ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՉԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

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ХИМИЯ ПОЛИМЕРОВ

INVESTIGATION OF THE CAUSES OF STABILITY VIOLATION OF PROPAGATING POLYMERIZATION HEAT WAVES IN THE PROCESS OF FRONTAL POLYMERIZATION

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In the work the causes of the stability violation of self-propagating heat waves in the process of frontal polymerization (FP) are studied. FP is an autowave process of the propagation of polymerization heat waves. One of the major factors for the practical implementation of FP is the necessity to establish the causes and boundaries of the stability violation of propagating heat waves in the process of FP. The paper clarifies one of the causes of stability violation during frontal polymerization of complexes of acrylamide with transition metals. Taking into account the fact that for the specified monomers the cause of stability violation and appearance of spin modes is shrinkage of polymer, we have investigated nanoparticle additions to the polymerizing media. It is shown that it is possible to regulate the stability violation during FP of the monomers depending on the amount of nanoparticle additions.

1. Introduction

In relation to the synthesis of functional gradient materials (FGM), which is one of the main advantages of frontal polymerization (FP) [1, 2], it has become necessary to study the stability of FP heat waves for the synthesis of high-temperature superconducting polymer composites with an objective of developing a strong linkage between superconducting composite and polymer according to a prescribed program. As it is known [3, 4], superconducting composites were obtained on the basis of cobalt- and nickel-complexes of acrylamide (AAm) using additions of superconducting ceramic, and studied for superconducting properties, transitions and electrical conductivity. However, in terms of the adhesion of these

composites to the required polymers for the synthesis of FGM, we faced the task of detailed investigation of the polymerization of metal-complexes of AAm both with and without additions. In Ref. [5], FP of the monomers as well as stability violation and appearance of spin modes were observed. It was shown that the main cause of the above-mentioned phenomena was shrinkage of polymer in the process of FP. To verify this, we specifically carried out FP in strict adiabatic conditions and confirmed that there was no heat loss from the walls of the reaction vessel [5]. A possible mass transfer from a hot polymeric part to a cool monomeric was checked as well. To that end, experiments were carried out where FP was initiated both from the top down and from the bottom up. The data obtained were consistent and the possibility of mass transfer was also excluded. Thus, in the work [5], the main causes of stability loss as a result of shrinkage of polymer were established.

Accordingly, the investigations with the additions of nanoparticles make it possible to synthesize compatible components of FGM by the method of FP.

2. Experimental Section

Reagents used: acrylamide (>99%) (AAm), cobalt nitrate hexahydrate (99.5%) (Co(NO₃)₂ · 6H₂O), nickel nitrate hexahydrate (99.5%) (Ni(NO₃)₂ · 6H₂O), silicon dioxide nanoparticles (10 nm, 99.9%) (all purchased from Sigma – Aldrich), bentonite of the local origin (63-80 μ m, 99.5%).

Synthesis of cobalt- and nickel-containing acrylamide complexes $(Co(AAm)_4(NO_3)_2, Ni(AAm)_4(NO_3)_2)$ was carried out according to the method described in [6].

The FP of the monomers was carried out in glass ampoules with a diameter of 8mm. The mechanical mixtures of the monomer and nanoparticles and bentonite were prepared by mixing the substances for a long time to thoroughly distribute the nanoparticles in a monomeric medium. The prepared mixtures were then loaded into the ampoules. To start the FP reaction of the monomeric mixtures, an instant heat was locally applied on the upper end of the ampoules.

The measurements were taken using thermocouples located in the recess holes on the reaction ampoules.

The samples obtained were examined on microscope MB30.

3. Results & Discussion

The FP of the monomers was investigated using thermocouples. The temperature profiles of the processes are given in Figures 1 and 2 (the thermocouples were located at a distance of 3mm from each other).



Figure 1. Temperature profiles of FP of Ni (curve 1) and Co (curve 2) complexes of AAm.

As can be seen from the Figures, the temperature of the waves reaches the adiabatic heating temperature for the polymerizing monomer and, at a certain moment, a part of the polymer formed during FP shrinks and gets detached from the monomer. At this detachment zone the wave temperature declines, which in turn decreases the polymerization rate. When sufficient amount of heat, released from the exothermic polymerization, transfers to the neighboring layer of the monomer on account of thermal conductivity, the FP process is restored and the temperature again reaches the adiabatic heating temperature.



Figure 2. Temperature profiles of FP of Ni-complex of AAm in comparison with spin rings formed on the samples as a result of polymer shrinkage.

Figure 3 shows the temperature profiles of FP of Co(AAm)₄(NO₃)₂ with additions of different amounts of SiO₂ nanoparticles. As can be seen from the Figure, FP of Co(AAm)₄(NO₃)₂ proceeds with formation of instabilities modes (curve 1). The addition of and spin up to 5 wt% of SiO₂ nanoparticles leads to a decrease in the gap between the polymer and monomer (curve 2), which, in turn, may be resulted by intermolecular interactions of the nanoparticles with the polymer chains [6].



Figure 3. Temperature profiles of FP of $Co(AAm)_4(NO_3)_2$ with the additions of 0 (curve 1), 5 (curve 2), 10 (curve 3), 15 (curve 4), and 20 (curve 5) wt% of SiO₂ nanoparticles.

Next, the further increase (10-15 wt %) in the amount of the nanoparticles leads to a uniform propagation of the FP heat waves (curve 3, 4) with a decrease in both the rate and maximal adiabatic heating of the polymerization process. The behavior of the curves in relation to the adiabatic heating of the FP of $Co(AAm)_4(NO_3)_2$ is shown in Figure 4.



Figure 4. Dependence of the maximal adiabatic heating temperature of FP of $Co(AAm)_4(NO_3)_2$ on the concentration of SiO₂ nanoparticles.

Figure 5 shows the samples of nanocomposites obtained by FP of $Co(AAm)_4(NO_3)_2$ with the additions of 0 (1), 5 (2), 10 (3), 15 (4), and 20 (5) wt% of SiO₂ nanoparticles. It is clearly seen from the Figure that addition of the nanoparticles up to 10 wt% gives the samples a homogeneous structure (Figure 5-2, 5-3). The fact is that, as mentioned above, the nanoparticles interacting with the polymer chains, attract them to each other and change the structure of the resulting composite. Nevertheless, with a further increase in the amount of nanoparticles, the structure of the obtained composites becomes inhomogeneous with the formation of uneven ruptures of the polymer matrix of the composite (Figure 5-3, 5-4).



Figure 5. Samples of nanocomposites obtained by FP of $Co(AAm)_4(NO_3)_2$ with the additions of 0 (1), 5 (2), 10 (3), 15 (4), and 20 (5) wt% of SiO₂ nanoparticles.

The samples of the obtained nanocomposites were also examined under the microscope MB30. The microimages of the composites (Figure 6) confirm the conclusions made. As can be seen from the microscope photographs, indeed, with additions of nanoparticles more than 15 wt% the structure of the nanocomposites becomes non-uniform and crumbly (Figure 6-3, 6-4).



Figure 6. Microscopic images of the samples of nanocomposites (at 100x magnification) containing 5 (1), 10 (2), 15 (3), and 20 (4) wt% of SiO_2 nanoparticles.

FP of $Co(AAm)_4(NO_3)_2$ with the addition of 5, 10, 15, and 20 wt% of bentonite as an inert filler was investigated as well. The results are demonstrated in Figure 7.



Figure 7. Temperature profiles of FP of $Co(AAm)_4(NO_3)_2$ with the addition of 5 (curve 1), 10 (curve 2), 15 (curve 3) and 20 (curve 4) wt% of bentonite.

As seen from the Figure, the shrinkage area decreases as the bentonite concentration increases. This phenomenon is caused by the dilution of the monomer with inert filler that reduces the front velocity, and consequently the shrinkage of the resulting composite.

4. Conclusion

The work presents investigations of stability loss of self-propagating heat waves in the process of FP. In the paper the effects of nanoparticles on the stationarity of FP heat waves were studied. From the presented data it can be concluded that the additions of nanoparticles diminish the effect of polymer shrinkage, and therefore instabilities and spin modes. At the same time denser filling disrupts the smoothness of the propagation of the heat waves, which is due to the agglomeration of the nanoparticles as a result of their very tight packing. From the presented data it can be concluded that by adjusting the quantity and quality of nanoparticles, it is possible to regulate the properties of the resulting composites. The results indicate that by means of nanoparticles it is possible to regulate the kinetics of the FP process, and therefore, obtain polymeric nanocomposites with prescribed properties and synthesize compatible components of FGM by the method of FP.

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ՖՐՈՆՏԱԼ ՊՈԼԻՄԵՐԱՅՄԱՆ ԳՈՐԾԸՆԹԱՅՈՒՄ ՏԱՐԱԾՎՈՂ ՊՈԼԻՄԵՐԱՅՄԱՆ ՋԵՐՄԱՅԻՆ ԱԼԻՔՆԵՐԻ ԿԱՅՈՒՆՈՒԹՅԱՆ ԽԱԽՏՄԱՆ ՊԱՏՃԱՌՆԵՐԻ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ

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Աչխատանքում ուսումնասիրվում են ֆրոնտալ պոլիմերացման ընթացքում ինջնատարածվող ջերմային ալիջների կայունության խախտման պատճառները: պոլիմերացման ջերմային Ֆրոնտալ պոլիմերագումը ալիքների տարածման ավտոայիջային գործընթաց է։ Ֆրոնտայ պոլիմերացման գործնական իրագործման գյխավոր նախապայման է Հանդիսանում գործընԹացի ընԹացքում տարածվող ջերմային ալիքների կայունուԹյան կորստի պատճառների պարդումը և դրանդ սաՀմանների Հաստատումը: Աշխատանքում ըննարկվում է անցումային չարքի մետաղների Հետ ակրիլամիդի կոմպլեջոների ֆրոնտալ պոլիմերացման ընթացքում իՀայտ եկած անկայունությունների պատճառներից մեկը: Հաչվի առնելով, որ նչված մոնոմերների Համար կայուուԹյան կորուստի և սպինային ռեժիմների առաջացման պատճառ է Հանդիսանում պոլիմերի նստեղման երևուլԹր, ուսումնասիրվել են պոլիմերացվող միջավայրում նանոմասնիկների Հավելումների ազդեզուԹլունը գործընԹազի կայունու-Թյան վրա: Ցուլց է տրվել, որ տվլալ մոնոմերների ֆրոնտալ պոլիմերացման ընԹագջում Հնարավոր է կառավարել դործընԹացի կայունուԹյունը կախված ռեակցիոն միջավայրում նանոմաասնիկների Հավելումների քանակից:

ИССЛЕДОВАНИЕ ПРИЧИН НАРУШЕНИЯ СТАЦИОНАРНОСТИ РАСПРОСТРАНЯЮЩЕЙСЯ ТЕПЛОВОЙ ВОЛНЫ В ПРОЦЕССЕ ФРОНТАЛЬНОЙ ПОЛИМЕРИЗАЦИИ

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В работе исследуются причины нарушения устойчивости самораспространяющихся тепловых волн в процессе фронтальной полимеризации (ФП). ФП – это автоволновый процесс распространения тепловых волн полимеризации. Одним из важнейших факторов практической реализации ФП является необходимость установления причин и границ нарушения устойчивости распространяющихся тепловых волн в процессе ФП. В статье выяснена одна из причин нарушения устойчивости при фронтальной полимеризации комплексов акриламида с переходными металлами. Учитывая, что для указанных мономеров причиной нарушения стабильности и появления спиновых мод является усадка полимера, нами были исследованы добавки наночастиц в полимеризующиеся среды. Показано, что можно регулировать нарушение стабильности при ФП мономеров в зависимости от количества добавок наночастиц.

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