or semi-synthetic clays have been produced with $p = 30 - 6000$; the ones with large platelets do not follow Gaussian curve.¹

1. **Semi-synthetic clays** are prepared by modification of natural minerals, *e.g.*, talc or obsidian. For example, a powdery mixture of 10 to 35-wt% of a sodium hexafluorosilicate (Na_2SiF_6) and natural talc is heated for about 1 hr at $T \approx 900^\circ\text{C}$ producing fluoro hectorite (FH) or

fluoro mica (FM). During this time, Na^+ or Li^+ partially replace Mg^{+2} in the talc Oc layer and fluorine partially replaces the $-\text{OH}$ groups on the clay surface.^{8, 9}

2. **Fully synthetic clays** are formed starting with metal salts or oxides in appropriate proportions. Several sub-categories are distinguished:
 - a. Low temperature, high pressure hydrothermal synthesis that starts with aqueous solutions of appropriate salts, co-precipitated into crystallizing slurry.^{10, 11}
 - b. High temperature melt process that starts with a mixture of, *e.g.*, Li_2O , MgO , SiO_2 and MgF_2 ; or SiO_2 , MgO , and Na_2SiF_6 , mixed in proper proportion, heated at $1300 - 1500^\circ\text{C}$ for 3 h and then allowed to cool for 10 h, yielding HT or FH.¹²
 - c. Synthesis of the layered double hydroxides (LDH) by co-precipitation of di-valent and tri-valent metal ions in an alkaline, aqueous medium.^{13, 14}
3. **Templated synthetic**, based on organic templates, which after synthesis may be pyrolyzed, or left in as intercalants (non-commercial).¹⁵

Recent three clays were tested (1) the natural MMT from Southern Clay Products Cloisite®- Na^+ (C- Na^+), (2) the semi-synthetic fluoro-mica or fluoro-hectorite, Somasif ME-100 from CBC Co., Japan (ME-100), and (3) the fully synthetic fluoro-tetrasilicic mica from Topy Industries, Japan (Topy- Na^+). Their properties are listed in Table 1.

Table 1. Properties of the clays.⁴

Property	C- Na^+	ME-100	Topy- Na^+
Specific/bulk density, g/mL	2.86/0.34	2.6/-	2.6/-
Particle diameter, d (μm)	2 to 13	5 to 7	4 to 10
Interlayer spacing, d_{001} (nm)	1.17	0.95	1.23
Platelets thickness, t (nm)	0.96	0.91	
Cation exchange capacity, CEC (meq/g)	0.92	1.2	0.80
Nominal aspect ratio, p (-)	280	≤ 6000	≤ 5000
Clay reference	16	17	9

Three sets of information characterize the clays:

1. Size, size distribution and shape of the clay platelets
2. Chemical composition
3. Impurities: type and quantity

2.1 Size, size distribution and shape of the clay platelets

Clay sodium salt was exfoliated in demineralized water and a droplet of suspension deposited on a membrane filter with pore size = 220 nm. Three orthogonal measures of platelets, L , W and t , as well as their distribution, were determined in a scanning (SEM), transmission (TEM) or atomic force (AFM) microscope. Figure 1 displays an examples and Table 2 the statistics.

Figure 1. Left: SEM image of ME-100 clay platelets (the diameters of circular holes in the PC membrane are $d = 220$ nm). Right: SEM/EDX spectrum of ME-100.¹⁸

Table 2. Statistical analysis of three clays.⁴

Clay	Length L (nm)		Width, W (nm)		Ratios	
	L_n	L_w	W_n	W_w	$(L/W)_n$	$(L/W)_w$
Natural, C- Na^+	290	350	183	219	1.58	1.60
Semi-synthetic, ME-100	872	1097	572	743	1.52	1.48
Synthetic, Topy- Na^+	1204	1704	761	1186	1.58	1.44
Error					± 0.2	± 0.2

2.2 Chemical composition of clays

The Scanning Electron Microscopy and Energy-Dispersive X-ray analysis (SEM/EDX method) probes $ca. 1 \mu\text{m}^3$ of material at a time;¹⁹ see SEM/EDX spectrum in Figure 1. SEM/EDS method analyzes the chemical composition and its crystalline cell size. A characteristic X-ray is produced when outer shell electrons replace the inner shell ones. Since clay may have locally-

diverse composition, it is important that several particles are sampled from at least five locations, each. An example of results is presented in Table 3.

Table 3. Elemental composition of C-Na⁺ and ME-100 clays ⁴

Source	C-Na ⁺	ME-100
Nominal	[Al _{3.34} Mg _{0.66} Na _{0.66}](Si ₈ O ₂₀)(OH) ₄	(NaF) _{2.2} (MgF ₂) _{0.1} (MgO) _{5.4} (SiO ₂) ₈
Found	[Al _{2.9} Fe _{0.6} Mg _{0.35} Na _{0.72}](Si ₈ O ₂₀)(OH) ₄	(NaF) _{0.94} (MgF ₂) _{2.3} (MgO) _{2.7} (SiO ₂) ₈

The composition of minerals of micron-sized particles depends on their size (a core-shell compositional structure). Since there is a particle size distribution in commercial clay powders a large scatter of values (error = ± 5 – 15%) has been reported.²⁰

2.3 Impurities

Purification of natural clays into a polymer-grade material is a laborious, time consuming process of about 300 steps. The patented method leads to clay sodium-salt, which contains ≤ 5 wt% (“preferably less than about 2% by weight”) of impurities, such as amorphous silicates, stacks of welded (by a crystallographic defect) platelets and the residual 0.3 – 2 wt% quartz particles with size exceeding 300 nm.²¹ Furthermore, the commercial clay contains about 2 wt% of moisture and 7 wt% of “loss on ignition”, LOI (comprising organics, hygroscopic and bound H₂O, carbonic acid, etc.).

Table 4. Impurities in C-Na⁺ and ME-100 from XRD.²²

C-Na ⁺	ME-100
Vermiculite, Quartz, Cristobalite, Rutile, Albite, Microcline, Aragonite, Vaterite, Dolomite, Gypsum, Anhydrite, Alunite, Sylvite	Vermiculite, Gypsum

Table 4 lists impurities identified in natural (C-Na⁺) and semi-synthetic (ME-100) clays. For the analysis of contaminants clay was dispersed in water and centrifuged. The sediment was analyzed by the X-ray diffraction method.

3 Pressure-volume-temperature (PVT) measurements

3.1 Transitions

Within the full temperature range from 0 (K) to the thermal decomposition temperature, $T_{\text{dec}} = 380 - 1170$ (K)²³ polymers undergo several transitions. Of these the best known are, the melting temperature of crystalline polymers, T_m , and the glass transition temperature for amorphous, T_g – the former is the first-order thermodynamic transition whereas the latter is a kinetic one. In addition to these major transitions there are others smaller ones detectable on the derivative properties, *e.g.*, the compressibility and the thermal expansion coefficients (κ and α , respectively):

$$\kappa \equiv (\partial \ln V / \partial P)_{T, P^0, q} \quad ; \quad \alpha \equiv (\partial \ln V / \partial T)_{T^0, P, q} \quad (1)$$

where P^0 and T^0 are solidification pressure and temperature, respectively, and q is the rate of heating or compressing.

Thus, the first transition at $T < 80$ K was theoretically predicted by Simha *et al.*²⁴ who assumed that at these low temperatures the inter-segmental interactions follow the Einstein's equation for harmonic oscillators with the universal Einstein reduced quantum temperature. Good agreement between the theory and experiments was demonstrated at ambient P for several chemically different polymers. At higher temperatures (but below T_g) there are other glass-glass transition transitions, identified by letters of the Greek alphabet.²⁵ Of these $T_\beta \approx 0.8 T_g$ is the most important as it limits the region of physical aging of vitreous materials.²⁶

Also at $T > T_g$ there are transitions such as the cross-over transition, $T_c/T_g \approx 1.15 - 1.35$. The magnitude of this ratio was found dependent on the fragility index:^{27, 28}

$$m = \left(\frac{1}{T_g} \right) \left(\frac{d \log \eta}{d(1/T)} \right)_{T=T_g} \quad (2)$$

The transition at T_c is readily observed by neutron scattering and other vibrational spectra, in dielectric or rheological measurements, but not readily in *PVT*. The mode-coupling theory (MCT) considers liquid as an assembly of particles enclosed in cages formed by their neighbors

with α -relaxation controlling the behavior. Only at $T > T_c$ the molecular vibrations dominate. Götze and Sjogren wrote: “ T_c seems to be an equilibrium parameter of the system, which separates the supercooled liquid state in two regions”.²⁹ Semi-crystalline polymers have a dual nature, in part being amorphous in part crystalline. In most such polymers $T_m \approx 1.5 T_g$.³⁰

3.2 Determination of PVT

The PVT data are often represented as a surface in $V = V(T, P)$ coordinates. The measurements are carried out in two steps: 1. Determination of the specific volume under well-defined ambient conditions, V_o , and 2. Measurements of changes, ΔV , caused by programmed variation of T and P , thus:

$$V(T, P) = V_o(T_o, P_o) + \Delta V(T, P) \quad (3)$$

ΔV measurements are carried out in a pressure dilatometer. Several of these have been described in the literature, home-made or commercial, but most of the results originate from the Gnomix dilatometer (from Gnomix Inc., Boulder, CO).^{31, 32} This fully automated instrument is based on the principle of confining the tested specimen in Hg. The pressure ranges from ambient to 200 MPa, the temperature from ambient to 400 °C. Variations of ΔV may be determined with accuracy of 0.0002 ml/g at the heating or cooling rate ≤ 5 °C/min.

Before PVT test, polymer samples need to be dried, and then V_o determined. Dry samples are loaded to dilatometer, pre-molded at $T \geq 130^\circ\text{C}$, and then cooled to room temperature (RT) at a rate of ca. 1°C/min. The pre-molded specimens are tested following selected procedure within the range of temperatures, $T = 300\text{--}590$ K, and pressures, $P = 0.1$ to 190 MPa. For example, following the “standard” procedure at each T -level P is increased from ca. 10 to 190 MPa in steps of 20 or 30 MPa. The T is increased from RT in steps of about 10°C. Depending on the selected rate of heating or cooling, the measurement of 350 to 750 data points takes 16 to 36 h. The four procedures used for PVT tests are listed in Table 5.

Table 5. Procedures of *PVT* measurements

Procedures	Constant variable	Adjusted variable
Isothermal heating ("standard")	T is kept constant until P -sweep is completed, then increased to another level between the ambient and the maximum level, $T_{\max}$.	P increases from 10 to 200 MPa.
Isothermal cooling	Initially $T \approx T_g + 30^\circ\text{C}$ is constant until P -sweep is completed, then decreased to another level toward the ambient T	P increases from 10 to 200 MPa.
Isobaric heating	P is kept constant until T -sweep is completed, then increased to another level between 10 and 200 MPa	T increases from ambient to $T_{\max}$.
Isobaric cooling	P is kept constant until T -sweep is completed, then increased to another level between 10 and 200 MPa	T decreases from $T \approx T_g + 30^\circ\text{C}$ to ambient

Note: As P increases the resulting adiabatic heating increases the set T by up to 5°C . In principle, the experiments may also be conducted reducing P .

Figure 2. PVT dependencies of polystyrene (PS) measured following procedures: A. isothermal heating, B isobaric heating, and C isobaric cooling. For clarity only five constant- P curves are displayed with 20% of experimental point shown.

Distinctly different *PVT* plots obtained from three procedures are seen in Figure 2. The “standard” test in Figure 2A and the isobaric cooling one (at high cooling rate of $10^\circ\text{C}/\text{min}$) in Figure 2C show large transitory regions below T_g . Only the isobaric heating in Figure 2B resulted in a regular behavior with nearly constant slopes (a measure of the thermal expansion coefficient, α) in the vitreous and molten phase. Evidently, different procedures are used for different purpose. For example, the standard procedure guarantees that specimens see the highest temperature only at the end of the test, thus the measurements are not affected by thermal

degradation. The isobaric cooling from $T \approx T_g + 30$ °C has been used for studying the thermodynamics of glass transition.^{33, 34}

3.3 Effects of clay, intercalant and compatibilizer

The discussion in the preceding parts focused on neat polymers. In the case of PNC the procedure needs to be slightly modified. The expandable clay contains ca. 7 wt% of moisture that may falsified the high- T response. Furthermore, PNC show barrier properties for vapors and gases dependent on the clay aspect ratio, its degree of dispersion, concentration and orientation. Consequently, the drying time of PNC samples may be significantly longer than that of neat resin. For example, to reach constant weight during vacuum drying at 80°C PA-6 required 48 h but its PNC with 2-wt% organoclay 161 hrs.^{35, 36}

Commercial organoclay may contain 25 – 40 wt% excess of the intercalating onium salt. This low molecular weight compound brings into PNC large amount of free volume that may significantly affect the PVT behavior. Highly polar PA-6 strongly interacts with crystalline clays having high surface energy.³⁷ The interactions are so strong that PA-6 expels intercalant from clay surface and forms 4 – 6 nm thick solid layer of polymer, followed by about 100 nm thick layer of organic molecules with increasing mobility as the distance from the clay surface increases.^{35, 38} In these PNCs adsorption and solidification reduce the free volume by ca. 15%.

As in polymer alloys and blends (PAB), also in PNC the two principal components, polymer and organoclay, are thermodynamically immiscible and compatibilization is desirable. The thermodynamic theories of PNC treats nano-sized clay platelets and polymeric macromolecules as statistical elements of the network, thus if exfoliation is required, system miscibility must be assured. Since macromolecular diffusion into the clay gallery decreases the entropy, $\Delta S < 0$, the miscibility might be expected only if enthalpy is negative, $\Delta H < 0$, *i.e.*, if the specific interactions are strong.³⁹ However as in PAB, compatibilizers may also be used for modifying the PNC performance, *e.g.*, by toughening the matrix, changing permeability, etc. Thus their overall effect on the PVT behavior is not necessarily predictable.

4 Derivatives; compressibility and thermal expansion coefficient

4.1 Interpolating the data

The raw data that come from automatic dilatometers usually have well defined, constant P -values, but because of adiabatic effect T is different at each P level. Thus, if the derivatives α and κ are required, one need to have evenly spaced data points at constant T and P . Three methods have been applied to accomplish this:

- I. Fitting the data to an equation and then computing the function value at desired intervals of T and P ; for that an empirical Tait equation has been used.^{40, 41}
- II. As an alternative to the first method, one may fit the data to a polynomial, which subsequently is differentiated according to definitions in Eq. 1.
- III. The third approach is a simple interpolation to the same T -value at $P = \text{constant}$, thus correcting for the adiabatic heating. The interpolation may be linear or polynomial.

All three methods may find their usefulness, but if derivatives are to be used for detecting small transitions, that only the last interpolative method III is acceptable.

4.2 Computation of the thermal expansion and compressibility coefficients, α and κ

According to definition in Eq. 1, α and κ are slopes of $\ln V$ as a function of T or P , respectively, while keeping the second independent variable constant. The experience shows that most objective method for extracting these derivatives from PVT data is direct numerical differentiation of data at constant value. There are numerous computer programs that perform differentiation by “moving arch” method, but the ones that is most convenient permits selection of number of data points used in each differentiation step. For fitting a curve, the minimum data points is 3 and usually the maximum is 9 – the smaller the number the larger the scatter, but high sensitivity to small functional variation, while the larger the number of data points the smoother the differential, but with danger of erasing important local information.^{42, 43} Most popular is the “5 point formula”, equivalent to locally fitting a 4th degree polynomial. The error of the derivation depends on the symmetry of the computation method, the number of data points in formula, and the distance between the abscissa independent variable, Δx . Thus, for symmetric computation with 5 points the derivative is computed as:

$$y_o' = [y_{-2} - 8y_{-1} + 8y_1 - y_2]/12\Delta x \quad (4)$$

The error depends on the size of the step Δx and the form of the $y = y(x)$ dependence.

4.3 Polymer α and κ from PVT

Numerical differentiation of dependencies displayed in Figure 2 leads to the temperature-dependent thermal expansion and compressibility coefficients presented in Figures 3 and 4, respectively.

Figure 3. Volumetric thermal expansion coefficients vs. T , computed from data in Figure 2 For clarity only five constant- P curves and every 4th point are shown.

It is noteworthy that at $T > T_g$ the numerical values of α are similar for neat PS-686 and PS-667 with lubricant. The different PVT test procedure is reflected in the lower- T data. The sequence of data collection during “standard” isothermal heating starts with data point at lowest T and P , then zigzagging down and up for each isothermal step ends in the uppermost point at the highest T . For $P > 40$ MPa the procedure results in densification of the vitreous phase and reduction of α to zero. For PS-686 the *beta*-temperature increases with pressure as: $T_\beta = 265 + 0.59 P(\text{MPa})$ with $r = 0.991$, *i.e.*, for the range P it ranges from 265 to 378 K.³⁴ When $T_\beta \leq T \leq T_g$ the compressed glass may relax. The simplest α -dependencies were obtained by isobaric heating (Figure 3B) where the over-compression evident in Figure 3A is absent. In these two test procedures the data were collected at a rate of ≤ 25 min/data point, *i.e.*, *ca.* 2°C/h. The rate used during the isobaric cooling (Figure 3C) was higher, *ca.* 10°C/h. Upon cooling at $P > 40$ MPa below T_g the coefficient α decreases down to negative values (volume expansion) then increases to the value

typical for the vitreous phase. This kinetic effect is related to the presence of non-equilibrium fractal structure of PS melt in the vicinity of T_g .^{44, 45}

Figure 4. Volumetric compressibility coefficients vs. T , computed from data in Figure 2. For clarity only curves for $P = 0.1$ and 190 MPa (with every 4th point) are shown.

Figures 3 and 4 show that while the thermal expansion coefficient, $\alpha = \alpha(T)$ within the vitreous and molten phase varies little with T , the compressibility coefficient, $\kappa = \kappa(T)$ increases in both phases. A transitory behavior of these two coefficients at $T \leq T_g$ is evident for isothermal heating and isobaric cooling PVT procedures at $P > 40$ MPa. It is worth noting that all three procedures lead to acceptable agreement of $\kappa = \kappa(T)$ dependencies at $T > T_g$, especially at lower P . Characteristically, in Figures 2 – 4 there is a weak evidence for the presence of other transitions than T_g , at $T_c \approx 475 \pm 5$ K. On the other hand, $T_\beta \approx 0.8T_g = 290$ K is near the lowest temperature of the PVT scans and thus is impossible to observe.

4.4 Effect of clay on α and κ in PS-based PNC

In the following parts the data obtained from the “standard” PVT isothermal heating procedure will be discussed.

The PS-based CPNC were prepared by melt compounding commercial, slightly lubricated PS-1301 ($M_w = 270$ kD) with 0 – 17.1 wt% of Cloisite® 10A organoclay (C10A = MMT + 39-wt%

of di-methyl-benzyl hydrogenated tallow ammonium chloride, 2MBHTA) in a twin screw extruder (TSE). The details have been published by Tanoue *et al.*^{46, 47, 48} As it will be repetitively shown in this Chapter, in PNCs there are two critical concentrations: w_1 limits possibility of free rotation of exfoliated clay platelets and w_2 , at which all matrix molecules are adsorbed by dispersed clay stacks. For the PS/C10A system, $w = 1.1$ and 3.6 wt% clay.

Figure 5. Temperature dependence of the volumetric thermal expansion coefficient at two pressures and four concentrations.

Figure 6. The thermal expansion coefficient at $T < T_g$ and $P = 0.1, 100$ and 190 MPa vs. clay content.

Figure 7. The thermal expansion coefficient at $T > T_g$ and its pressure gradient as function of clay concentration, w .

Figures 5 – 7 display computed values of α as function of P , T and w . In the vitreous state α_g shows two types of behavior. For clay loadings $w \leq 2\%$ it has low value decreasing with P to about zero, whereas for $w > 3.6\%$ its values are negative, *i.e.*, heated specimen shrinks with T instead of expanding. The magnitude of α_g at $T < T_g$ strongly depends on the cooling process from the melt. In the molten state the isobaric values of α_m are nearly constant, independent of T . As shown in Figure 6, addition of clay reduces α_g in the full range of the investigated P . However, the decrease is non-uniform –in the vicinity of $w_2 = 3.6$ wt% the function takes a dip. A similar, but stronger local decrease is observed in the melt; Figure 7 displays $\alpha_m = \alpha_m(w)$ at ambient pressure and its pressure gradient.

Figures 8 and 9 display computed from PVT the compressibility coefficients, κ , as functions of P , T and w . By contrast with α , compressibility tends to increase with T . However, the temperature dependence of κ decreases with P virtually to zero at the highest P and w . This observation is confirmed by the $\kappa = \kappa(w)$ dependencies shown in Figure 9 – excepting a local dip

of the function near $w_2 = 3.6$ wt% at constant T and P the function is nearly constant. The dip observed in vitreous and molten state in $\alpha = \alpha(w)$ is also evident in $\kappa = \kappa(w)$.

Figure 8. The compressibility coefficient vs. T at $P = 0.1$ and 190 MPa for PNC containing: $w = 0, 2, 5$ and 17 wt%.

Figure 9. The compressibility coefficient at $T < T_g$ as function of clay concentration, w .

4.5 Effect of clay on α and κ in PA-6 based PNC

There are two transitions of interest in dry PA-6: the glass transition temperature $T_g(\text{PA-6}) \approx 323$ K and the melting point at $T_m(\text{PA-6}) \approx 500$ K, both dependent on P as well as on the method of material preparation. The PVT measurements of PA-6 ($M_w \approx 22$ kD), its PNC-2 and PNC-5 containing 2.29 ± 0.13 and 4.91 ± 0.24 wt% of clay (inorganic content), respectively, were carried out at $T = 300 - 580$ K and $P = 0.1 - 190$ MPa.⁴⁹ The PNC's were prepared reacting ϵ -caprolactam in the presence of MMT pre-intercalated with ω -amino-dodecyl-acid, thus forming a bonded structure: $\text{MMT} \leftrightarrow \text{ADA} \leftrightarrow \text{PA-6}$.

The derivatives α and κ were computed by numerical differentiation of the PVT isobaric or isothermal dependencies, following Eq. 1. Because of the closeness of T_g to the starting temperature, this transition was ignored – the attention was focused on T_m and its variation with independent variables, P , T and w .

Figure 10. The thermal expansion coefficient vs. T at $P = 0.1 - 190$ MPa for PA-6 and two its nanocomposites with 2 and 5 wt% of clay.

The thermal expansion coefficient for PA-6 and its PNCs is shown in Figure 10. For ease of comparison the three graphs are on the same scale – the crystalline phase is separated from the melt by a “chimney-like” melting zone. It is evident that addition of clay affects both phases – it reduces α of the solid phase, and significantly modifies the melt behavior. Comparing PNC-2 with PA-6 at $T > T_m$ one note that while shape of the dependencies are similar, the low- P expansion is larger. By contrast, PNC-5 behavior at $T < T_m$ is similar to that of PA-6, but above T_m the function $\alpha = \alpha(T)$ decreases instead of increasing. This behavior might be related to the presence of high crystallinity regions in the vicinity of the MMT high energy surface.

Figure 11. The compressibility coefficient vs. T at $P = 0.1 - 190$ MPa for PA-6 and two its nanocomposites PNC-2 and PNC-5

The compressibility coefficient vs. T for PA-6 and its two PNCs is displayed in Figure 11. The data points were computed from PVT , whereas the lines represent polynomial fitted to all data except those in the melting zone at 470 – 500 K. Two aspects are noteworthy: (1) The dependence $\kappa = \kappa(T)$ follows the same dependence on both sides of T_m , and (2) at low P

compressibility slightly increases with clay content (at high P the behavior of all three materials is the same). As it will be shown in part 7 of this chapter, the first aspect is fully predicted by the theoretical analysis of α and κ as functions of P and T .^{50, 51} The enhanced compressibility at low P might be related to the presence of the ADA intercalant cushioning the MMT platelets in the PA-6 matrix.

5 Thermodynamic theories

Up to this point all discussion was based on experimental data: measuring the PVT surface and then differentiating it for extracting the α and κ derivatives as functions of P , T and w . However, with adequate theory one may determine other thermodynamic quantities such as binary interaction parameters, cohesive energy density, solubility parameters, internal pressure, and others. Furthermore, since the theory relates the material behavior to the presence of free volume, it offers valuable insight into the thermodynamic equilibrium and non-equilibrium behavior such as diffusivity, rheology, positron annihilation lifetime spectroscopy (PALS), etc.⁵²

5.1 Simha-Somcynsky cell-hole theory

Any functional relation between volume, V , pressure, P , and temperature, T , belongs to the family of equations of state, eos.⁵³ While the early relations were empirical, applied to condensed gases, later on Lennard-Jones and Devonshire generalized the concept of intermolecular interactions in gases and liquids. Prigogine *et al.* cell model for s -mer linear molecules was a big step toward development of eos suitable for polymeric systems.⁵⁴ The cell model offered good description for condensed fluids, where the intermolecular distance is comparable to the lattice size, but progressively deviated with increased T . This problem was successfully treated in 1969 by Simha and Somcynsky by introduction of non-occupied cells in the lattice model.^{55, 56}

The Simha and Somcynsky (S-S) cell-hole theory is based on the lattice-hole model. The molecular segments of s -mer occupy y -fraction of the lattice sites, while the remaining randomly distributed sites, $h = 1 - y$, are left empty accounting for free volume. The theory was derived assuming thermodynamic equilibrium, thus its direct applicability is to liquids: non-polar or polar solvents, solutions, melts and diversity of mixtures (alloys, blends, composites, foams,

nanocomposites). However, assuming that at $T < T_g$ part of the free volume is frozen, the theory was extended to the vitreous and semi-crystalline non-equilibrium states.^{34, 57}

The derivation starts with configurational partition function in the form:

$$\begin{aligned} Z &= g(N, y) [v_f(V, y)]^{cN} \exp\{-E_o(V, y) / k_B T\} \\ g(N, y) &\propto y^{-N} (1-y)^{-Ns(1-y)/y} \\ E_o(V, y) &= (yNqz\varepsilon^*/2) \left[A(v^*/\omega)^4 - 2B(v^*/\omega)^2 \right]; \quad \omega \equiv yV / (Ns) \end{aligned} \quad (5)$$

where g is the combinatorial factor. L-J “6-12 potential” cast in volume terms is incorporated as the potential energy of the system, E_o , with two interaction parameters: the maximum attractive energy, ε^* , and the segmental repulsion volume, v^* . Next, assuming the corresponding states principle (CSP), the variables are divided by the characteristic reducing parameters:

$$\left. \begin{aligned} \tilde{V} &\equiv V / V^* \\ \tilde{T} &\equiv T / T^* \\ \tilde{P} &\equiv P / P^* \end{aligned} \right\} \Rightarrow M_s \frac{P^* V^*}{RT^*} = \frac{c}{s} \Leftarrow \begin{cases} P^* = zq\varepsilon^* / (sv^*) \\ T^* = zq\varepsilon^* / (Rc) \\ V^* = v^* / M_s \end{cases} \quad (6)$$

where $zq = s(z-2)+2$ is the number of interchain contacts between s segments (each of molecular weight: $M_s = M_n/s$) in a lattice of the coordination number z , and $3c$ is the number of the external degrees of freedom. The reduced free volume function v_f in Eq. (5) is taken as a volume-average of the solid-like and gas-like contributions:

$$\tilde{v}_f = \left[y(\tilde{\omega}^{1/3} - 2^{-1/6}) + (1-y)\tilde{\omega}^{1/3} \right]^3 \quad (7)$$

The configurational Helmholtz free energy is obtained as:

$$\begin{aligned} \tilde{F} &= \tilde{F}[\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T})] = -RT \ln Z \\ \tilde{F} / k_B T &= N \ln y + sN \left[(1-y)/y \right] \ln(1-y) - \\ &3cN \left\{ \ln \left[(y\tilde{v})^{1/3} - 2^{-1/6} y \right] + Nqz(\varepsilon^*/2kT) \left[A(y\tilde{v})^{-4} - 2B(y\tilde{v})^{-2} \right] \right\} \end{aligned} \quad (8)$$

In Eq. 8 the numerical values of the coefficients $A = 1.011$ and $B = 1.2045$ are for the assumed face-centered cubic lattice with the coordination number $z = 12$. It is noteworthy that in addition to the usual volume and temperature dependence, $\tilde{F}$ contains the hole fraction $h = h(\tilde{V}, \tilde{T})$.

The S-S eos is obtained by differentiation of the Helmholtz free energy:

$$(\partial \tilde{F} / \partial h)_{\tilde{T}, \tilde{V}} = 0 \quad \text{and} \quad \tilde{P} = -(\partial \tilde{F} / \partial \tilde{V})_{\tilde{T}} \quad (9)$$

The first partial derivative on Eq. 9 assumes presence of the thermodynamic equilibrium at which the free volume content is at optimum, while the second is a standard definition of pressure. Thus, the differentiation leads to eos in form of coupled equations:

$$\begin{aligned} \tilde{P} \tilde{V} / \tilde{T} &= (1 - \eta)^{-1} + 2y(AQ^4 - BQ^2) / \tilde{T} \\ 3c \left[(\eta - 1/3) / (1 - \eta) - y(3AQ^4 - 2BQ^2) / 6\tilde{T} \right] + (1 - s) - (s/y) \ln(1 - y) &= 0 \\ Q &\equiv 1 / (y\tilde{V}); \quad \eta \equiv 2^{-1/6} yQ^{1/3} \end{aligned} \quad (10)$$

The Helmholtz free energy also leads to the cohesive energy density, $\widetilde{CED}$, solubility parameter, $\delta = \delta(T, P)$, and the internal pressure, $\tilde{p}_i$:^{58, 59}

$$\begin{aligned} \widetilde{CED} &\equiv \tilde{U} / \tilde{V} = (y / 2\tilde{V}) [AQ^4 - 2BQ^2]; \quad \delta = \sqrt{\widetilde{CED}} = \sqrt{\widetilde{CED} \times P^*} \\ \tilde{p}_i &\equiv (\partial \tilde{U} / \partial \tilde{V})_{\tilde{T}} = -\frac{1}{2} [3AQ^4 - 2BQ^2] (\partial y / \partial \tilde{V}) + (2y / \tilde{T}) [AQ^4 - BQ^2] \end{aligned} \quad (11)$$

where $U = F + TS$ is the internal energy of the system.

The S-S theory (in form of the Eqs. 5 – 11) is valid for a single component liquid at equilibrium. Its advantage over others eos is the explicit incorporation of the hole fraction, $h = 1 - y$, a measure of the free volume fraction, $f(P, T) \equiv 1 - V_o/V(P, T)$.⁶⁰ Eq. 10 stipulates that all liquids cast in reduced variables obey the CSP. Once the characteristic parameters (P^* , V^* , T^* , and $3c/s = 1 + 3/s$) are known, the V , h , L-J interaction parameters and derivative properties may be computed in the full range of P and T . For linear polymers, where $s \gg 3$, the external degree of freedom $3c/s \cong 1$, and only knowledge of P^* , V^* , and T^* is required.⁶¹

5.2 Simha-Somcynsky eos for multicomponent systems

In the early 1980's Jain and Simha published an important extension of the S-S theory to homogeneous, binary mixtures.^{62, 63} Assuming that in multicomponent fluids there is only one type of vacancies and one cell size for all components the authors showed that Eq. 10 is applicable to multicomponent systems provided that the reducing and interaction parameters are expressed as composition-dependent averages indicated by the angular brackets $\langle \rangle$:

$$\begin{aligned} \langle P^* \rangle &= qz \langle \varepsilon^* \rangle / (\langle s \rangle \langle v^* \rangle); \quad \langle T^* \rangle = qz \langle \varepsilon^* \rangle / R \langle c \rangle; \quad \langle V^* \rangle = \langle v^* \rangle / \langle M_o \rangle \\ \langle P^* \rangle \langle V^* \rangle / R \langle T^* \rangle &= (\langle c \rangle / \langle s \rangle) (1 / \langle M_o \rangle) \\ \langle c \rangle &= \sum_i c_i x_i; \quad \langle s \rangle = \sum_i s_i x_i; \quad \langle M_o \rangle = \sum_i M_{si} s_i x_i / \sum_i s_i x_i \\ X_i &= zq_i x_i / \sum zq_i x_i; \quad zq_i = s_i(z-2) + 2; \quad z = 12 \end{aligned} \quad (12)$$

where the interacting site fractions, X_i , depend on the lattice interchain contact, zq_i , and the mole fraction x_i . The average interaction parameters $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$ are related to binary ones via:

$$\langle \varepsilon^* \rangle \langle v^* \rangle^m = \sum_{i,k} X_i X_k \varepsilon_{i,k}^* (v_{i,k}^*)^m; \quad m \in (2, 4) \quad (13)$$

where the two values of m reflect the assumed Lennard-Jones 6-12 potential. The S-S theory for multicomponent systems well describes the phase equilibria, CED, solubility as well as PVT behavior of polymer mixtures with gases (PS foam with physical foaming agents⁶⁰), liquids [PS blends with poly(2,6-dimethyl phenyl ether), PPE⁶⁴], or solids (composites^{65, 66, 67} and nanocomposites^{1, 52}).

Eq. 13 has six parameters, out of which up to four are accessible from the PVT measurements of neat components (e.g., polymer-1 and polymer-2), while the two cross-interaction parameters, ε_{12}^* and v_{12}^* , may be computed from the two relations in Eq. 13. The PNC behavior was analyzed for systems with PA-6^{35, 36}, PS⁶⁸ or polypropylene, PP⁶⁹, as the matrix. Details of the calculations are provided in the cited articles.

Figure 12. Relative free volume vs. T and P for PNC with 2 wt% clay [Simha et al., 2001].³⁵

Figure 13. Loss of free volume vs. clay content in PS-based PNC at $P = 0.1$ MPa and $T = 360$ and 560 (K).

Figure 14. Concentration dependence of the volume-average L-J interaction parameters for PS and its PNC

Figures 12 and 13 illustrate the effect of clay on the free volume parameter h in molten PNC with PA-6 and PS matrix, respectively. At constant clay loading of 2% reduction of the free volume parameter is related to the interlayer spacing, d_{001} :⁴⁶

$$\Delta h = 2.51 + 0.833d_{001} ; \quad r = 1.000 \quad (14)$$

Since the reactively-prepared PA-6 based PNCs are the closest to full exfoliation, here the addition of 2 wt% clay has the largest effect – it reduces h by about 15%. In Figure 13 for PS-based PNCs h vs. w dependence goes through a local minimum of about 6% at $w_2 = 3.6$ wt% clay – further addition of organoclay reduces the interlayer spacing and dilutes the intercalated stacks. It is noteworthy that the shape of dependencies presented in Figure 13 resembles the effects of clay on the derivative properties in Figures 7 and 10, indicating that α and κ dependencies are indeed related to the hole fraction in the S-S lattice-hole theory. However, fundamentally h is a result of interactions, thus it is interesting to see how the L-J interaction parameters vary with w .

The results of computations using Equations 10, 12 and 13 presented in Figure 14 again show the expected similarity of behavior with the maxima for $\langle \epsilon^* \rangle$ and $\langle v^* \rangle$ at $w_2 \approx 3.6$ wt%. Table 6 lists the reducing and L-J interaction parameters for a series of PNC with PA-6, PP and PS matrix. It is noteworthy that the effect of clay addition depends on its intercalant and the method of PNC manufacture.

Table 6. The characteristic reducing parameters for PNC with PA-6, PP and PS matrix.⁷⁰

Polymer	Clay (wt%)	$\langle P^* \rangle$ (MPa)	$\langle T^* \rangle$ (K)	$10^4 \times \langle \nu^* \rangle$ (mL/g)	M_s (g/mol)	$\langle \varepsilon^* \rangle$	$\langle \nu^* \rangle$	r^2
1	2	3	4	5	6	7	8	10
PA-6	0	1257.4 ± 8.2	11134 ± 32	8919.3 ± 9.6	27.51	31.23	24.54	0.999999
PA-6	0.8	1185.7 ± 11.1	11364 ± 49	8943.1 ± 14.3	29.70	31.49	26.56	0.999998
PA-6	1.6	1163.9 ± 12.6	11307 ± 54	8888.6 ± 16.2	30.29	31.71	26.92	0.999998
PA-6	0	1232.8 ± 6.0	11157 ± 22	8935.5 ± 6.9	28.07	30.92	25.08	0.999998
PA-6	1.6	1310.4 ± 6.9	10962 ± 22	8779.3 ± 7.4	26.41	30.98	23.18	0.999998
PA-6	4.0	1312.0 ± 8.6	10956 ± 28	8685.2 ± 9.2	26.64	30.36	23.14	0.999997
PA-6	0	1064.1 ± 10.8	12287 ± 61	9199 ± 15	34.78	34.05	32.00	0.999999
PA-6	2.29	1180.8 ± 12.2	11338 ± 52	8895 ± 15	29.82	31.42	26.52	0.999998
PA-6	4.91	1217.3 ± 14.3	11204 ± 57	8795 ± 17	29.00	31.05	25.51	0.999998
PP	0	572.7 ± 6.8	10449 ± 57	11728 ± 22	43.1	28.95	50.56	0.999998
PP	1.14	516.9 ± 10.3	10712 ± 98	11874 ± 37	48.4	29.68	57.43	0.999998
PP	1.59	545.7 ± 5.5	10775 ± 49	11712 ± 18	46.7	29.86	54.70	0.999998
PP	2.42	502.8 ± 9.3	10917 ± 92	11857 ± 34	50.7	30.25	60.17	0.999997
PS	0	743.5 ± 2.6	11723 ± 22	9525.9 ± 4.7	45.87	31.98	43.03	0.999999
PS	1.4	749.2 ± 5.2	11938 ± 46	9583.7 ± 9.6	46.08	33.07	44.02	0.999998
PS	2.8	747.5 ± 3.2	12010 ± 29	9567.8 ± 5.9	46.54	33.29	44.53	0.999999
PS	5.7	755.6 ± 5.6	11975 ± 48	9458.8 ± 9.8	46.43	33.29	44.26	0.999998
PS	10.6	747.1 ± 8.4	11834 ± 74	9259.6 ± 15.1	47.41	32.83	43.95	0.999994
PS	17.1	751.0 ± 8.9	11711 ± 73	9011.2 ± 14.6	47.77	32.48	43.29	0.999992

Before leaving discussion on the *PVT* behavior in molten phase it is worth mentioning that contrary to the earlier concept that equilibrium liquid exists at $T > T_g$, there are experimental evidences from several different test methods that indicate the presence of dynamic solid-like aggregates near-but-above T_g – only above the crossover temperature, T_c , the true liquid-like behavior was found. For example, Wool and his colleagues used the atomic force microscopy (AFM) in the tapping-mode for detecting the percolating twinkling fractal solid aggregates in PS below and above T_g .^{71, 72} Given that the tapping mode detects variation of substrate modulus, the results evidence the presence of the twinkling solid clusters in liquid matrix.

Analysis of the *PVT* surface by means of the S-S eos leads to the hole content, h , which should correlate with liquids viscosity following the dependence:^{73, 74, 75, 76}

$$\ln \eta_{\sigma_{ij}=const} = a_0 + a_1 Y_s; \quad Y_s \equiv 1 / (h + a_2) \quad (12)$$

The relation predicts that $\eta_{\sigma_{ij} = \text{const}}$, i.e., the zero-shear or constant stress quantity is a function of T and P only through $h = h(T, P)$. This indeed was observed for low molecular weight n -paraffins or silicon oils; good superposition was found at $T = 20 - 204^\circ\text{C}$ and $P = 0.1 - 500$ MPa, with constants: $a_1 = 0.79 \pm 0.01$ and $a_2 = 0.07$. The method was applied to eight molten polymers, whose PVT and $\eta = \eta(P, T)$ were measured.⁷⁷ By contrast with the previously found superposition for solvents and silicone oils, the polymer data plotted as $\log \eta$ vs. $1/h$ did not superposed on a “master curve”. The discrepancy could be eliminated by introducing an empirical characteristic reducing pressure, $P^*_R = \zeta P^*$, with ζ ranging from 1 to 2.1. The origin of the behavior difference between solvents and molten polymers is the presence of structures in the latter's at $T_g \leq T \leq T_c$. The TFT model supports this explanation as the liquid entrapped within the aggregate does not contribute to flow. The presence of structure at $T_g \leq T \leq T_{LL}$ has been postulated by Boyer and his colleagues; only above T_{LL} the melt behaved as regular liquid.^{30, 78, 79, 80}

The positron annihilation lifetime spectroscopy (PALS) has been also used for determining the free-volume holes. The method is based on the rate of annihilations of *ortho*-positronium by external electrons (*o*-PS) of a free volume cavity. The method has been applied to polymer and is well reviewed in Part III of ref. 52. In particular Dlubek has discussed correlation between the hole volume obtained from PALS and the hole volume fraction obtained from PVT .⁸¹ The chapter reviews a decade of intensive research in the field, to a large extent focused on the determination of hole density through the use of S-S eos. The specific volume obtained from the high pressure dilatometry is divided into the specific occupied volume, $V_{\text{occ}} = yV$ and the specific hole free volume, $V_f = hV$. Differentiation leads to α and κ coefficients for the occupied and free volume parts, what leads to setting $\alpha_{\text{occ}} = 0$ and $\kappa_{\text{occ}} = \text{constant}$. The interrelation between PVT volume, V , and PALS average hole volume, $\langle v_h \rangle$, is set up by calculating the effective number of holes from: $N_h = V_f / \langle v_h \rangle = (V - V_{\text{occ}}) / \langle v_h \rangle$. Thus, correlation of information from these two methods and their analysis using S-S eos leads to consistent description of material behavior. Furthermore, a connection between the hole-size distribution and relaxation phenomena was noted.⁸²

5.3 The vitreous region

Properties of the vitreous phase vary with the way they were produced by cooling or compressing the molten phase.⁸³ The analysis follows the procedure developed by Simha and his colleagues.^{34, 68, 84, 85, 86} Accordingly, from *PVT* data the hole fraction was calculated for the molten and vitreous phase (omitting the transitory region). For the glasses, $h_{\text{glass}} = h(T', P')$ was computed substituting $V = V(T', P')$ into Eq. 10 with known $\langle P^* \rangle$, $\langle T^* \rangle$ and $\langle V^* \rangle$ parameters from the $T > T_g$ data (*nota bene*, the variables with prime refer to the vitreous region). The hole fraction that the melt would have at the vitreous state at T' and P' , $h_{\text{extrapol}} = h(T', P')$, was computed the S-S eos. Next, the frozen fraction of free volume, FF , was computed from the relation:

$$FF = 1 - (\partial h / \partial T')_{P, \text{glass}} / (\partial h / \partial T')_{P, \text{extrapol}} \quad (13)$$

Evidently, since FF is a fraction its value should be $FF < 1$. Figure 15 displays the $FF = FF(w)$ dependence at several pressures calculated for PS + C10A.

Figure 15. Free volume frozen fraction, $FF = FF(w)$, for PS-1301 with 0 – 17 wt% of C10A at the selected (for clarity) five pressures, $P = 0.1 - 190$ MPa. See text.

Only in low clay content, $w < w_2 = 3.6$ wt%, $FF < 1$ is found; at higher clay concentration $FF > 1$. This behavior stems from rapid adsorption and solidification during cooling from the melt, which takes place at $T \leq T_g + 50^\circ\text{C}$ for samples with higher w . In other words, once the free PS melt is exhausted additional incorporation of organoclay brings along a large quantity of free

volume associated with the 2MBHTA intercalant. Additionally, while in neat polymer h always increases with increasing T , in the highly loaded PNC-17 glass it decreases at $T/T_g \approx 0.86 \pm 0.02$, thus above but near T_β .

5.4 Equation of state for semi-crystalline PNC

Thermodynamic theory for semi-crystalline polymeric systems originates from several sources: theory of polymeric glasses at $T \leq 80$ K by Simha *et al.*⁸⁷, Prigogine *et al.* cell-model for condensed systems⁸⁸, cell model for crystals Midha and Nanda⁸⁹, and Simha and Jain refinements.^{90, 91} Thus, the MNSJ theory has five parameters: P^* , T^* , V^* , c/s and the characteristic frequency at $T = 0$ K, ν_0 . The cell lattice does not have holes, thus the reducing parameters (P^* , T^* , V^*) are different than those computed using S-S eos cell-hole theory for equilibrium liquids. The theory for crystalline solids in reduced variables is:

$$\begin{aligned} \tilde{P}\tilde{V} = & \left(2/\tilde{V}^2\right)\left[\left(A/\tilde{V}^2\right) - B\right] + 3\gamma_G F_1(\tilde{\theta}, \tilde{T}) - (9s/4c)ab\tilde{V}^2\tilde{\theta}'^2 \left[\frac{1}{2} + \frac{2X}{(X-1)^2}\right] + \\ & (9s/8c)\gamma_G b\tilde{V}^2\tilde{\theta}'^2 \left[\frac{1}{2} + \frac{3X+1}{(X-1)^2} - (\tilde{\theta}/\tilde{T})\frac{X(3+X)}{(X-1)^3}\right] \end{aligned} \quad (14)$$

With the secondary functions given by:

$$\begin{aligned} \gamma_{G,0} = & -(\partial \ln \nu_0 / \partial \ln V)_T = 4/3 + A_1 / (A_1 - 2B_1 V^2) \\ \gamma_G = & \gamma_{G,0} \left\{ 1 - (s/2c)b\tilde{V}^2 \left[F_1(\tilde{\theta}_0, \tilde{T}) - (\tilde{\theta}_0^2/\tilde{T}) \frac{X_0}{(X_0-1)^2} \right] \right\} - (s/c)ab\tilde{V}^2 F_1(\tilde{\theta}_0, \tilde{T}) \\ \tilde{\theta}_0(\nu_0) = & h\nu_0 / kT^* = 4.794 \times 10^{-11} \nu_0 / T^* = 13.189 (c/s) V_0^{-4/3} \frac{(A_1/2V_0^2 - B_1)^{1/2}}{M_0^{5/6} \sqrt{T^*} \sqrt[3]{V^*}} \\ X(\tilde{\theta}, \tilde{T}) = & \exp\{\tilde{\theta}/\tilde{T}\}; \quad F_1(\tilde{\theta}, \tilde{T}) = \tilde{\theta} \left[\frac{1}{2} + \frac{1}{X-1} \right]; \\ Y = & (3s/8c)(\tilde{\theta}_0/\tilde{\theta}')^2 (\tilde{\theta}_0\tilde{V})^2 b/\tilde{T} \\ \tilde{\theta} = & \tilde{\theta}' \left[1 + (3s/8c)b\tilde{V}^2\tilde{\theta}' \right]; \quad \tilde{\theta}' = \tilde{\theta}_0 \left[1 + (4\tilde{T}/3\tilde{\theta}_0^2) F_1(\tilde{\theta}_0, \tilde{T}) Y \right] + 0(Y) \\ a = & 1 - \frac{A_2}{[A_2 - 2B_2\tilde{V}^2]} + \frac{2A_1}{[A_1 - 2B_1\tilde{V}^2]}; \quad b = \left[(A_2/\tilde{V}^2) - 2B_2 \right] / \left[(A_1/\tilde{V}^2) - 2B_1 \right]^2 \end{aligned} \quad (15)$$

In the above relations $A_1 = 22.1060$, $B_1 = 5.2797$, $A_2 = 200.653$ and $B_2 = 14.334$ are lattice constants

Equations 14 and 15 have been derived for the crystalline phase at $T_g \leq T \text{ (K)} \leq T_m$. Their applicability for describing the PVT dependencies has been examined for PE^{90, 91} and more recently for PA-6.^{49, 50, 51, 51} In the latter publications the additivity of the crystalline and non-crystalline domains was assumed. For rigorous calculations the crystalline content should be determined as $X = X(T, P, w)$. However, owing to the non-availability of high pressure calorimeter, only the ambient P tests could be conducted. These data were supplemented by the pressure effect on crystallinity, deduced from the difference, $\Delta V_{m,c}$, in specific volume, V , between the experimental PVT data and computed from the assumption of additivity of crystalline and molten phases. The results are displayed in Figure 16 with lines given by second-order polynomials. The sequence of the computation steps and the assumed models are detailed in the original publication.⁴⁹ Example of the final fit is presented in Figure 17.

Figure 16. Incremental volume of PA-6 with $w = 0 - 5 \text{ wt\%}$ clay at $P = 0.1 - 190 \text{ MPa}$. Error bars of the computer fit are marked.

Figure 17. Experimental (points) and computed (lines) specific volume of PA-6 with $5 \text{ wt\%}$ clay at $P = 0.1 - 190 \text{ MPa}$.

6 Thermodynamic interaction coefficients

All theories discussed in this chapter employ the L-J potential, initially written in the general form: $E_o = (\lambda/r^n) - (\mu/r^m)$ with the adjustable exponents: $m = 10 - 13$, $n = 6 - 7$.^{92, 93, 94}

$$E_o(r) = 4\varepsilon_{ij} \left[A \left(\frac{\sigma_{ij}}{r} \right)^m - B \left(\frac{\sigma_{ij}}{r} \right)^n \right]; \quad m = 12; \quad n = 6$$

or

$$E_o(V, y) = \left(\frac{yNqz\varepsilon^*}{2} \right) \left[A \left(\frac{\omega}{v^*} \right)^4 - 2B \left(\frac{\omega}{v^*} \right)^2 \right]; \quad \omega \equiv yV / (Ns) \quad (16)$$

where ω is cell volume. The present form of the “6-12 potential” originates from the quantum mechanics derivation of attractive forces between H-H atoms that lead to $n = 6$, while the exponent for the short-range repulsive interactions was taken as $m = 2n$.⁹⁴ The 6-12 potential was incorporated into the S-S cell-hole theory in the form given by the second relation in Eq. 16.

In the text above the inter-segmental L-J interaction parameters, ε^* and v^* are for single component systems, and averaged, $\langle \varepsilon^* \rangle$ and $\langle v^* \rangle$, for multi-component ones (see Eq. 12). For extracting the individual binary interactions from these averages one needs a model. Note that Simha-Jain assumption was for random-mixed two systems, $i = 1$ customarily assigned for the major phase and $i = 2$ for the dispersed one.

The situation is relatively simple for the single-phase polymeric systems such as solutions^{58, 59}, mixtures of molten polymer with a foaming agent⁶⁰ or miscible polymer blends⁶⁴. In case of immiscible binary polymer blends, where PVT of each component can be measured directly, only the heterogeneous ones, ε_{ij}^* and v_{ij}^* , must be determined from the blend behavior. It is noteworthy that such a treatment ignores the presence of the interphase which importance increases with the enhanced dispersion and is unacceptable for micron-sized dispersions.⁹⁵

PNCs are complex systems comprising matrix, nano-sized particles, intercalant, compatibilizer(s) and various industrial additives. Furthermore, the clay usually exists in a wide spectrum of dispersion ranging from fully exfoliated to micron-size aggregates. Clay also

adsorbs the organic phase creating a gradient of molecular mobility stretching up to 120 nm from the clay surface.¹ During the last 20 years PNCs with immiscible polymer blends became of interest.⁹⁶ Thus, it is a challenge to convert these systems into a model mixture of matrix and dispersed in it solid particles that will realistically simulate the physical behavior.

The organic-phase adsorption on the high energy solid surface has been observed using the surface force analyzer (SFA) and the neutron scattering method.^{97, 98, 99, 100} Similarly, molecular dynamics (MD) and Monte Carlo (MC) computations predicted formation of the solidified layer.^{101, 102, 103} Thus, in the z -direction perpendicular to clay surface there are two layers with reduced molecular dynamics: $z_1 \approx 2\text{--}9$ nm thick solid layer of organic molecules followed by $z_2 - z_1 = 100\text{--}120$ nm thick layer where molecular mobility progressively increases from z_1 to z_2 . Luengo *et al.* determined that on a freshly cleaved mica flake polybutadiene (PBD) forms 5–6 nm solid layer, followed by about 100 nm thick layer of increasing mobility. Thus, the bulk melt behavior of PBD (*e.g.*, steady-state or dynamic viscosity) was observed only at $z_2 \geq 110$ nm from the mica surface.³⁸

Accordingly, the basic model of PNC should specify the composition of the matrix and dispersed solid phase. Evidently, the solid particles are made off clay platelets or their stacks covered with $z_1 \approx 4\text{--}6$ nm thick, solidified organic layer (intercalant, compatibilizer and/or polymer). Their L-J interaction parameters are ε_{22}^* and v_{22}^* . Consequently, the remaining materials must be treated as a matrix, *i.e.*, the organic layer at $z > z_1$ having variable molecular mobility, with the L-J parameters ε_{11}^* and v_{11}^* . In consequence, the model implicitly assumes that the L-J parameters depend on the clay content. Obviously, the variability may be observed only at low clay content, below its second critical value ($w_2 = 3.6$ wt% in PS matrix; see part 4.4) at which the molten polymer with the bulk properties disappears. The expression used for describing variation of L-J parameters with distance from the clay surface, $\varepsilon_{ij}^*(z)$ or $v_{ij}^*(z)$, is:⁶⁹

$$y(z) = \frac{y_1 y_2}{y_1 - (y_1 - y_2) \exp\{n[(z - z_1)/(z - z_2)]\}}; \quad z_1 \leq z < z_2; \quad y \in [\varepsilon^*, v^*] \quad (17)$$

In this expression the steepness index $n \approx 2$ is adjustable, and y represents the L-J parameters at $z_1 \leq z \leq z_2$. At the low limit: $y(z) = y_1 \in [\varepsilon_{22}^*, v_{22}^*]$ and at high limit: $y(z) = y_2 \in [\varepsilon_{11}^*, v_{11}^*]$.

Because of differences in clay-polymer interactions, one should not assume that a single model will be applicable to all PNCs. For example, owing to polarity of PA-6 and strong interaction with negatively charged clay platelets, the PA-based PNC are relatively easily prepared with high degree of exfoliation following the synthetic or compounding method. However, since the intercalant location and molecular structure are different, the model for extracting the L-J parameter should account for the difference.¹⁰⁴ Flow analysis of these PNCs led to the “hairy clay particles” (HCP) model.¹⁰⁵ By contrast with these PNCs, the ones with polyolefin (PO) or PS matrix, which does not bond to clay surface, are also immiscible with most intercalants, thus they need compatibilizer.

In conclusion, before devising a realistic model for tested PNC, information about composition, thermodynamic interactions and resulting degree of dispersion is needed. **Error! Bookmark not defined.**⁷⁰ Considering the adopted definition of the solid and liquid phase the molar and site fractions (x_i , and X_i in Eq. 12, respectively) must be recalculated, e.g.:

$$x_1 = \frac{(m_1 / M_{s1}) - (m_{l,solid} / M_{s1})}{(m_1 / M_{s1}) + (m_2 / M_{s2})}; \quad x_2 = \frac{(m_2 / M_{s2}) + (m_{l,solid} / M_{s1})}{(m_1 / M_{s1}) + (m_2 / M_{s2})} \quad (18)$$

where m_i is the weight fraction of the polymer, $m_{l,solid}$ is the weight fraction of solidified matrix, m_2 is the weight fraction of clay, and $M_{si} = M/s_i$ is the molecular weight of a statistical segment of component “i”.

The interrelation between the L-J parameters and site fractions X_i is given by Eq. 13, which for ease of computation was transformed into:

$$\begin{aligned} \langle v^* \rangle^2 &= v_{11}^2 \Xi_4 / \Xi_2; \quad \text{and} \quad \langle \varepsilon^* \rangle^2 = \varepsilon_{11}^* \Xi_2^2 / \Xi_4 \\ \Xi_2 &\equiv X_1^2 + 2X_1X_2e_{12}v_{12}^2 + X_2^2e_{22}v_{22}^2 = (\langle v^* \rangle / v_{11}^*)^2 \cdot (\langle \varepsilon^* \rangle / \varepsilon_{11}^*) \\ \Xi_4 &\equiv X_1^2 + 2X_1X_2e_{12}v_{12}^4 + X_2^2e_{22}v_{22}^4 = (\langle v^* \rangle / v_{11}^*)^4 \cdot (\langle \varepsilon^* \rangle / \varepsilon_{11}^*) \\ e_{12} &\equiv \varepsilon_{12}^* / \varepsilon_{11}^*; \quad e_{22} \equiv \varepsilon_{22}^* / \varepsilon_{11}^*; \quad v_{12} \equiv v_{12}^* / v_{11}^*; \quad v_{22} \equiv v_{22}^* / v_{11}^* \end{aligned} \quad (19)$$

For PNCs out of the six parameters only two (ε_{11}^* and v_{11}^*) can be measured directly. The two cross-interaction parameters, ε_{12}^* and v_{12}^* , follow the Berthelot's rule and the algebraic average, respectively: ¹

$$\varepsilon_{12}^* = \sqrt{\varepsilon_{11}^* \varepsilon_{22}^*}; \quad \text{and} \quad v_{12}^* = \left[v_{11}^{*1/3} + v_{22}^{*1/3} \right]^3 / 8 \quad (20)$$

The remaining two parameters, ε_{22}^* and v_{22}^* , are then calculable from the two relations in Equations 13 or 19. Concentration dependence of ε_{22}^* for PS-based PNC is displayed in Figure 18. The solid line is a smooth curve fitting dependence with the expected maximum at the critical concentration, $w_2 = 3.6$ wt%. ⁶⁸ Figure 19 displays the concentration dependence of the computed binary interaction parameters in the full range of clay content, $w = 0 - 100$ wt% for PP-based PNC with MMT pre-intercalated with *di*-methyl *di*-hydrogenated tallow ammonium chloride. The computations lead to ε_{11}^* and v_{11}^* for all points, excepting the two last ones at $w = 100$ wt% clay corresponding to ε_{22}^* and v_{22}^* interactions. From these two sets of numbers the cross-interactions, ε_{12}^* and v_{12}^* , can be calculated according to Eq. 20.

Figure 18. Computed stack-stack interaction in intercalated PS-based PNCs

Figure 19. L-J interaction parameters in PP-based PNCs

Eq. 6 suggests that the L-J parameters may not be independent, viz.:

$$v^* P^* = \varepsilon^* (zq/s); \quad \text{where} \quad zq/s = z - 2 + 2/s \rightarrow 10 \quad (21)$$

Since for a given polymer P^* vary by about $\pm 5\%$ one may expect that parameters are interrelated $\varepsilon^* \propto v^* P^*$.⁶¹ Indeed, Figure 20 ε^* vs. v^* for PS and its PNCs. The data seem to follow a linear dependence, but as for each set the range of values is limited the observation may not be always valid, although similar linear dependencies have been obtained for other polymers, blends and composites.

Figure 20. L-J interaction parameters for PS and PS-based PNCs

The binary interaction parameters for the matrix (ε_{11}^* , v_{11}^*) and for the solid phase (ε_{22}^* , v_{22}^*) are listed in Table 7. The cross-interaction parameters, ε_{12}^* and v_{12}^* , can be calculated using Eq. 20. On a first sight it may seem odd that the difference between the interaction parameters of the matrix and solid part is small. However, for solids there is no clay-clay interaction, but rather between the polymeric solid layers that enrobe the high energy solid platelets.

Table 7. The binary interaction parameters for PNC with PA-6, PP and PS matrix.

Polymer	Matrix		Solid		Refs.
	ε_{11}^*	v_{11}^*	ε_{22}^*	v_{22}^*	
PA-6	34.1 ± 0.3	32.0 ± 0.1	31.2 ± 0.3	25.9 ± 0.3	36, 49
PP	28.9 ± 0.1	50.6 ± 0.4	30.7 ± 0.4	59.9 ± 0.3	69
PS	32.0 ± 0.6	43.0 ± 1.7	33.0 ± 0.1	44.2 ± 0.1	68

7 Theoretical predictions

Theories are constructed following assumptions that on the one hand should represent the phenomenon and on the other still permit derivation of analytical expressions and their use for comparison with experiment. The notorious assumptions for theories of polymer systems is omission of polydispersity, the presence of “customary” industrial additives and the non-random distribution of properties, *e.g.*, introduced by mixing or temperature gradients. Furthermore, the thermodynamics theories assume thermodynamic equilibrium within a phase located between two transitions while in practice the transitions are complex, introducing serious physical changes even to such first order transition as T_m .

It is interesting to check how well the accepted theories represent the PVT data, in particular their derivatives, α and κ . Figure 20 show variability of their properties within a wide range of independent variables. The variables are expressed in reduced form – one need to multiply these by the reducing parameters (*e.g.*, see Table 6) to convert these to SI variables such as $^{\circ}\text{C}$, MPa, 1/K and 1/MPa. Thus, the variables for PS range: $T = 20 - 313^{\circ}\text{C}$, $P = 11 - 189 \text{ MPa}$, $10^4\alpha = 3.52 - 8.44 \text{ (1/K)}$ and $\kappa = 0.07 - 0.60 \text{ (1/kPa)}$. Similarly, for PA-6 these ranges are: $T = 5 - 284^{\circ}\text{C}$, $P = 25 - 314 \text{ MPa}$, $10^4\alpha = 3.35 - 8.02 \text{ (1/K)}$ and $\kappa = 0.13 - 1.01 \text{ (1/kPa)}$. In short, they do represent the customary ranges of variables.

Comparing the theory with experiment one may look for similarities in pairs of Figures

- #1. The pair 20A & 3A (PS) shows similar effects of P on both sides of T_g , but while the experimental data are nearly constant on both sides of the transition, the theory predicts a slight increase seen in Figure 5 for another PS.
- #2. The pair 20B & 11 (PA-6) show that on both sides of T_m α increases with T , but while theory increases across the transition, the experimental data are horizontally displaced.
- #3. For neat PS the pair 20C & 8 show a similar behavior – better agreement for κ than for α .
- #4. An excellent agreement between theory and experiment is observed comparing 20D & 12 (PA-6) – κ vs. T follow the same dependence across the first order melting point transition.

Figure 20. Theoretical predictions of the thermal expansion and compressibility coefficients in reduced variables for amorphous glass/melt (left column) and semi-crystalline/molten polymeric systems computed from S-S eos and from combination of S-S and MNSJ eos'.^{50, 51}

The comparison of the four theoretical plots of α and κ for PS and PA-6 with the dependencies extracted from the *PVT* data is acceptable. For the amorphous polymer (PS) the experimental plots well compare with predictions of the S-S eos. Considering the difficulties with numerical differentiation of the *PVT* data the agreement is considered good. The theoretical dependencies for PA-6 were computed assuming the presence of PA-6 crystals dispersed in molten polymer, thus using MNSJ and S-S theories, respectively. The agreement with experiments is excellent.

8 Summary and conclusions

This discusses the use of high pressure dilatometry for characterization of the clay-containing polymer nanocomposites. The central six parts of the chapter deal with:

1. Characterization of clays
2. *PVT* measurements
3. Derivative properties
4. Thermodynamic theories
5. Interaction parameters
6. Theoretical predictions

Over the last 80 years or so there has been an evolution in the approach to experimental polymer physics, reflected in the ossified statement “used without further purification”. Indeed, the early research on polymers inherited from physics and physical chemistry the need to work with well characterized substances, fractionated polymers, rectified or re-crystallized additives, well characterized ingredients, etc. At the same time, the industrial materials are getting progressively complex, loaded with diverse additives designed to stabilize the polymer during forming, facilitate production by incorporation of internal lubricants, extend the lifetime of the finished part or modified the performance by blending in small (≤ 5 wt%) of another polymer. As a result, results of measurements of supposedly the same polymer originating from different manufacture may show significant differences. PNC characterization is even more complex, especially of these containing natural minerals.

8.1 Characterization of clays.

Natural clays significantly differ depending on the geographical location and local strata in: platelet shape, size and size distribution, chemical composition and impurities. For example:

1. The average clay platelet dimensions in three orthogonal directions are: thickness $t \approx 1$ nm, width $W \approx 20 - 4000$ nm, length $L \approx 30 - 6000$ nm, and the nearly universal ratio $L/W \approx 1.5 \pm 0.1$. The distribution of clay platelet size is approximately Gaussian.
2. The chemical composition of varies greatly due to: (a) non-uniform atomic substitution in the crystalline cells, (b) tendency of natural clays to vary composition with particle size, (c) presence of mineral impurities. The chemical heterogeneity may cause batch-to-batch

variability of the mechano-chemical sensitivity during compounding, degradability, weatherability, sensitivity or lack of it toward antioxidants and stabilizers, etc.

3. The natural clays contain 2 – 5 wt% of impurities, such as < 300 μm diameter quartz, cristobalite, rutile, and other particles, may seriously affect the reproducibility of PNC performance. Since they do not bond to the matrix, they may initiate premature specimen fracture, reduction of the barrier property of PNC films, etc.

In short, characterization of PNC should start with examination of the three aspects of the reinforcing clay.

8.2 *PVT* measurements

Four test procedures may be used for the determination of the *PVT* surface: isothermal or isobaric increasing or decreasing the second independent variable. Under thermodynamic equilibrium conditions, all four procedures should and mostly do lead to the same results. However, the test results show significant influence of the test procedure in the vitreous phase, as well as near the transition temperature, T_g or T_m . The most regular $V = V(P, T)$ behavior is obtained in the isobaric heating, but for thermally sensitive material the “standard” isothermal heating procedure is recommended. Evidently, the test strategy should depend on the reason for testing, dictated by a part application. It is recommended that the transient behavior of polymer at and below the transition temperatures will be disregarded.

Since PNCs are multicomponent systems, their behavior depends on the concentration and the nature of the additives, *e.g.*, clay, intercalant, compatibilizer. In particular, since the intercalant has low molecular weight and large free volume its effect on *PVT* and its derivatives may be disproportionately large.

8.3 Derivative properties

The thermal expansion and compressibility coefficients, α and κ are important derivatives of the function: $\ln V = \ln V(P, T)$. They are of interest for the processing and application of PNCs as well as for detecting finer variations of the material structure reflected in specific volume. The numerical differentiation of raw data is recommended, preceded by an interpolation step assuring

constant values of V for selected level of P and T . Care must be taken that the fine structure of experimental data is not affected.

There is significant difference in α and κ behavior for the amorphous and semi-crystalline polymers. The former ones show large transient effect for both coefficients below T_g , which depend on the test procedure. For the latter systems there is also a transient effect in α , originating in variability of the crystalline content and structure near T_m . However, the temperature variation of κ is smooth right across T_m .

8.4 Thermodynamic theories

Simha-Somcynsky (S-S) cell-hole theory was developed for equilibrium single-component liquids, the extended to multicomponent systems (alloys, blends, foams, micro and nanocomposites) in the molten and vitreous state. Since the theory explicitly includes free volume parameter, its application was extended to rheology, PALS, physical aging, diffusion, surface/interface tension and other phenomena.

Midha and Nanda cell theory (no free volume!) was developed for crystalline polymers and subsequently modified by Simha and Jain by incorporating elements of the earlier theory for polymers at $T < 80$ K, in which the inter-segmental interactions followed the Einstein's equation for harmonic oscillators. The modified theory was used to describe the PVT behavior of the crystalline part of PNC based on semi-crystalline PA-6. However, since crystallinity amounts to ca. 40%, the molten fraction was described by the S-S theory. The combined theories well followed the observed PVT behavior.

8.5 Interaction parameters

For a single or bi-component system the interaction parameters can be directly calculated from the derived equations. However, for PNCs one must define what part of composition belongs to the solid phase and which one to the matrix. Furthermore, owing to adsorption of the organic phase on high energy clay surface the progressive variability of molecular mobility with distance from the surface must be taken into account.

Depending on the system, *i.e.*, polymeric matrix and dispersed solids, the interaction parameters and their relative magnitude changes. Thus for example, exfoliated clay in polar polymer (PA-6) matrix shows a significant difference between matrix and solid parameters. By contrast, the

interactions between clay stacks in PS matrix for these two components are similar. In PP systems the energetic interaction are small, but the volumetric expulsion contribution is large, as it could be expected from the low polymer density.

8.6 Theoretical predictions

The last part compares the measured and theoretically predicted α and κ coefficients for the amorphous polymer and its PNC and for the semi-crystalline system. Good agreement between these two sets of data was found.

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