

Study and analysis of the IR spectra of a composition based on polyamide filled with iron nanoparticles

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Abstract. A complex of studies was carried out to study the chemical composition of the initial components and compositions: polyamide and nanocompositions based on it, filled with iron particles. The paper presents an analysis of the IR spectra of the developed polymer nanocomposites.

1 Introduction

The rapid development of industry and increasing its competitiveness requires the creation of new materials, including polymer composites. Recently, there has been growing interest in the creation of nanocomposites based on thermoplastic matrices. It is economically expedient to create composite materials based on such polymers, which are characterized by the availability of capacities for their production, for example, aliphatic polyamides (PA). The introduction of dispersed or fibrous fillers into polyamides significantly increases the operational characteristics and expands the possibilities of their application. The use of dispersed fillers improves some characteristics of polymeric materials, in particular, tribological ones, but, in most cases, reduces the strength properties of composite materials, which imposes significant restrictions on the scope of products. But the introduction of nanoparticles can significantly change their properties. This article is devoted to the development and study of such compositions. The development and manufacturing technology of nanocomposite samples based on polyamide are described in [1–3].

2 Result and discussion

Based on these studies, the features of the intermolecular interaction of the components in the composite were evaluated. As is known [4], phenylones belong to the class of aromatic heat-resistant polyamides and are linear heterochain polymers whose macromolecules are built from aromatic fragments of various structures linked by amide bonds. The presence in the spectrum of polyamide of wide strong bands with a fine weak structure in the region of 3600–2700 cm^{-1} both in pure (Fig. 1) and metal-filled (Fig. and intermolecular hydrogen bonds between amide groups. In the spectrum of polyamide, bands of stretching NH

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vibrations are unambiguously identified (broad band with a maximum at about $3300\text{--}3450\text{ cm}^{-1}$), Amide-I (split band with maxima at 1643 cm^{-1}), Amide-II (also split, $1547\text{--}1572\text{ cm}^{-1}$) and Amide-III (band $1250\text{--}1260\text{ cm}^{-1}$). In the metal-filled composition based on phenylone, this band narrows and intensifies with the appearance of a maximum \sim at $3420\text{--}3430\text{ cm}^{-1}$ Amide II bands ($\delta(\text{N-H})$ associat. $1547\text{--}1572\text{ cm}^{-1}$) and Amide V band (700 and 727 cm^{-1}). It is possible that the maximum at $3450\text{--}3300\text{ cm}^{-1}$ groups: , C O N H C N OH, since the “Amide II” band $\delta(\text{N-H}) = 1548\text{ cm}^{-1}$ associated with bending vibrations of the free NH group in amide bonds disappears at the same time.

The choice of iron nanoparticles as a filler was determined by both its strength characteristics and the expected affinity for polyamides. Analysis of the IR spectrum of a nanocomposition based on polyamide filled with iron nanoparticles, Figures 2-4 showed the following. A broad strong band in the region of $3700\text{--}2500\text{ cm}^{-1}$ characterizes the presence of a delocalized π -electron cloud. There is a fine, weak structure ($3421, 2923, 2857\text{ cm}^{-1}$), indicating both an intermolecular hydrogen bond between amide groups and an electrostatic interaction of quartered immonium nitrogens (according to $\text{R NH}_2 \oplus \text{RC NH}_2 \oplus$ and carboxylate ions (carbonate, sulfate).

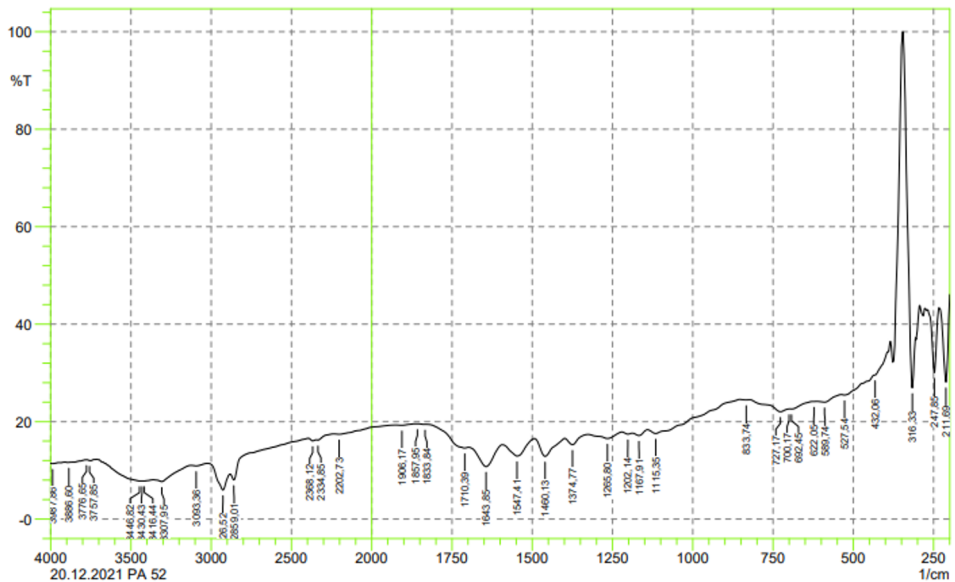


Fig. 1. IR spectra of pure polyamide

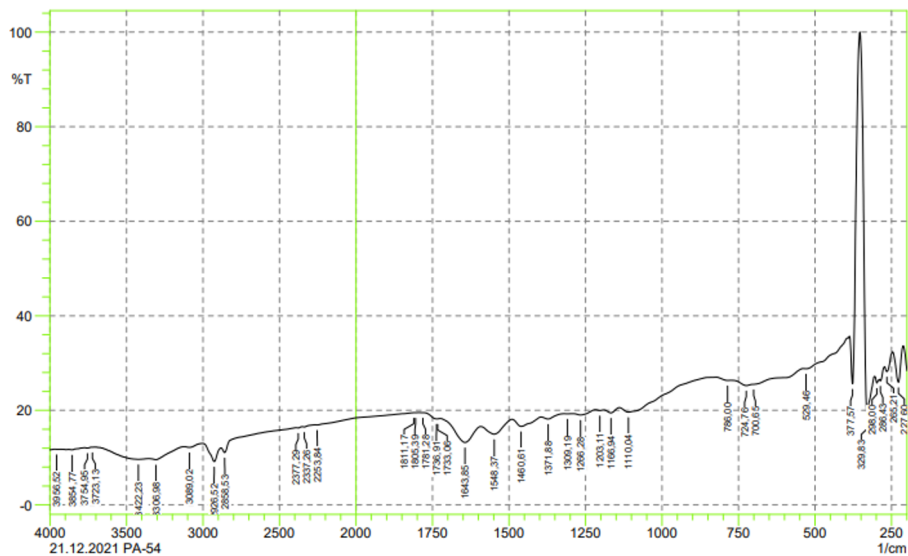


Fig. 2. IR spectra of a composition based on polyamide filled with iron nanoparticles (RA + 5.19% Fe)

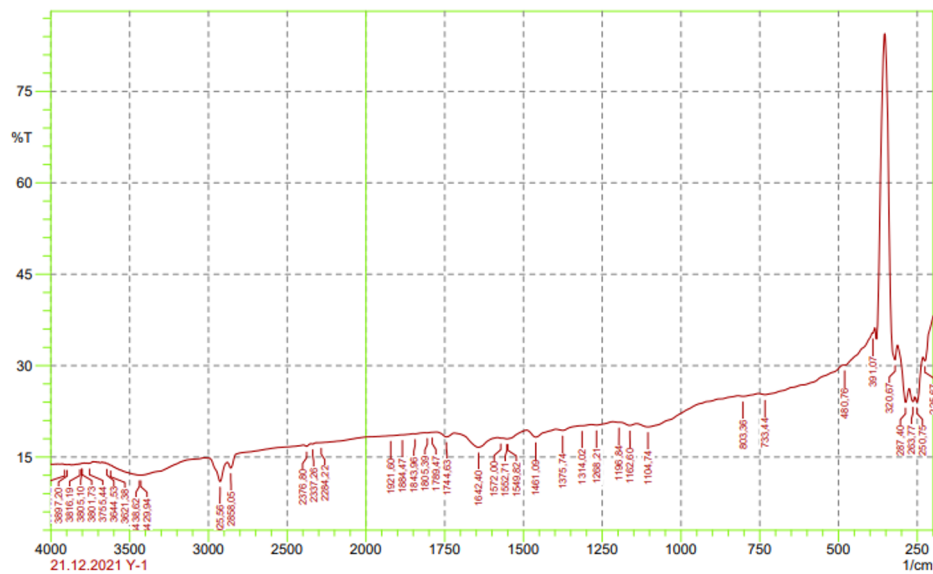


Fig. 3. IR spectra of a composition based on polyamide filled with iron nanoparticles (RA + 20% Fe)

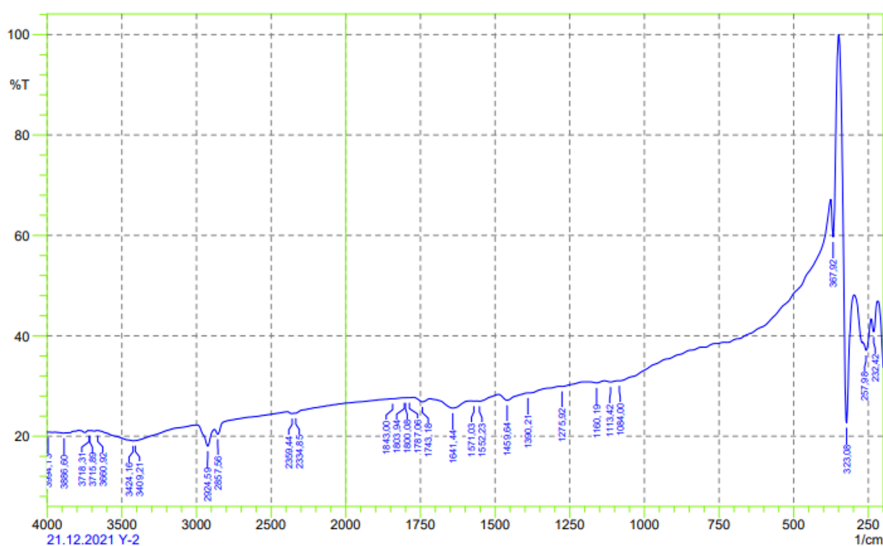


Fig. 4. IR spectra of a composition based on polyamide filled with iron nanoparticles (RA + 30% Fe)

The presence of a broad strong band with a fine structure at 1750-1450 cm^{-1} additionally testifies in favor of the presence of the $\text{R}_2\text{C}=\text{NH}$ ($\delta(\text{N-H})$, $\nu(\text{C-N})$) group, which takes part in the extended conjugation system.

Peaks $\nu_1=1747\text{cm}^{-1}$; $\nu_2=1459\text{cm}^{-1}$ and $\nu=708\text{cm}^{-1}$ indicate the presence of imide cycles ("Imid-I", "Imid-II", "Imid-III" bands, respectively). But the presence of an "immonium band" at 1688cm^{-1} , as well as a shoulder on the Imid-I band (1714cm^{-1}), absorptions at 1688cm^{-1} ($\nu_{\text{as}} - \text{RCO}_2$), 1459cm^{-1} ($2- \text{CO}_3$ or $\nu(\text{C-N})$ in amides), 1268cm^{-1} ($\nu(\text{C-N})$ in amides) indicate the presence of "defects" in cyclization, i. in the formation of imide cycles - under-cyclized and, apparently, containing CO_2 - ($2-\text{CO}_3$, $-\text{HCO}_3$) groups adsorbed according to the type of anhydride bond or $-\text{SO}_2$ ($-\text{SO}_3\text{H}$) - acid residues. It was found that there is no water in the sample, since there is no absorption in the region of 3710cm^{-1} . As a result of the studies, it was found that in the IR spectrum of the composite, interaction occurs both along "defective" non-cyclized imide cycles and along the imide cycles themselves. Analyzing Figures 2-4, we can conclude that bands appear at 1688cm^{-1} in the composite sample, which indicates the formation of a carboxyl group from the former imide group in the arimide fiber. The disappearance of the band at 1460cm^{-1} ($\nu(\text{CN})$ in amides) in organoplasty indicates the interaction of non-cyclized $\text{C}=\text{N}$ - groups in the arylamide with the amide and terminal amino groups of phenylone, since the concentration of hydrogen bonds decreases in this case (the region $3300-3900\text{cm}^{-1}$) and the intensity of the Amide-II band ($\delta(\text{NH})$), associated with the vibrations of the associated hydrogen bond of the NH group, decreases (region 1375cm^{-1} , 1549cm^{-1}). Thus, changes in the spectrum of phenylone (an increase in the intensity of the band at 1076cm^{-1} and the appearance of a weak band at 1280cm^{-1}) as a result of pressing indicate a decrease in the degree of ordering in the polymer structure, and also, possibly, additional deformation of the chains (formation of folded structures).

The absence of these features in the spectrum of the composite can be interpreted as the result of the influence of the fiber, which somehow prevents the mentioned structural changes. Interpretation of the spectra of the initial phenylone and composites based on it, containing iron nanoparticles, allows us to conclude that the intermolecular hydrogen bonds

of amide groups in phenylene are disturbed and that the fiber interacts with the matrix at the molecular level [168].

Polyamide 6 belongs to polymers whose structure is relatively well studied. It, like other aliphatic polyamides, can crystallize in several crystalline modifications, among which δ and γ are the most stable. Modification α is built from almost completely elongated flat zigzag macromolecules interconnected by hydrogen bonds.

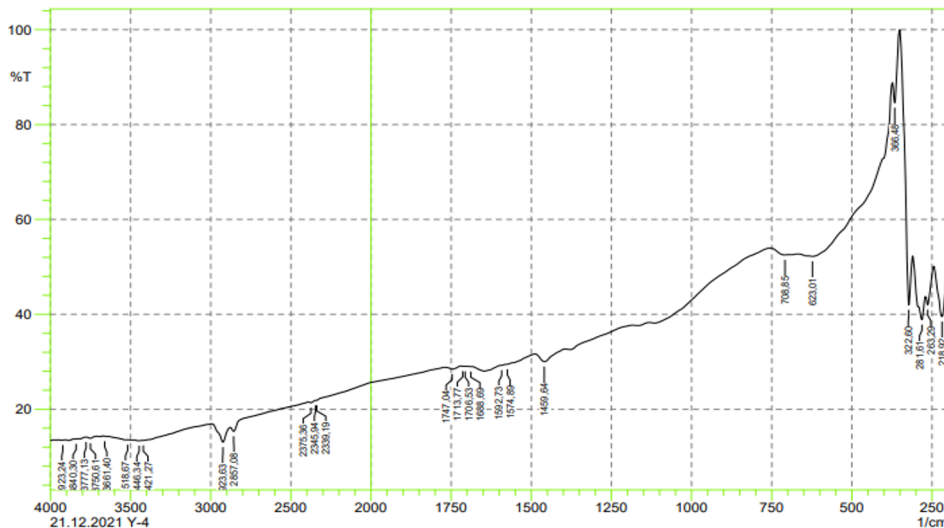


Fig. 5. IR spectra of a composition based on polyamide filled with iron nanoparticles (RA + 60% Fe)

The study and analysis of the wavenumbers of the absorption bands of the spectra of PA 6 and the composite (60% Fe) (Fig. 5) shows that four peaks characteristic of PA 6 are observed in the range of hydrogen stretching vibrations: 3315 cm^{-1} , 3090 cm^{-1} (stretching vibrations hydrogen bonded groups N–H) and 2936 cm^{-1} , 2873 cm^{-1} (stretching vibrations of CH_2). The band at 3315 cm^{-1} is broadened due to the superposition of the moisture absorption band and stretching vibrations of the terminal primary amino groups. The bands at 1647 cm^{-1} and 1551 cm^{-1} refer to the Amide I and Amide II vibrations, respectively. The bands are noticeably split; a possible cause of the splitting can be assumed to be the superposition of the band of bending vibrations of the $-\text{NH}_2$ end groups. The presence of a weak component at 1665 cm^{-1} in the Amide I band was mentioned earlier by the authors of [170] without discussing its nature. The Amide III band has two components: a stronger one at 1264 cm^{-1} and a weaker one at 1203 cm^{-1} , which is typical of the α form of the polymer [170]. The Amide V and Amide VI bands are structurally dependent and in the spectrum obtained by us have a position characteristic of the α -form of PA 6 – 697 cm^{-1} and 583 cm^{-1} , respectively. The fact that pure polyamide is in the crystalline state and in the α -modification is also indicated by a typical poorly resolved group of bands at $1410 - 1470\text{ cm}^{-1}$ and the characteristic shape of the band at 1264 cm^{-1} . The spectrum of polyamide 6 obtained by us is almost identical to the spectrum of this polymer in the crystalline α -modification described in the literature [170, 172]. Spectra of composites with 15 and 30 wt. % filler differ little from the spectrum of pure PA 6 [173]. We can only note a change in the contour of the band at 1264 cm^{-1} (the intensity of the low-frequency shoulder increased), an increase in the peak at 733 cm^{-1} due to the superposition of the band at 718 cm^{-1} of arimide, and the appearance of weak peaks at 823 cm^{-1} and 886 cm^{-1} . The absorption of arimide-T in composites is somewhat different from the absorption of pure

fiber. Differences are noticeable in the range of stretching vibrations of hydrogen atoms, which indicates a change in the nature and number of hydrogen bonds, which, in turn, is caused by the interaction between the matrix and the fiber. The interaction of the polymer and filler can also explain the changes in the spectral region $1660 - 1300 \text{ cm}^{-1}$.

As for the nature of the mentioned interaction, it can include both the redistribution of hydrogen bonds and the chemical interaction of the non-cyclized sites of poly-N, N-bis (phenoxyphenyl) pyromellitimide with terminal amino and carboxyl groups of the polyamide. Purely electrostatic interactions of charged functional groups - carboxylate ions and ammonium ones - are also not excluded. The consequence of this interaction is the homogenization of the composite. The spectrum of the composite containing 45 wt. % of the filler, has significant differences compared to the two previous ones and with the spectrum of pure PA 6. First of all, fiber bands are clearly distinguished (shoulders 1780 cm^{-1} and 1726 cm^{-1} on the Amide I band, 1086 cm^{-1} , 702 cm^{-1}). The peaks at 1035 cm^{-1} (due to the superposition of the band at 1352 cm^{-1} iron) and 817 cm^{-1} (due to the superposition of the band at 796 cm^{-1} iron) increase strongly. In addition, the spectrum of this composite has features that allow us to conclude that with an increase in the filler content to 40%, changes occur in the structure of the matrix. Thus, the Amide V band merges with the iron band at 718 cm^{-1} and is observed at 700 cm^{-1} , while the Amide VI band shifts towards higher frequencies and is observed at 600 cm^{-1} . The intensity of the bands in the region of $1000 - 1100 \text{ cm}^{-1}$ increases significantly. All of these features allow us to conclude that with a fiber content of 40 wt. % PA 6 in the composite either forms an amorphous phase or is in the γ form (according to [170], these states are difficult to distinguish). It should be noted that the spectrum of this composite contains a fairly strong band at 1503 cm^{-1} , which is absent both in the spectra of both modifications of PA 6 and in the spectrum of the fiber. The appearance of this band, in our opinion, indicates the formation of C=N and N=N double bonds (cis position), i.e., partial decyclization and destruction of the arimide-T structure. A comparative analysis [173] of the IR spectra of PA 6, iron, and composites based on them shows that there are interactions between the polymer matrix and the filler, in which the non-cyclized regions of the fiber polymer and the terminal carboxyl and amino groups of PA 6 take part. Interactions may include the formation of hydrogen bonds, chemical interactions and electrostatic interactions. The consequence of chemical interactions is the enolization of carbonyl groups of non-cyclized sites, the cis-addition of polyamide molecules, which leads to a change in the structure of PA 6 and its amorphization with an increase in the filler content to 40 wt. %.

3 Conclusions

Thus, the analysis of the IR spectra revealed the presence of the interaction of non-cyclized amide groups of the fiber and amide, terminal amino and carboxyl groups of the binders, as well as additional formation of intermolecular hydrogen bonds due to the interaction of the amide groups of the fiber and binders. The presence of the same type of functional groups in the composition of fiber macromolecules and matrices provides the possibility of the formation of both chemical and additional physical bonds, which should help improve the performance properties of products. The performance characteristics of composite materials are determined not only by the characteristics of the initial components, but also by the interactions between them on the interfacial surfaces. Such interactions, on the one hand, determine the adhesion forces that ensure the solidity of the structure, and, on the other hand, they can affect the properties of the polymer matrix and change the properties of the composite. Additional evidence of chemical and physical changes in the structure of the developed composites are characteristic changes in the shape of the thermomechanical curve, which can be used to judge the transformations that have occurred in the polymer

[176]. The thermomechanical curve determines the transition temperatures of the polymer from one physical state to another. Our studies presented in [177] show that the introduction of fiber leads to a change not only in the softening temperature of the binder, but also in the general character of the thermomechanical curve. For the initial phenylone, the thermomechanical curve runs parallel to the abscissa axis up to the softening temperature, after which it rises sharply.

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