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Interphase between nanoparticles and molten polymeric matrix: pressure–volume–temperature measurements

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Abstract—The pressure–volume–temperature (*PVT*) dependence of commercial polymers (*viz.* poly- ϵ -caprolactam, PA-6, polystyrene, PS, polypropylene, PP, and epoxy), and of nanocomposites based on these resins, was studied in the molten state. Incorporation of 2-wt% organoclay decreases the specific volume by about 1.0%. The Simha–Somcynsky (S–S) lattice-hole theory provided excellent description of the *PVT* behavior. Congruence between the theory and experiment yielded an explicit measure of the free volume. It has been found that in polymeric nanocomposites (PNC) the reduction of the free volume, Δh , correlated with the degree of clay dispersion (e.g. expressed as the interlayer spacing, d_{001}), or more precisely with total clay surface area accessible to macromolecules. The free volume reduction originates in adsorption and solidification of macromolecules on the high-energy clay surface – the phenomenon observed in the Surface Force Analyzer. The solidification offers consistent explanation for several reported puzzling behaviors of PNC.

Keywords: *PVT*; free volume; equation-of-state; interphase in PNC; nanocomposites; molecular mobility; solidification; interlayer spacing.

1. INTRODUCTION

The structural polymer nanocomposites (PNC) usually contain 2 to 5 wt% organoclay, or 0.6 to 1.5 vol% of clay. Since the aspect ratio of clay platelets ranges from about 100 to 5,000 the encompassed volume of freely rotating platelets starts overlapping at about 1 wt% – above this limit the clay platelets must form domains with locally ordered stacks. In other words, to profit from the effects of fully exfoliated layered silicates, the clay concentration near this low encompassed volume limit is most often used [1].

One of the earliest commercial clay-containing PNC is Ube PA1015C2; a polyamide-6 (PA-6) based clay-containing PNC, prepared by reactive exfolia-

tion. The method of preparation and performance are well described in the patent and open literature [2–4]. Thus, the PNC has been prepared by intercalation of MMT with ω -amino-dodecanoic acid and ε -caprolactam, and then compounding the adduct in a twin-screw extruder (TSE) with *ca.* 70-wt% of PA-6. In comparison to the matrix polymer, the resulting PNC shows 40% increase of the tensile modulus, 14% of strength, 65°C of heat deflection temperature, 200% reduction of oxygen permeability, etc. It is difficult to comprehend how incorporation of 0.64 vol% of clay into the PA-6 may cause these substantial changes of properties.

The explanation of this puzzling behavior must be related to the structure of PNC, to the degree of clay dispersion, its effect on the matrix, and most of all to the size and properties of the interphase.

It is desirable to maximize the degree of clay dispersion in polymeric matrix, i.e. to exfoliate it, or in other words to reach the ultimate interlayer spacing: $d_{001} > 8.8$ nm. Under these circumstances, the nano-filler particles have the largest aspect ratio, and the largest surface area may interact with matrix. Addition of crystalline solids to polymeric matrix may enhance its crystallinity, it may form physically or chemically crosslinked structures, etc.

However, it is noteworthy that crystalline solids have high surface energy; about 100 times higher than of organic liquids (e.g. the surface energy of freshly cleaved mica is $\gamma = 4,500$ mN/m) [5, 6]. Incorporation of such particles into organic matrix affects its molecular mobility. For example, sorption of polymers onto a solid surface has been studied using neutron scattering [7, 8], or a Surface Force Analyzer (SFA) [9–11]. The studies indicated that polymer solidifies on the crystalline surface from solutions or from the melt. The thickness of the adsorbed, solidified layer varied within a narrow range of 6 ± 3 nm, being similar for solvents or polymeric molecules. Furthermore, between the solidified layer and the matrix bulk behavior there is a second layer in which the molecular mobility exponentially increases with distance from the clay surface for a distance of $z \leq 120$ nm. The measurements have been well reproduced in different laboratories. In addition, the ‘solidification’ on the clay surface was predicted by molecular dynamics [12].

To examine the PNC melt structure, the pressure-volume-temperature (PVT) behavior was used. These properties of polymeric systems have been measured mainly to determine compressibility and the thermal expansion coefficients. However, by means of an adequate theory, the PVT relation provides insight into intermolecular interactions, and the free volume content. Several equations of state (eos) for liquids have been proposed [13–19]. Curro [20], Zoller *et al.* [21], Rodgers [22], and others evaluated their suitability. Of all the theoretical expressions the one derived by the Simha and Somcynsky (S–S) lattice-hole theory is considered the most apposite – it not only provides excellent fit to the PVT data, but in addition it describes the free volume variations with independent variables, and determines the binary Lennard-Jones internal interaction parameters. During the last few years the Simha–Somcynsky (S–S) eos has been used to describe the PVT behavior of sev-

eral PNCs, namely, that with PA-6 as the matrix [23], with polypropylene (PP) [24], with polystyrene (PS) [25], and with epoxy [26].

The present paper focuses on the different *PVT* behavior observed of these systems. The aim is to propose a common interpretation for the diversity and thus, based on the clay-polymer interphase, to show how the variation of the degree of clay dispersion affects the free volume and the macroscopic performance.

2. EXPERIMENTAL

2.1. Materials

The composition of the tested PNCs is given in Table 1. Full details are given in the original papers (see the cited References).

2.2. Equipment

The *PVT* surfaces were measured in a pressure dilatometer from Gnomix Inc. (Boulder Co, USA), within the molten state, at $T = 300$ to 590 K and $P = 0.1$ to 200 MPa. Prior to testing, the materials were dried. Since the instrument measures only the incremental changes of the specific volume as a function of P and T , first an absolute value of V under ambient conditions was measured with accuracy of $\Delta V \leq \pm 0.001$ ml/g in a glove compartment under positive pressure of dry N_2 .

The degree of clay dispersion was determined by X-ray diffraction (XRD; using a Brüker D8 Discover) and high-resolution transmission electron microscopy (HRTEM; Hitachi H9000). Information from these two sources was complementary, and consistent.

Table 1.

The CPNC studied

Polymer	Organoclay		Ref.
	Type	Content (wt%)	
PA-6	MMT-ADA	0 & 2	[23]
PP	C15A	0, 2, 4	[24]
PP + $X\%$ of grafted PP	C15A	$X = 0, 2, 4$	[24]
PS-1301 (Nova Chem.)	C10A	0–11	[25]
Epoxy (Vantico)	TiO ₂ (23 & 1,500 nm)	10	[26]

Organoclay type in column 2: ADA – amino dodecanoic acid; C15A and C10A are commercial Cloisite 15A, and Cloisite 10A from SCP, containing Wyoming montmorillonite pre-intercalated with dimethyl dihydrogenated tallow ammonium cation and dimethyl benzyl hydrogenated tallow ammonium cation, respectively.

3. THEORY

3.1. Simha–Somcynsky theory

The Simha–Somcynsky lattice-hole theory [16] models an amorphous, condensed system as a random mixture of sites occupied by chain segments (or small molecules) and empty sites (a measure of disorder). The configurational entropy of mixing is expressed in the manner of Huggins and Flory. The inter-segmental interactions are described by a Lennard-Jones-Devonshire 6-12 potential with a maximum attraction energy, ε^* , and repulsion volume, v^* . Following Prigogine and colleagues [13, 14], a number $3c$ of external, volume-dependent degrees of freedom is assigned to each species.

The variables of state, and derived quantities, such as the *PVT* surface, or the cohesive energy density (*CED*), are scaled. For large s , the principle of corresponding states is obtained. For the macromolecular species, $3c/s \Rightarrow 1$ is usually assumed. The three characteristic scaling parameters of pressure, temperature, and volume are expressed respectively as:

$$\left. \begin{aligned} P^* &= zq\varepsilon^*/(sv^*) \\ T^* &= zq\varepsilon^*/(Rc) \\ V^* &= v^*/M_s \end{aligned} \right\} (P^*V^*/T^*)M_s = Rc/s \Rightarrow R/3, \quad (1)$$

with M_s the molar segmental mass, $zq = s(z - 2) + 2$ the number of interchain contacts in a lattice of coordination number $z = 12$, and R the gas constant. From equation (1) the interaction parameters are calculated. In this manner a scaled configurational free energy in reduced variables (indicated by tilde) is derived:

$$\tilde{F} \equiv F/F^* = \tilde{F}[\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T})], \quad (2)$$

where h is the free volume parameter. From equation (2) the eos is derived by minimization of $\tilde{F}$, and the customary definition of pressure. In consequence, the S–S eos is expressed in form of coupled equations:

$$\begin{aligned} &3c[(\eta - 1/3)/(1 - \eta) - yQ^2(3.033Q^2 - 2.409)/6\tilde{T}] \\ &+ (1 - s) - s \ln[(1 - y)/y] = 0, \\ &\tilde{P}\tilde{V}/\tilde{T} = (1 - \eta)^{-1} + 2yQ^2(1.011Q^2 - 1.2045)/\tilde{T} \end{aligned} \quad (3)$$

with $y = 1 - h$; $Q = 1/(y\tilde{V})$; $\eta = 2^{-1/6}yQ^{1/3}$. The coupled equation (3) has been found successful in describing the *PVT* behavior of over 50 polymer and copolymer melts [20–22], as well as blends [27] and composites [28, 29]. Under random mixing conditions, the mean-average interaction parameters are interrelated [30]:

$$\langle \varepsilon^* \rangle \langle v^* \rangle^p = X_1^2 \varepsilon_{11}^* v_{11}^{*p} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*p} + X_2^2 \varepsilon_{22}^* v_{22}^{*p}, \quad p = 2, 4, \quad (4)$$

where the site fractions, X_1 and $X_2 = 1 - X_1$, are defined in terms of the mole fractions x_i . However, since equation (4) implies that the binary interaction parameters, $\varepsilon_{ij}^*, v_{ij}^*$ ($i, j = 1, 2$), are independent of composition, whereas in CPNC

the degree of dispersion depends on it, a model is required for extracting realistic values of the interaction parameters.

3.2. Model of molten CPNC

The ‘hairy clay platelet’ (HCP) model [31] assumes that flat MMT plates are covered with a uniform layer of solidified polymer to specified thickness – solidification means low segmental mobility and low free volume. Above the solidified layer, the polymer forms a layer with variable segmental mobility. Thus, macromolecules progressively (with the increasing distance from the clay surface) gain mobility up to the neat matrix values. As a consequence, the characteristic interaction parameters of the matrix vary with the interparticle distance, hence with clay content. The HCP model was quite successful not only for the interpretation of the *PVT* behavior, but also that of strongly non-linear viscoelastic PNC flows [31]. Accordingly, the limiting distances from the clay platelet of the solidified organic phase, $z_0 = 6$ nm, and that of the variable matrix properties $z_\infty = 100$ nm are adopted.

The *PVT* measurements of neat matrix provide ε_{11}^* and v_{11}^* of the matrix at a distance: $z > z_\infty = 100$ nm. The cross-interaction parameters, ε_{12}^* and v_{12}^* , may be approximated by the geometric (Berthelot’s rule) and algebraic averages, respectively. However, the assumption of a solidified layer on the surface of MMT platelet embedded in a polymeric matrix still requires a functional description of the property changes within the distance ranging from z_0 to z_∞ [24]:

$$y(z) = \frac{y_0 y_\infty}{y_0 - (y_0 - y_\infty) \exp\{2[(z - z_0)/(z - z_\infty)]\}}, \quad z_0 \leq z < z_\infty, \quad (5)$$

where y_0 is the matrix interaction parameter at the solidified polymer layer (at $z_0 = 6$ nm): $\varepsilon_{22}^*(z)$ or $v_{22}^*(z)$. For large values of z the function $y(z)$ approaches a constant value of y_∞ , characteristic of the neat matrix, $\varepsilon_{11}^*(z)$ or $v_{11}^*(z)$. Thus, at the lower limit: $y(z) = y_0$ characterizes the polymer-covered clay, ε_{22}^* , v_{22}^* , while for the upper, the neat matrix are obtained: ε_{11}^* , v_{11}^* .

4. RESULTS

The characteristic reducing parameters (P^* , T^* and V^*) were computed by fitting the experimental *PVT* data to the S–S eos. The fitting was carried out using MicroMath Scientist commercial software for the non-linear squares fit. The computer program extracted the model parameters, along with the fitting statistics. An example of data fit is presented in Fig. 1. The statistical evaluation of the fit for neat polymer or PNC invariably indicated that S–S eos provides excellent description of *PVT*. Abbreviated evidence is presented in Table 2; for details see the original papers [23–26].

Figure 1. Specific volume for PA-6 and its PNC vs. temperature at 20 pressure levels, from ambient (top) to 190 MPa. Points are experimental while the values computed from S–S eos are indicated by squares. There is good reproducibility between non-consecutive runs.

Table 2.
Composition and properties of PP-based PNC samples

Sample	Clay (%)	P^* (bar)	$10^4 V^*$ (ml/g)	T^* (K)	r^2	σ
PA-6	0	12574	8919	11134	0.999999	0.0011
PA-6	2	11639	8889	11307	0.999998	0.0013
PP	0	5727	11728	10449	0.999998	0.0016
PP-2	2	5169	11874	10712	0.999998	0.0019
PP-4	4	5028	11857	10917	0.999997	0.0023
PS	0	7435	9526	11723	0.999999	0.0011
PS-2	2.8	7475	9568	12010	0.999999	0.0009
PS-6	5.7	7556	9459	11975	0.999998	0.0015
Epoxy	0	9741	8585	12407	0.999999	0.0010
Epoxy	10	9835	8180	12291	0.999998	0.0010

Column 2 lists organoclay content in wt%; columns 3 to 5 the *PVT* characteristic parameters, and the last two columns the correlation coefficient squared (r^2) and the standard deviation (σ) of the *PVT* data fit to S–S eos.

5. DISCUSSION

The two sets of information obtained from the eos analysis of *PVT* behavior are: (1) the binary interaction parameters expressed as the maximum attraction energy and the repulsion volume, ϵ_{ij}^* , v_{ij}^* ($i, j = 1, 2$), and (2) the free volume parameter, h . However, the importance of the first set of information extends beyond the determination of the numerical values – consistency of the data provides means of model validation, thus it reflects on the type of structure existing within the PNC.

5.1. Interactions

The HCP model assumes that in PNC there is a pseudo-three phase structure:

- (1) The solid particles composed of mineral solid and adsorbed on it $z_0 = 6$ nm thick layer of polymer;
- (2) The intermediate layer stretching from $z = 6$ to 100 nm above the mineral surface, where the polymer chain mobility increases with distance z ; and
- (3) The homogeneous polymer phase, away from the clay platelets by $z_\infty > 100$ nm, where the chain mobility is the same as in neat, molten polymer.

Thus, in the HCP model, the interphase between the clay platelet and polymeric matrix is composed of adsorbed layers with reduced molecular mobility, stretching for about 100 nm.

As an example of the consistency of the model, Fig. 2 displays changes in the interaction parameters as a function of clay content for PP-based PNCs. In accord with the adsorption concept, it is the solidified polymer that interacts with the molten matrix, and the high energy of solid mineral is only responsible for forming the solidified layer, but not for the direct interaction between the dispersed phase and the matrix. As a consequence the binary interaction parameters (clay–clay, clay–polymer and polymer–polymer) are similar in magnitude.

Evidently, an assumption of different limiting values, z_0 and z_∞ , will affect the numerical values of the interaction parameters, but the overall properties of the PNC and structure of the interphase will be qualitatively the same.

Figure 2. Variation of the matrix interaction parameters as functions of the PP site fraction, X_1 , for CPNC of PP with C15A [24].

5.2. Free volume parameter, h

The S–S eos also provides the hole fraction $h = h(V, T)$. At constant organoclay loading of 2 wt%, the loss of free volume, Δh , well correlates with the interlayer spacing determined by XRD (see Fig. 3). Thus, as the interlayer spacing expands, more macromolecules are adsorbed onto the clay surface, and their segmental mobility; hence the free volume content is reduced. Evidently, the maximum loss of free volume is expected when the interlayer spacing exceeds the thickness of two solidified layers and thickness of the inorganic layer (t):

$$d_{001}^{\max} \geq 2z_o + t. \quad (6)$$

For the values of $d_{001} < d_{001}^{\max}$, less polymer can be adsorbed, which results in a smaller decrease of the free volume. However, it is important to note that under these circumstances the stack of intercalated clay platelets is covered with a 6 nm layer of solidified polymer, hindering the mechanical exfoliation.

At low clay loadings the Δh values are proportional to the clay content. For example, in PP-based PNCs, the loss of free volume at 4 wt% loading of organoclay was twice as large as that at 2 wt% [24]. However, as the organoclay concentration exceeds a critical value for given system, the interlayer spacing starts to decrease and Δh tends toward zero. This is illustrated in Fig. 4 – similar dependencies were observed for others PNCs.

Figure 3. Correlation between Δh and d_{001} for three types of CPNC at the corresponding organoclay loading of 2 wt% [24].

Figure 4. Loss of free volume vs. organoclay concentration at $T = 360$ K and $P = 10$ bar, for PS1301 with Cloisite® 10A [25].

However, it is important to recognize that for some systems incorporation of inorganic filler may lead to increased free volume. This is illustrated in Fig. 5 for dispersion of 10 wt% TiO_2 in epoxy; for micro-dispersed filler the expected decrease of free volume was observed, but for the nano-dispersed one, the free volume parameter increased. For coated particles repulsive interactions could provide an explanation, but the authors prepared the nano-powder without any coating. Thus, the most likely explanation is the presence of aggregates with occluded air pockets [26].

5.3. Consequences

The HCP model offers a simple explanation for several difficult to understand PNC properties. For example, incorporation of *ca.* 0.4 vol% of clay results in an increase of matrix modulus by about 20% [1]. However, while the clay platelet thickness is nearly $t = 1$ nm, the solidified polymer increases it to $t + 2z_0 \cong 13$ nm, greatly increasing the solid filler content and its effect. In addition, the second layer of variable mobility enhances the effect.

The relative tensile strength of PA-based PNC is significantly higher than the value calculated from the most optimistic relations using the volume fraction of inorganic component, but virtually identical to the value calculated assuming matrix solidification on clay [32]. In short, to predict the tensile strength, one order of magnitude larger filler volume fraction had to be assumed.

Figure 5. Relative free volume parameter, $h = h(P, T)$ for nano- and micro-sized TiO_2 dispersed in epoxy matrix [26].

Another example of performances that are readily understood on the basis of the HCP model is the barrier property of PNC containing a large amount of clay. For example, permeability of dichloromethane through PCL-based PNC was studied for clay content of up to 18 vol% [33]. The dependence predicted by the theory was obeyed only up to about 5 vol%; at higher clay concentration the permeability reduction was significantly higher than predicted. Evidently, as the clay concentration increases, the solidified polymer domains start to be interconnected, providing additional obstacles to the molecular diffusion [1].

6. CONCLUSIONS

The Simha–Somcynsky eos provides a good description of the *PVT* behavior for molten polymers and their nanocomposites. The free volume parameter computed from fitting the theory to experimental data indicates that incorporation of clay reduces the free volume of the matrix – the reduction is related to the total clay surface available for interacting with the matrix polymer. Thus, at low clay concentration the decrease of free volume, Δh , is proportional to concentration. At constant concentration within this region, Δh is proportional to the interlayer spacing, d_{001} . As the concentration increases, the interlayer spacing decreases and so does Δh .

The eos analysis of the *PVT* behavior of PNC validates the HCP model, with adsorbed, solidified layer of polymer on the clay surface, followed by another layer of polymer with segmental mobility that gradually increases with distance from the clay surface. In consequence, the binary interactions between the two components of the PNC, the matrix and the clay platelets covered by solidified polymer, are similar; hence the interaction parameters are of similar magnitude.

The HCP model predicts that, at sufficiently low clay content, the two-layer entities might be freely dispersed in the polymeric matrix. However, at higher clay content, e.g. $\phi_{\text{clay}} > 0.005$, the low mobility domains interact – the polymeric matrix with its characteristic behavior disappears. Furthermore, at still higher clay concentration, e.g. $\phi_{\text{clay}} > 0.08$, the solidified polymer domains start interacting; this seriously affects the transport properties.

Evidently, the above description is valid for miscible PNC, in which there are strong thermodynamic interactions between matrix and organoclay – the so-called exfoliating systems. For the more common, intercalated systems the above discussion is still valid, provided that instead of individual clay platelets the clay stacks are considered. The corollary to this is that stacks are covered with solidified matrix polymer, which makes their dispersion by mechanical means difficult. The only way to solve this conundrum is to ensure good thermodynamic interactions between matrix and organoclay. Furthermore, it should be noted that, at the 2 wt% organoclay loading, the loss of free volume by about 15% is equivalent to reduction of temperature by about 50°C. This suggests that compounding should be carried out at as high a temperature as possible for the given polymer/organoclay system. For example, compounding PP with PP-MA and organoclay at 180°C and 200°C showed that better dispersion and mechanical performance was obtained at the higher temperature [25]. However, since the thermal degradation of intercalants starts at about 180°C there is a low limit on the processing temperature.

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

eos	equation of state
FTIR	Fourier transform infrared spectroscopy
MW	molecular weight
NMR	nuclear magnetic resonance
PALS	positron annihilation lifetime spectroscopy
PNC	polymeric nanocomposites
<i>PVT</i>	pressure–volume–temperature dependence
SCP	Southern Clay Products, Inc.
SEM	scanning electron microscopy
SFA	Surface force analyzer
S–S	Simha–Somcynsky cell-hole theory or eos

Materials

ADA	amino dodecanoic acid
C10A	Cloisite® 10A (MMT-dimethyl benzyl hydrogenated tallow ammonium chloride)
C15A	Cloisite® 15A (MMT-dimethyl dihydrogenated tallow ammonium chloride)
MMT	montmorillonite
PA-6	polyamide-6 (poly- ϵ -caprolactam)
PP	polypropylene
PP-MA	maleated polypropylene
PS	polystyrene

Symbols

$\tilde{F}$	Helmholtz free energy in reduced variables
$3c$	the external, volume-dependent degrees of freedom per macromolecule
$3c/s$	the flexibility parameter
CED	cohesive energy density
d_{001}	interlayer spacing
h	free volume parameter in S-S eos; $h = h(V, T)$
$M_s = M_n/s$	molecular weight of statistical segment
M_n, M_w	number- and weight-average molecular weight
P, P^*	pressure and the characteristic pressure reducing parameter
R	the gas constant
r^2	correlation coefficient squared
s	number of statistical segments per macromolecule
T, T^*	temperature and the characteristic temperature reducing parameter
v^*	L-J segmental repulsion volume per statistical segment
V, V^*	specific volume and the characteristic volume reducing parameter
x_i	mole fractions
X_i	site fractions
y	occupied volume fraction in S-S eos; $h = 1 - y$
$z = 12$	coordination number
z_0, z_∞	limiting distances from the clay platelet for the two adsorbed layers
zq	the number of interchain contacts in a lattice; $zq = s(z - 2) + 2$
ϕ	volume fraction
ε^*	L-J maximum attractive energy
Δ	difference between values, increment
σ	standard deviation

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