Intermolecular Interactions in Complex Systems "Polyamide-Silica Gel": The Quantum-Chemical Interpretation

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Abstract. The paper presents the results of quantum-chemical studies of polymer composite materials based on aromatic polyamide phenylon C1 filled with silica gel. The initial compounds recreating the structure features of monomer units of macromolecules are given. Theoretical models of complexes with hydrogen bonds describing the most probable interactions of the polymer matrix with the filler are proposed. The adequacy of the structures was confirmed by the results of IR spectroscopy. It is established that the chemical interaction of polymer molecules with the filler is carried out by forming strong hydrogen bonds with the participation of bridged amide groups interacting with some active hydroxyls on the surface of silica gel.

Keywords: Polymers · Polymer composite materials (PCM) · Polymer matrix · Quantum-chemical interpretation

1 Introduction

The polymers and polymer composite materials (PCM) based on them have become widespread in all branches of human activity over the past 30 yrs [1–4]. Particularly interesting are special-purpose polymers [5–7], which are close to metals and their alloys in terms of their properties, but are 3–5 times lighter, have a high level of wear resistance and chemical resistance, are able to withstand alternating loads, etc. One of these polymers is aromatic polyamide, whose strength reaches 230 MPa, and heat-distortion temperature and thermal fastness are 290 and 350° respectively. The main disadvantages of these polymers include their high cost. To reduce it, aromatic polyamides are filled with cheap fillers that can improve their physical, mechanical, thermal, and tribological properties compared to the original polymer [4, 5].

One of these fillers is silicon earth of the silica gel brand, which is capable of physical and chemical interaction with macromolecules of aromatic polyamide in the production of PCM and their processing into products [7]. In this case, physical interaction is

possible due to the fact that the filler has a well-developed surface (up to 300 m^2/g) with a large number of pores that contribute to the physical adsorption of the matrix polymer by the filler surface. Chemical interaction of silica gel with aromatic polyamide is possible due to the formation of chemical bonds between reactive hydroxyl groups on the filler surface and matrix polymer molecules. A number of papers, such as [8–10] and so on, describe PCM based on polyolefins, fluoropolymers, phenolics and silica gel with confirmation of their physical or chemical interaction.

The nature of some interaction between aromatic polyamide and silica gel has not been previously explored. The presence of interaction of these components was determined indirectly, starting from an increase in the level of physical, mechanical and thermal properties of PCM based on aromatic polyamides and silica gel. Therefore, the main purpose of our research is to determine the nature of the interaction of silica gel with aromatic polyamide. To solve this problem, it is necessary to study in detail the features of intermolecular interactions that occur at the level of individual macromolecule links using the broad capabilities of quantum-chemical calculation methods, as well as some vibrational spectroscopy.

2 Experimental Procedure

Aromatic polyamide of the phenylon C1 brand (TU 6-05-221-101-71) was used as a polymer matrix. This polymer is created by a polycondensation reaction when diamines (75% m-phenylenediamine and 25% p-phenylenediamine) react with isophthalic acid dichloroanhydride. The structural formula of phenylon C1 is shown in Fig. 1.
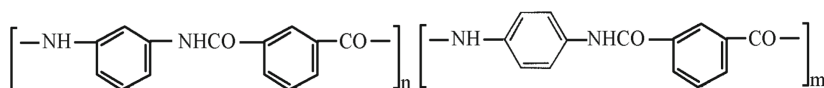

Fig. 1. The structural formula of phenylon C1

In its initial state, it is a fine pink-white granular molding compound with a bulk density of 0.2–0.4 g/cm^3 and a basic particle size of 40–60 μ. As a filler, amorphous silicon earth silica gel was used, which obtained from dried, washed and crushed gel formed during acidification of an aqueous-alkaline solution of sodium metasilicate. In its initial state, it is a fine white granular molding compound with a bulk density of 0.3–0.6 g/cm^3 and a basic particle size of 5–10 μ.

The IR absorption spectra of phenylon were recorded on the SPECTRUM ONE (PerkinElmer) instrument. Samples for recording are pressed from the powder of the initial polymer, as well as a composite material based on it, according to the standard method with KBr [11]. The effective diameter of the tablets was about 12 mm with a thickness of about 1 mm. In this case, it is advisable to have a polymer powder content of no more than 3 wt%. The quantum-chemical calculations at the *ab initio* level of theory were performed using the software package Gaussian 03, Revision E.01 with further visualization of the results in GaussView 3.0. Some statistical data processing was performed using ORIGIN Professional 6.0.

3 Results and Discussion

At the initial stages of the study, the question of choosing typical model compounds that would provide the possibility of adequate reproduction of the structure and inter-molecular interactions occurring in the systems under study, and at the same time were characterized by such important features as simplicity and convenience in terms of quantum-chemical calculations becomes very important. In this case, the primary task is to create such theoretical models that would take into account the presence of basic structural fragments of macromolecules and characteristic interactions between them without significantly detailing the internal structure of individual components of super molecular systems.

As evidenced by our previous studies of the structure of polymer composites based on aramidic binders and fillers [12], the structure of N-phenylbenzamide (**1**) is quite consistent with the composition of the monomer link of polymers of this type. As for the filler, which was silica gel, the best model compound in the simplest approximation can be the structure of the composition $H_4[Si_4O_{10}]$ (**2**), which is a tetracyclic cage system built of silicon and oxygen atoms, on the surface of which isolated from each other four hydroxyl groups are situated. Taking into account the amorphous nature of silica gel, which is characterized only by local symmetry in certain fragments of the structure (clusters), this approach to the choice of a modified molecular model, in our opinion, is justified. On the other hand, the cluster method is effective not only for modeling localized condition state, but also for numerous surface effects that can be fundamentally important in the conditions of active intermolecular interactions.

Using a three-parameter hybrid density functional in the B3LYP/6-311++G(d,p) approximation, we optimized the geometry of model compounds (**1**, **2**) *in vacuo* while simultaneously calculating the corresponding sets of vibrational frequencies, according to which localized stationary points were characterized as minima on the potential energy surface. The electron density distribution with the determination of atomic charges for the studied structures was established in the framework of natural bond orbitals (NBO) theory [13, 14]. The results are shown in Fig. 2.
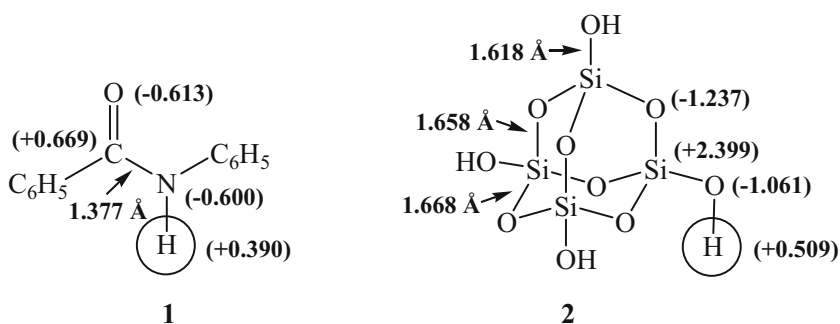

Fig. 2. The structures of model compounds with certain values of NBO atomic charges as well as some bond lengths (Å)

The obtained data have generated great interest both in terms of the structure of individual sections (structural fragments) of the phenylon polymer matrix, and their interaction with silica gel with the possible formation of typical hydrogen bonds. Based on this assumption, we have suggested theoretical models that recreate the direct interaction of N-phenylbenzamide (**1**) molecules with the tetracyclic cage structure of $H_4[Si_4O_{10}]$ (**2**). Splitting the equilibrium geometry of dimers into separate components with their subsequent optimization in the B3LYP/6-311++G(d,p) approximation led to the formation of "isolated" structures that were obtained earlier. The calculation of vibrational frequencies for all intermolecular complexes indicated the absence of imaginary vibrations, which allowed us to characterize them as minima on the potential energy surface. When evaluating the energy parameters of localized structures, special corrections for the basis set superposition error obtained according to the Boys-Bernardi procedure were taken into account [15]. The calculation results are shown in Fig. 3.
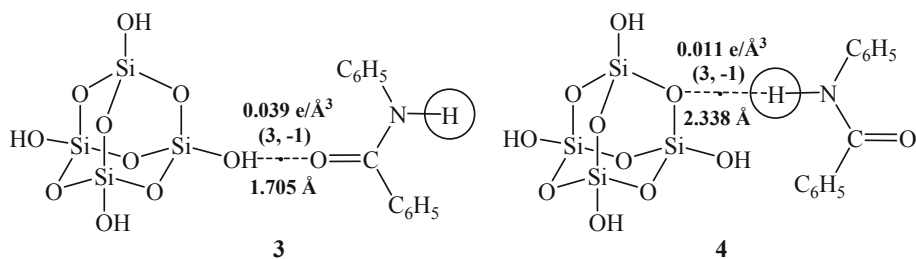

Fig. 3. The structures of complexes in the system "polyamide-silica gel" with some hydrogen bond lengths (Å) as well as electron densities in (3,–1) critical points

It should be noted that the greatest contributions to the stabilization energy of structures (**3**, **4**), along with weak interactions of an electrostatic nature, are made by strong hydrogen bonds formed with the participation of a bridged amide group and a hydroxyl (~77%), as well as the oxygen atom of the cage fragment (~23%), which were evaluated in the framework of the atoms-in-molecules (AIM) Bader's theory [16]. The calculated stabilization energies are 32.4 and 12.5 kJ/mol, respectively. Considerable attention was also paid to the determination of the general energy effects for solvation of unrelaxed geometries of intermolecular complexes using the polarizable continuum method *PCM*-B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) ($\varepsilon = 78.4$) without any detalization of the structure for individual hydrate shells. In this case, the energy difference for the structures (**3**, **4**) was at least 12.0 kJ/mol in favor of the first type interaction.

To confirm the crucial role of hydrogen bonding effects in the PCM structure, we performed a detailed analysis of the vibrational spectra of the previously described isolated (**1**, **2**) and dimerized (**3**, **4**) forms in order to further compare them with each other, as well as with the available experimental data. The latest theoretical models quite adequately reflect the structural situation in which interacting molecules, along with the hydrogen-bound groups (>C=O) and (>NH), contain their unrelated analogues. As we know, the harmonic vibrational frequencies calculated by quantum-chemical methods usually turn out to be much larger in comparison with the similar parameters obtained

experimentally. In this case, the main source of errors, according to the authors [17], is the neglected an harmonicity effects, as well as the lack of completeness of the description of electronic correlations due to the use of limited sets of basis functions. To improve the accuracy of the calculated data in their reproduction of the main spectral characteristics of the studied systems, we used some additional values of the scale factors, which in the case of the three-parameter hybrid functional B3LYP were 0.9580 and 0.9688 for the basis sets 6-311+G(d) and 6-311+G(d,p), respectively. The results are in Table 1 and Fig. 4.

Table 1. Harmonic vibrational frequencies (cm^{-1}) obtained experimentally as well as calculated in approximation DFT-B3LYP/6-311 ++G(d,p)

| Intensity, band shape[a]	C1[b]	C1SG15[b]	C1SG30[b]	Model (3)	Model (4)	Interpretation[c]
w., wd.	3405	3410	3419	3788	3790	$\nu_{(OH)}$ of cage fragment or capacity of moisture
	3267	3345	3345	3507	3459	$\nu_{(NH)}$ of amido groups
v. w.	2921	2925	3000	3092	3093	$\nu_{(CH)}$ of benzene rings
	2851	2914	2897	3084	3086	(the same one)
s.	1649	1652	1655	1647	1673	$\nu_{(CO)}$ of amido groups
v. s.	1605	1609	1611	1586	1588	$\nu_{(CC)}$ of benzene rings with $\delta_{(NH)}$ of amido groups
	1526	1539	1539	1567	1568	
	1474	1486	1486	1517	1520	
s.	1412	1408	1412	1480	1479	$\delta_{(CH)}$ of benzene rings
	1307	1319	1319	1423	1420	(the same one)
	1237	1250	1224	1305	1294	$\nu_{(CN)}$ with $\delta_{(CH)}$ of benzene rings
v. s., wd.	–	1084	1091	1056	1024	$\nu_{(SiO)}$ of cage fragment
w.	–	782	785	781	767	$\delta_{(OH)}$ of cage fragment
	719	717	719	697	698	$\delta_{(CH)}$ of benzene rings
	684	684	686	688	689	(the same one)
v. w.	570	568	571	586	624	$\delta_{(NH)}$ of amido groups
s.	–	459	467	341	343	$\delta_{(SiO)}$ of cage fragment

[a] s. – strong; w. – weak; wd. – wide; v. – very.
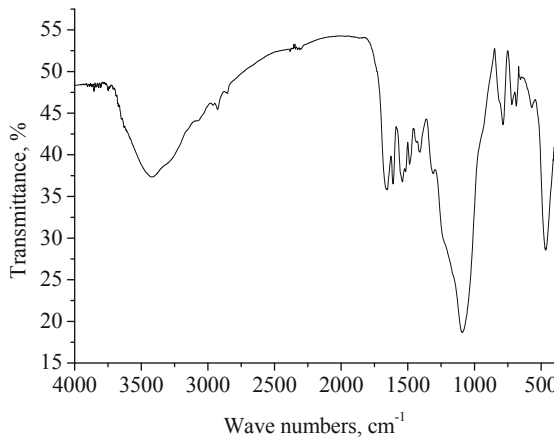[b] C1 – pure phenylon; C1SG15 and C1SG30 – polymer composites with 15 and 30 wt% of silica gel.
[c] ν – stretching vibrations; δ – bending vibrations.
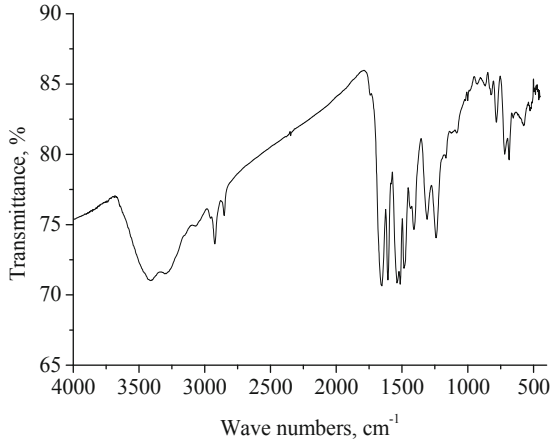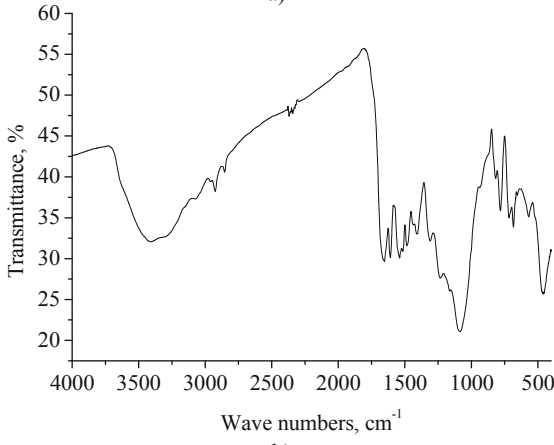
Fig. 4. IR absorption spectra of pure powder phenylon C1 (a) as well as composites C1SG15 (b) and C1SG30 (c)

According to the literary data [18], the structural identification of aliphatic polyamides usually includes consideration of characteristic absorption bands with reliable signal attribution in the regions of 3280, 2900, 1640, 1550 and 1545 cm^{-1}. Analysis of the obtained results (Table 1) indicates the presence of wide bands at 3267 or 3345 cm^{-1}, which correspond to the stretching vibrations of bonds (>NH) of amide groups. In the region of ~1650 cm^{-1} there is an intense band "Amide I", which is characteristic of carbonyl with a significant contribution of hydrogen binding. Indeed, in the case of the calculated structures (**3**, **4**), there is a noticeable shift of this absorption band from 1673 cm^{-1} for the "isolated" group (>C=O) to 1647 cm^{-1} in a complex with a hydrogen bond. A similar displacement of the signal $\nu_{(NH)}$ occurs from 3507 to 3459 cm^{-1}. In the field of ~1530 cm^{-1} observed band "Amide II", corresponding to the stretching vibrations of carbon-carbon bonds of aryl fragments, with the participation of $\delta_{(NH)}$. The characteristic strip "Amide III" is observed near 1237 cm^{-1} corresponds to $\nu_{(CN)}$ with $\delta_{(CH)}$ of benzene rings. From this point of view qualitative identification signals of silica gel also become crucial, a wide and intense band around ~1090 cm^{-1} and narrow absorption bands of lesser intensity at 780 and 460 cm^{-1}, and in the first case contributions of the stretching vibrations of individual bonds (SiO) are upmost, and in the second one $\delta_{(OH)}$ and $\delta_{(SiO)}$ in terms of effective hydrogen binding. It should be noted that the stretching vibrations of hydroxyl groups can also be reflected in the spectrum section 3405–3419 cm^{-1}, which is usually responsible for the presence of trace amounts of water in the studied polymer and composite samples. The averaged sets of wave numbers obtained for the entire range of polymer systems under study correlate well with each other, which indicates an adequate reproduction of the spectral characteristics of the materials under consideration within the selected computational approximation:

$$\nu, \delta(\text{expt.}) = (99.16 \pm 25.17) + (0.90 \pm 0.01) \cdots \nu, \delta(3); \ r = 0.998; \ S_0 = 54.98; \ n = 17 \quad (1)$$

$$\nu, \delta(\text{expt.}) = (94.02 \pm 27.85) + (0.91 \pm 0.01) \cdots \nu, \delta(4); \ r = 0.998; \ S_0 = 60.66; \ n = 17. \quad (2)$$

4   Conclusions

The results of quantum-chemical research presented in this paper indicate that it is possible to apply quantum chemistry methods and techniques to study the features of intra- and intermolecular interactions at the level of individual sites – structural fragments of macromolecules. The results of calculations are well within the spectral studies data of the structure of polymer materials and may be fundamentally important in terms of preliminary assessment of the affinity of individual components when creating new composites based on them.

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