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SOME PECULIARITIES OF OBTAINING COMPOSITIONS ON THE BASIS OF ALICYCLIC POLYIMIDE AND NATURAL MINERAL MONTMORILLONITE

Abstract. In this work, an analysis was conducted of research on the production of materials on the basis of alicyclic polyimide with plasticizing additives in the presence of the inorganic filler is montmorillonite by the method of IR-spectroscopy. Installed some of the features of their production, namely, compositions based on alicyclic polyimide with additives alkylated montmorillonite and polyacrylic acid formed intercalated structure. In the ternary compositions of alicyclic polyimide with polyethylene glycol and alkylated montmorillonite, a natural mineral, apparently, forms a complex with terminal groups of polyethylene glycol. The presence of a complex in the ternary composition based on polyimide, polyethylene glycol and montmorillonite, is reflected in the DSC diagram, which manifests itself 2 the specific heat jump corresponding to the polymer-polimer interactions and polymer-low-molecular substance.

Key words: polyimide, montmorillonite, composition, intercalation, complex.

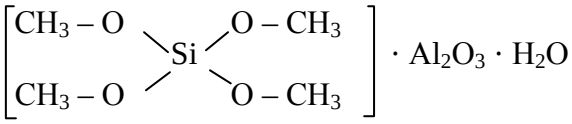
Obtaining composite materials based on polyimides with additives of natural mineral montmorillonite are currently, is a promising direction [1]. As such materials, due to the large surface of the filler particles of nanoscale range, enhanced interaction of polymer matrix with the inorganic component, thereby increasing the thermal and mechanical properties of the composition as a whole [2].

In the literature there are publications on the development of composite material based on various polyimides, for example, in [3] use particles of Na-montmorillonite (exfoliating filler) to activate the process of imidization of polymetakrilate aromatic structure. Known composite materials based on polyimide derived from dianhydride 3,3',4,4'-oxydiphthalic and 1,3-bis-(4- aminophenoxy)-2-propanol silica [4,5], it is shown that the synthesized nanocomposites covalently bound silica is distributed in the PI of the active amino groups. The obtained thermoplastics based on poly[4,4'-bis(4''-N-phenoxy)-diphenylsulfone]imide 1,3-bis(3',4 dicarbofenoxy)benzene with modified montmorillonite [6].

It is known that composite materials based on layered silicates are classified into three main types, depending on the nature of initial components, conditions and the production method [1]. This is a traditional microcomposite, in which the particles retain their original size, which is formed under the condition that the polymer does not penetrate into the interlayer space of the silicate. Another type of the composite when the material is formed intercalated structure, i.e., the polymer penetrates between the layers of silicate. In this case, there is an increase in the interlayer distance, but while maintaining an orderly layered structure of the

mineral. The third type is the so-called exfoliating nanocomposite in which the silicate delamination of the individual layers dispersed in the polymer matrix. The latest nanocomposite is formed in the harsh conditions of the modified clay an organic compound with the chemical reactions of polymerization of monomers (in the processes of mixing of the reaction) [7] or in the melt of polymers.

In this work, we used the alkylated montmorillonite (AMM), for which earlier [8] based on methods of IR spectroscopy, x-ray diffraction and differential scanning calorimetry were installed structure :



It was determined that AMM is a compound where the methyl group with silicon oxide are linked directly by a covalent bond. And thus, AMM is a holistic layered silicate.

Upon receipt of the ternary compositions based on PI, AMM and various polyfunctional polymers, such as PEG, and PAK, the formation of different types of nanocomposites. It was found that the formation of compositions from AMM+PAK for these investigated systems in the spectra (figure 1, curve 3, 4) observed deformation of the main characteristic bands of stretching vibrations of PAK (ν_{1683}^{-1}) [9].

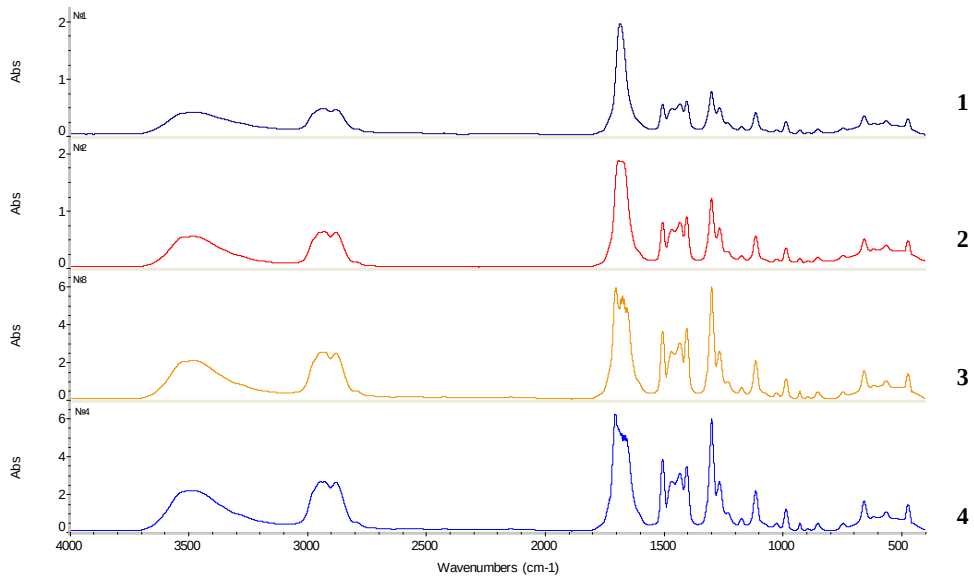


Figure 1 – IR spectra PAK (1) and compositions based on it with AMM when the ratio (wt.%) PAK: AMM = 1:0,25 (2); 0,5 (3); 1(4) in the solution of MP in glasses (KBr)

Whereas in the ternary composition PI+AMM+PEG these deformities stretching vibrations characteristic bands (figure 2, curve 1, 2; $\nu_{1638\text{-}1680\ см^{-1}}$, $\nu_{1645\text{-}1706\ см^{-1}}$) related to aminoacide and C-O groups [9] PI and PEG, respectively, does not occur. This implies that in the composite AMM+PAK intercalation occurs the entry of PAK into the interlayer space of a layered silicate.

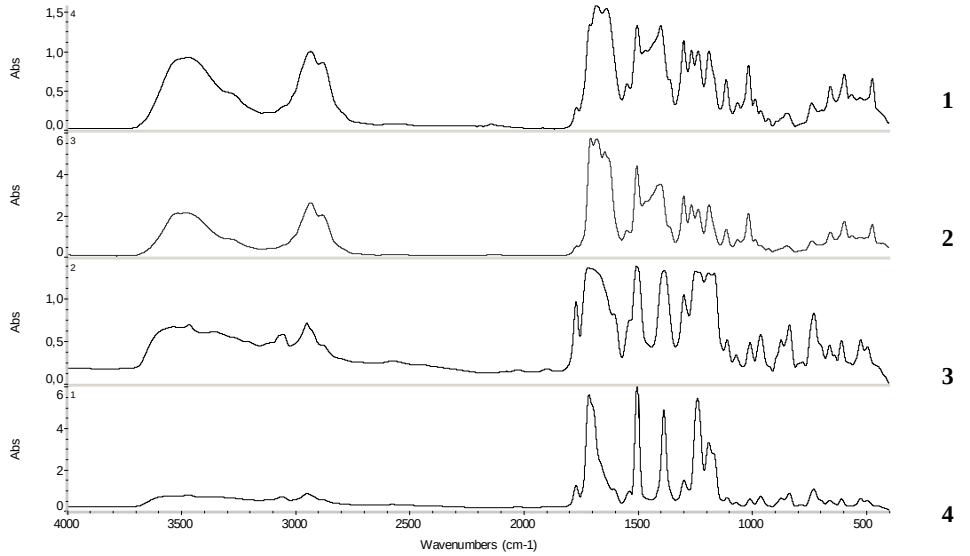


Figure 2 – IR spectra compositions based on PI+1.5 wt.%AMM+6 wt..%PEG(4)(2); PI+3 wt.%AMM+6 wt.%PEG(3)(1) 3.4 film, dried at 90°C; 1.2 the solutions of the ternary mixture in the glass (KBr)

This does not contradict the literary data [10], where in the polymerization of polyacrylice acid used layered silicate montmorillonite (MM). The study gives the following interpretation of the process of intercalation between layers MM there is a weak link at the level of Van der Waals, whereby a polar molecule PAK can be introduced between the layers of the mineral. X-ray diffraction analysis, it was shown that in this case, the structure of two-dimensional layers of MM is not changed, and only increases the distance between the layers.

Apparently, in this material system AMM+PAK, the penetration of PAK molecules in the interlayer space of a natural mineral of the montmorillonite leads to deformation of the stretching vibrations of the functional groups PAK on compositional spectra mixture. This pattern is observed for ternary compositions based on PI, MM and PAK (figure 3).

In the formation of a triple composition based on PI, PEG and AMM intercalation does not occur – deformation of stretching vibrations of functional groups of the components of the mixture have not been identified (figure 4). It can be assumed that the destruction of the layers of the AMM does not occur, because getting a double (PI+PEG) and the triple composite (PI+PEG+AMM) were not in hard conditions – mechanical method of mixing [11] at 40°C.

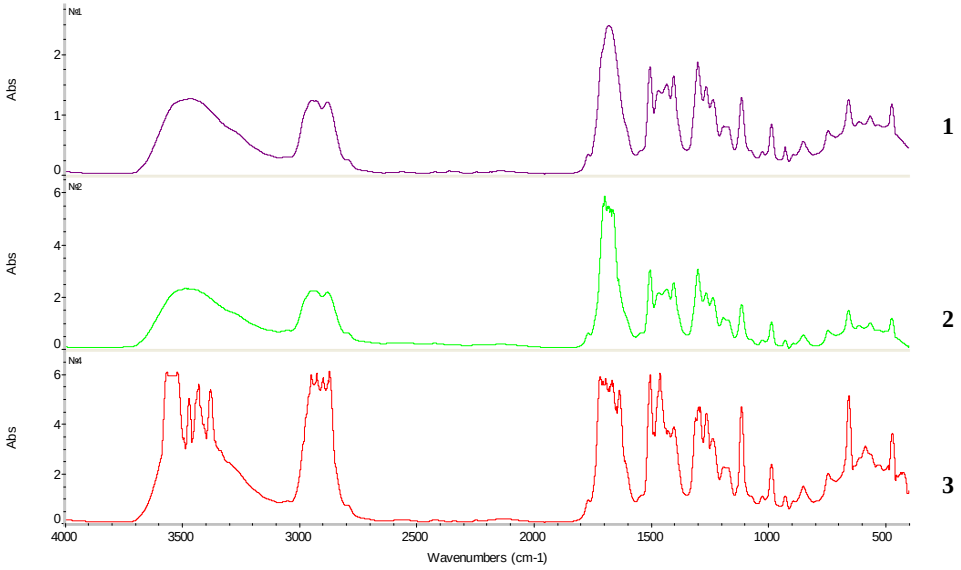


Figure 3 – IR spectra PI and PAC (1) and ternary compositions based
on PI, PAK and AMM at a ratio of PAK:AMM=2,7:0,7(2);
1,4; 2,7(3) wt.% in relation to PI (100 wt.%);
in the solution of MP in glasses (KBr)

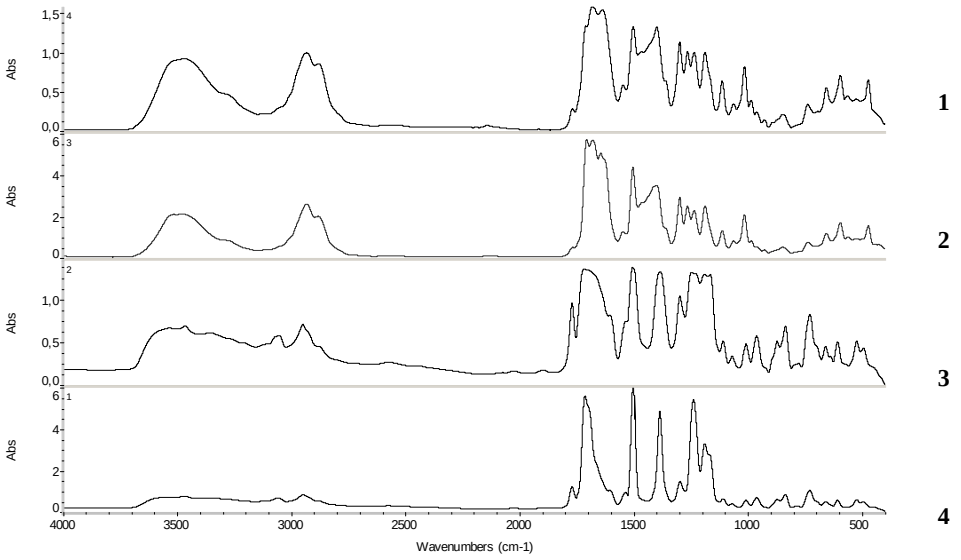


Figure 4 – IR spectra of the compositions on the basis of PI+1.5 wt.%AMM+6 wt.%PEG(4)(2);
PI+3 wt.%AMM+6 wt.%PEG(3)(1) 3.4 film, dried at 90°C;
1.2 the solutions of the ternary mixture in glasses (KBr)

Perhaps the particles of AMM, form a complex with PEG via the terminal hydroxyl groups. It is known that the oxides of silicon (in the silicon exhibits four valence) with oxygen-containing substances, silicon can exhibit a coordination number 5 and forming in this direction the complex [12]. The diagrams DSK ternary composition PI, AMM and PEG 2 is observed in the specific heat jump, the lower sheets stitched T_{g1}=343^{o}C, apparently, refers to the PI associated with the PEG partial cross-linking [13]. The second glass transition temperature T_{g2}=511^{o}C corresponds to the manifestation of the energy relations ternary mixtures of PI+PEG+AMM and the complex of PEG with AMM in particular, because the pure PI does not react with the particles of AMM [14].

It should be clarified that in polymer composite materials the criterion for the compatibility of components in the mixture is the glass transition temperature (T_g), namely, if the compatibility of components in polymer blends manifested a single glass transition temperature. For low molecular weight substances, this assessment is somewhat different. In this case, when the formation of complexes on the figures, changes in the heat capacity manifests the individual jumps corresponding to the different means of communication, as it was shown in [8]. Therefore, the chart of change in internal energy in the composition of PI+PEG+AMM were two of a specific heat jump corresponding relations of polymer-polymer and polymer-low-molecular substance. But while maintaining the compatibility of all components in the material, as evidenced by the transparency of the material, and it persists for a long time (2 years). Because, in the absence of the compatibility of components in the composite material, the particles of montmorillonite vipotest on the film surface for six months.

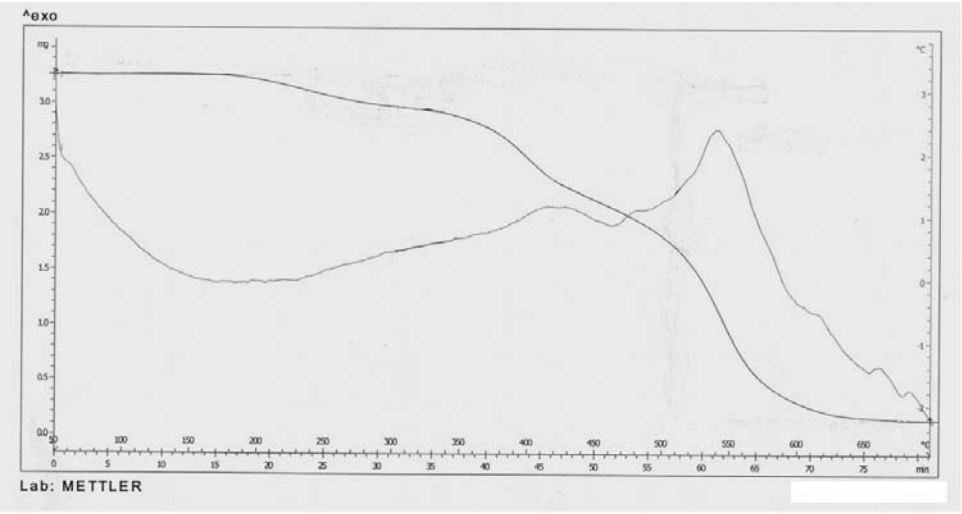


Figure 5 – Is a Thermogravimetric and calorimetric chart films triple compositions based on songs from the PI+3 wt.%AMM+6 wt.%PEG

On the basis of conducted research we can say that in the ternary compositions based on PI+PEG+AMM and PI+PAK+AMM form different types of nanocomposites, namely in the first case is the formation of a complex of a layered silicate with end groups of PEG, in the second case is formed intercalated structure of the mineral PAK. In both cases, the resulting nanocomposite in certain proportions are well aligned with PI.

Thus, to obtain thermodynamically compatible composites based on alicyclic polyimide particles of natural mineral montmorillonite, can be successfully used small additions of polyfunctional polymers, such as PEG, and PAK.

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Резюме

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АЛИЦИКЛДЫ ПОЛИИМИДТІ ЖӘНЕ ТАБИҒИ МИНЕРАЛ МОНТМОРИЛЛОНИТ НЕГІЗІНДЕГІ АЛЫНҒАН КОМПАЗИЦИЯНЫҢ КЕЙБІР ЕРЕКШЕЛІКТЕРІ

Жұмыста пластмассамен қанықкан алициклды полиимид негізінде алынған материалдарды монтмориллонитті бейорганикалық қоспасының қатысуымен ИҚ-спектроскопия әдісімен анализ жасалынды. Оларды алудың кейбір ерекшеліктері анықталды, атап айтсақ, алициклды полиимид негізіндегі композицияға алкилделінген монтмориллонитті және полиакрил қышқылды қоспалардың қатысында интеркалирленген құрылысы түзіледі. Алициклды полиимидті, полиэтиленгликольмен және алкилденген табиғи минерал монтмориллонитті үштік композиция композиция полиэтиленгликольдің тобымен аяқталады деген тұжырым бар. Монтмориллонит және полиэтиленгликоль, полиимид негізіндегі үштік композиция полимер-полимерлік өзара әрекеттесу және полимер-төменгі молекулалы заттарға сәйкес ДСК диаграммада 2 секірісті жылусиымдылығы бар.

Түйін сөздер: полиимид, монтмориллонит, композициялар, интеркаляция, комплекс.

Резюме

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НЕКОТРЫЕ ОСОБЕННОСТИ ПОЛУЧЕНИЯ КОМПОЗИЦИЙ НА ОСНОВЕ АЛИЦИКЛИЧЕСКОГО ПОЛИИМИДА И ПРИРОДНОГО МИНЕРАЛА МОНТМОРИЛЛОНИТА

Проведен анализ исследований по получению материалов на основе алициклического полиимида с пластифицирующими добавками в присутствии неорганического наполнителя монтмориллонита методом ИК-спектроскопии. Установлены некоторые особенности их получения, а именно в композиции на основе алициклического полиимида с добавками алкилированного монтмориллонита и полиакриловой кислоты образуются интеркалированные структуры. В тройной композиции из алициклического полиимида с полиэтиленгликолем и алкилированным монтмориллонитом природный минерал, по-видимому, образует комплекс с концевыми группами полиэтиленгликоля. Наличие комплекса в тройной композиции на основе полиимида, полиэтиленгликоля и монтмориллонита отражается на диаграмме ДСК, на которой проявляется 2 скачка теплоемкости, соответствующие взаимодействиям полимер-полимер и полимер-низкомолекулярное вещество.

Ключевые слова: полиимид, монтмориллонит, композиция, интеркаляция, комплекс.