

Stress – Strain Behavior Polymer Blends Of Poly(Vinyl Chloride) And Linear Copolymer Of Ethylene With Butene - 1

Elshod Khakberdiev, Nigmat Ashurov, Shukhrat Sadikov, Nurbek Ashurov

Abstract: In this work, non-polar polyethylene with polar poly(vinyl chloride) is considered as polymer-polymer mixers. Direct mixing of poly(vinyl chloride) and polyolefin's leads to the formation of incompatible mixtures that have weak complex properties. To achieve the compatibility of this mixture, chlorinated polyethylene and a copolymer of polyvinyl chloride with polyethylene were used as a compatibilizer. The elastic-strength properties for various composite mixtures under various exposure and type of compatibilizer were studied. For all components of the mixtures, a special role is noted for compatibilizers capable of causing the extraction and formation of a grafted copolymer of polyvinylchloride (PVC) with polyethylene (PE) in the process of dehydrochlorination, which enhances interfacial adhesion. A positive deviation of the elastic modulus at low polyethylene contents (5-20 wt.%) From the additive curve indicates optimal compatibilization of the mixtures.

Index Terms : additivity, chlorinated polyethylene, compatibilizer, grafted copolymer, linear low-density polyethylene, mechanical properties, polymer blends, polyvinyl chloride.

1 INTRODUCTION

Polyethylene (PE) and polyvinyl chloride (PVC), due to the wide range of operational characteristics, find a variety of applications in almost all industries. Low thermal stability of PVC [1-5], with satisfactory and variable (plasticization) elastic - strength characteristics and, on the contrary, small values of the elastic modulus of PE at high deformation rates and resistance to aggressive environments limit their application. The mixing of these polymers [6-10] makes it possible to strengthen a number of operational characteristics (elastic modulus, glass transition temperature, impact resistance, thermal stability, etc.) depending on the ratio of components in the mixture and their initial characteristics. Of significant interest is the effect of thermal stabilization of polyvinyl chloride (PVC) at low PE contents [10-12] due to interchain crosslinking of macroradicals formed during the mixing of components in the melt in the temperature range 150–180 °C. In a number of works, the problems of incompatibility of PVC and PE, the development of morphology are considered mixtures by varying the speed, temperature and mixing time and ways to optimize morphology by introducing compatibilizers (chlorinated polyethylene (CPE), nitrile and butadiene elastomers, but copolymers of butadiene with styrene and others) [8,13]. Despite conflicting data on the effect of morphology on various properties, chlorinated polyethylene, a copolymer of methyl methacrylate with butyl acrylate and a copolymer of ethylene with methacrylate are recognized as the most effective compatibilizers.

In this work, we investigated the elastic - strength characteristics of polymeric mixtures of PVC with a linear ethylene butene-1 copolymer of various compositions in the presence of two types of compatibilizers - a grafted copolymer of polyvinyl chloride with polyethylene(GC) and chlorinated polyethylene, taking into account the formation of macroradicals and the chemical reaction between the mixed polymers.

2 MATERIALS AND RESEARCH METHODS

In the work we used: PVC suspension grade S-7059-M. TU 2212-012-466963-2008 Manufacturer - Bashkir soda company Joint Stock Company, Russia, the Republic of Bashkortostan and LLDPE grade F-0320, $d = 0.920 \text{ g / cm}^3$, PTR = 2.5 g / 10 min (at a load of 2.16 kgf). Manufacturer - Shurtan gas

chemical complex of the Republic of Uzbekistan; n - dioctyl phthalate (DOP), GOST 8728-88, $M = 390.56 \text{ g / mol}$; colorless oily liquid; $d_{420} = 0.978 \text{ g / cm}^3$; chlorinated polyethylene CPE 3614A (Dow Chemical Co), chlorine content - 36 wt.%; a grafted copolymer of PE-PVC was obtained in an earlier work [14]. Polymer-polymer mixtures were obtained in a Brabender plastograph (Plasticorder Brabender OHGDUISBURG (Germany), at a rotation speed of 50 rpm, a temperature of $180 \pm 5^\circ \text{ C}$, for 15 min.

2.1 Mechanical Properties

Tensile properties: The tensile diagrams of the samples were determined on a universal test machine Instron 3366 (USA) in uniaxial tension mode with a set deformation rate in accordance with the requirements established by ASTM D638-99 "Standard Test Method for the Strength Properties of Plastics." For analysis, at least five samples of the studied material were used, made in the form of double-sided blades 2 mm thick. The strain rate of the samples was 20 mm / min.

2.2 Morphological Studies

The morphology of polymeric mixtures was studied using atomic force (scanning probe microscope Agilent 5500) microscopy at room temperature. Silicon cantilevers with a

- Elshod Khakberdiev, PhD student at the Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan.
- Nigmat Ashurov, D.Sc. in Technical sciences, professor. Head of the laboratory at the Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan.
- Shukhrat Sadikov, PhD in Chemical sciences, leading researcher at the Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan.
- Nurbek Ashurov, PhD in Physical-Mathematical sciences at the Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan.

stiffness of 9.5 N/m and a frequency of 145 kHz were used. The maximum scanning area on AFM on X, Y is 15x15 μm^2 , on Z - 1 μm .

3 RESULTS AND DISCUSSION

During the formation of mixtures in the melt and subsequent cooling, internal stresses arise due to the difference in the thermal expansion coefficients in the zones between the phases around the particles of the dispersed phase, which are responsible for the initiation of microvoids under the influence of external forces. The magnitude of stresses and the level of deformation for the development of this process are determined by the forces of interfacial interaction. Based on these considerations, three stages of deformation [15] of polymer mixtures were determined, pseudo-elastic (stage 1 — small deformation values that determine the elastic modulus), the second stage — exit to the flow process (in the form of increasing stress with a subsequent decrease, or without it - referred to as the limit yield strength) and the third stage — deformation independent of stress (cold flow, orientational crystallization) with an increase or decrease in the angle of inclination of the derivative of stress from deformation. Changes in the morphology of the system at these stages are accompanied by a slight detachment of the matrix from the surface of the filler (stage 1), the formation of micro voids in the matrix, comparable with the particle sizes of the second phase (stage 2), and coalescence of voids, resulting in the destruction of the sample (stage 3). The $\sigma - \epsilon$ curve for the components of the mixture and directly for mixtures in which PVC and PE acts as the matrix and dispersed phase are shown in Fig. 1.

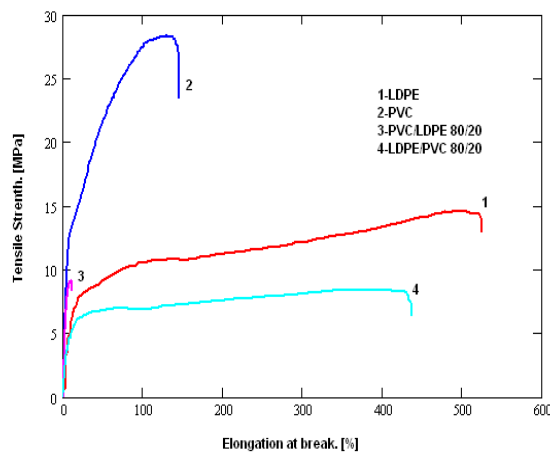


Fig 1. Curves $\sigma - \epsilon$: 1 - PVC; 2 - LLDPE; 3 - PVC / LLDPE 80/20; 4 - LLDPE / PVC 80/20.

As can be seen, these dependences for the initial components of PVC and PE are typical for pseudo-elastic and pseudo-plastic materials, respectively. For the first type of materials, relatively high yield strengths (σ_f) of 26 MPa and small elongation at break (ϵ_b) of 122% are characteristic, while for pseudoplastic PE these values are 12 MPa and 540%, respectively, i.e. polyethylene is inherent all stages of deformation described above. The introduction of polyethylene of various concentrations of 0–50 wt.% into PVC (Fig. 2) significantly changes σ_f and ϵ_b towards a significant decrease.

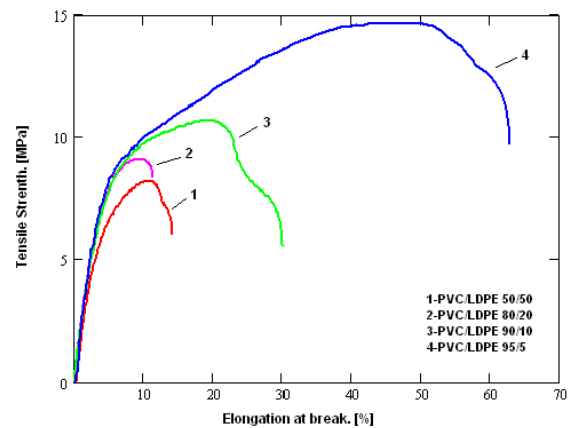


Fig 2. Curves $\sigma - \epsilon$: 1 - PVC / LDPE (50/50); 2 - PVC / LDPE (80/20); 3 - PVC / LDPE (90/10); 4 - PVC / LDPE (95/5).

This picture may be due to a number of reasons - acceleration of PVC degradation (intramolecular crosslinking and chain breaking) and due to the morphology of the mixture, violation of the continuity of the PVC matrix due to incompatibility of the components of the mixture. The form of the $\sigma - \epsilon$ curve for PVC corresponds to stage I with a sharp exit to the yield zone without the stage of plastic flow and subsequent fracture. This is due to the degradation of PVC. The presence of dispersed PE particles, due to the reasons described above, leads to a significant decrease in σ_f and ϵ_b . As the PE content in the mixture increases, σ_f decreases from 26 MPa to 10 MPa, ϵ_b from 122% to 15%. The introduction of a compatibilizer in the form of chlorinated polyethylene (CPE) into compositions with different PE contents in the range of 5-15 wt.% Noticeably affects the shapes of the $\sigma - \epsilon$ curves and the values of σ_f and ϵ_b . For almost all PVC / PE compositions, with the introduction of CPE, the effect of stress redistribution between the matrix and the dispersed phase is observed, which is expressed by a change in the $\sigma - \epsilon$ curve.

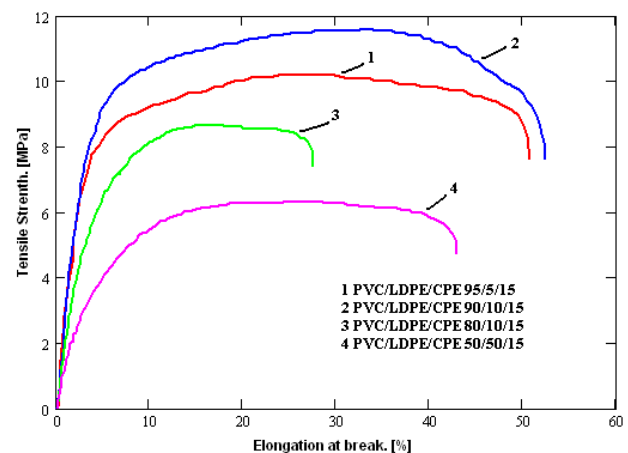


Fig 3. Curves $\sigma - \epsilon$: 1 - PVC / LLDPE / CPE (95/5/15); 2 - PVC / LLDPE / CPE (90/10/15); 3 - PVC / LLDPE / CPE (80/20/15); 4 - PVC / LLDPE / CPE (50/50/15).

Comparison of the $\sigma - \epsilon$ curves for PVC / PE compositions 95/5, 90/10, 80/20, 50/50, wt.% With the introduction of 15 wt.% CPE indicates an improvement in interfacial adhesion compared with mixtures without compatibilizer - the

appearance of the stage deformation, independent of external stress and orientational ordering, requiring a certain increase in the applied stress (Fig. 3.). These processes are most pronounced for the compositions PVC / PE 95/5 and 50/50 wt.% With a content of CPE - 5 wt.% (Fig. 4.)

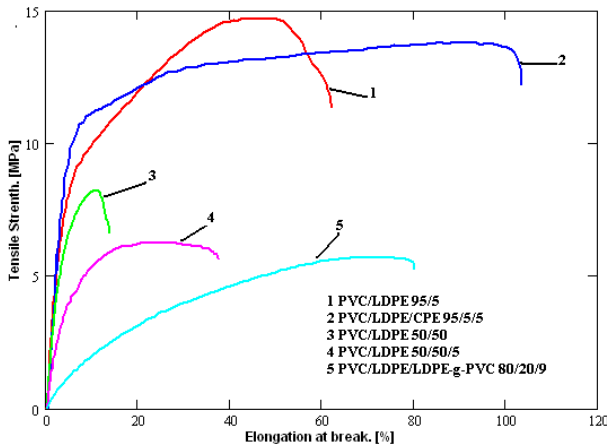


Fig 4. Curves $\sigma - \epsilon$: 1 - PVC / LLDPE (95/5); 2 - PVC / LLDPE / CPE (95/5/5); 3 - PVC / LLDPE (50/50); 4 - PVC / LLDPE / CPE (50/50/5); 5 - PVC / LLDPE / PVC-g-LLDPE (80/20/9).

The composition of PVC / LLDPE - 95/5 with chlorinated PE (5 wt.%) Exhibits good interfacial adhesion and the $\sigma - \epsilon$ curves exhibit combined stages of the onset of flow and a stage of orientational ordering with a delayed process of coalescence of microvoids, which contribute to deformation of the sample with high indicators of stress at the transition stage and elongation at failure (more than 100%). A similar picture is observed for the composition of PVC / LLDPE 50/50 wt.% With 5 wt.% CPE, but with a significantly low voltage when entering the stage of the flow. This result indicates a limited amount of CPE at the interface and poor adhesion between the phases. This situation significantly reduces the voltage required to initiate microvoids at the phase boundary. The enhancement of interfacial adhesion is accompanied by an increase in ϵ_p for almost all PVC / LLDPE compositions as the content of the compatibilizer increases (Table 1). When the PE content is in the range of 5–20 wt.%, This effect is pronounced for the composition of PVC / PE - 95/5 wt.%, For which the increase in ϵ_b is more than 20%. A more than twofold increase in ϵ_p is observed for the composition of PVC / PE - 50/50 wt.% With a CPE content of 15 wt.% With the mixture morphology in the form of two coexisting continuous phases (Fig. 5).

Table 1. The effect of the composition of the mixture on the elastic strength properties.

Name sample	σ Tensile Strength (Maximum load) [MPa]	σ Load at yield strength [MPa]	ϵ Elongation at break [%]	E Young's modulus [MPa]
PVC / PE95/5	14,28±0,71	14,36 ± 0,70	67,53±2,45	287,1±10,30
PVC/PE/CPE 95/5/5	14,73±0,63	14,71 ± 0,67	84,35±9,54	359,7±4,03
PVC/PE/CPE95/5/10	12,71±1,33	12,79 ± 1,32	77,28±16,41	355,3±24,58
PVC/PE/CPE95/5/15	10,22±1,34	10,17 ± 1,29	75,33±10,97	368,5±34,32
PVC / PE 90/10	10,21±0,70	10,32 ± 0,78	31,07±2,12	315,8±4,94
PVC/PE/CPE90/10/5	9,93±0,71	9,93 ± 0,71	32,65±1,76	316,7±8,11
PVC/PE/CPE90/10/10	10,63±1,24	10,64 ± 1,27	35,28±3,74	351,9±14,28
PVC/PE/CPE90/10/15	9,82±0,95	9,87 ± 0,96	53,35±0,49	329,9±20,11
PVC / PE 80/20	8,50±0,14	8,72 ± 0,10	15,71±0,54	254,7±3,49
PVC/PE/CPE80/20/5	10,00±0,47	10,06 ± 0,48	19,48±1,19	282,9±8,17
PVC/PE/CPE80/20/10	9,31±0,20	9,37 ± 0,20	26,84±1,26	262,8±5,61
PVC/PE/CPE80/20/15	8,68±0,16	8,71 ± 0,16	30,65±0,55	259,1±6,66
PVC/PE/PS 80/20/9	5,7±0,03	5,67±0,01	78,81±1,88	24,9±0,51
PVC / PE 50/50	8,14±0,22	8,09 ± 0,21	16,45±0,83	235,3±1,54
PVC/PE/CPE50/50/5	6,96±0,34	6,96 ± 0,35	38,78±3,53	146,1±2,30
PVC/PE/CPE50/50/15	7,36±0,70	7,38 ± 0,71	42,56±1,43	165,5±23,71
PVC/PE/PS50/50/3	8,37±0,47	8,35±0,51	22,13±1,11	214,61±5,09

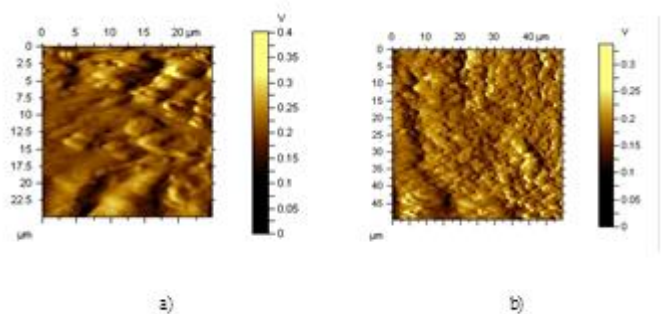


Fig 5. AFM micrograph of PVC/LLDPE blend for various CPE contents (a) 50/50/15, (b) 95/5/15 wt.%.

A completely different picture of the $\sigma - \epsilon$ curves is observed for mixtures with a polyethylene matrix, which also undergoes significant changes when a compatibilizer is introduced in the form of chlorinated polyethylene or a grafted copolymer of PVC and PE (Fig. 6).

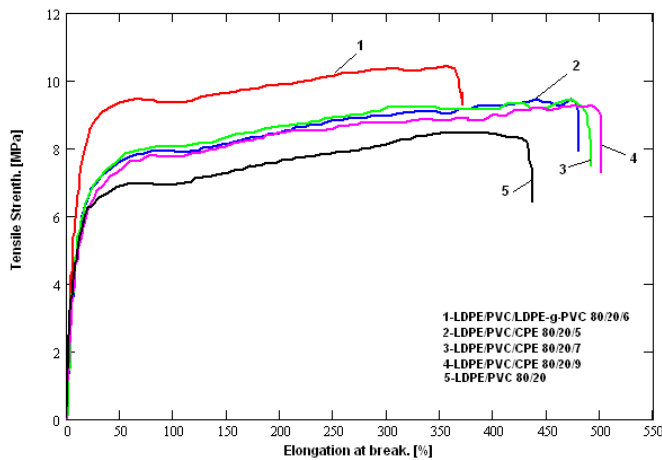


Fig 6. Curves $\sigma - \epsilon$: 1– LLDPE / PVC / LLDPE-g-PVC (80/20/6); 2 - LLDPE / PVC / CPE (80/20/5); 3 - LLDPE / PVC / CPE (80/20/7); 4 - LLDPE / PVC / CPE (80/20/9); 5 - LLDPE / PVC (80/20).

A comparison of the $\sigma - \epsilon$ curves for PVC and the composition of the mixture with a polyethylene matrix (dispersed phase content of 20 wt.%) Shows a significant difference in the deformation processes of these systems. In the first case, catastrophic destruction of the mixture is observed (ϵ_b is 15%) immediately after reaching the stage of fluidity (due to the large-scale formation of microvoids, comparable with the particle sizes of the dispersed phase and their simultaneous detachment from the matrix). For a mixture with a polyethylene matrix, the $\sigma - \epsilon$ curves include all the stages of deformation indicated above, with a deformation interval independent of the applied stress of 50–100% and a subsequent increase in stress to a strain value of more than 400%. Only the presence of sufficient interfacial adhesion can provide an extended zone of the orientation process without large-scale coalescence of microvoids at the interface. The reason for this behavior of the system under consideration, in our opinion, is associated with the formation of a certain amount of grafted copolymer of PE with PVC [16] and chlorinated polyethylene due to the capture of chlorine atoms during dehydrochlorination of PVC with polyethylene macroradicals. The special introduction of CPE from 5 to 9 wt.% During the mixing of the components practically does not change the shape of the $\sigma - \epsilon$ curves, except for a shift of the maximum σ to large deformation values, an increase in the nominal stress value at the stage of orientation processes of the polyethylene matrix and a noticeable increase in ϵ_b by more than 500%. These factors indicate enhanced interfacial adhesion, i.e. about the presence of an optimal concentration, formed and introduced by CPE. The introduction of a compatibilizer in the form of PS with the same concentration complements the enhancement of interfacial adhesion, which is manifested in the shift of the maximum σ to the region of 50% deformation (in PE in the region of 100%) and the stress itself 9.5 MPa (in PE - 8.0 MPa). The difference in the enhancement effect of the CPE

and GC is apparently due to the different localization of the compatibilizer at the phase boundary. It is obvious that, due to the similarity of the structure with the mixed polymers, GC is localized precisely at the interphase boundary, while the CPE is prone to localization in the vicinity of the polyethylene matrix. It is generally accepted that in the ideal case, a number of properties of two-phase systems follow the additive addition of similar properties, taking into account the ratio of components in the mixture (Fig. 7).

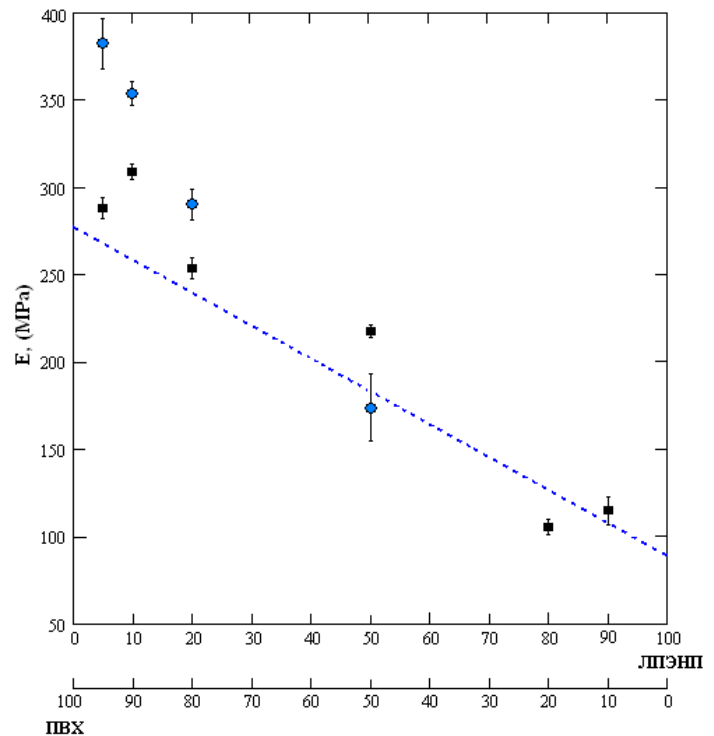


Fig 7. The dependence of the modulus of elasticity of a mixture of PVC / LLDPE on the ratio of components in the presence of compatibilizers.

■ - initial ● - in the presence of CPE

4 CONCLUSION

Based on the model representations of the deformation behavior of polymer mixtures, accompanied by the formation of microvoids (at small deformations), their coalescence at different scales, partially contributing to the deformation of the sample, the $\sigma - \epsilon$ curves were analyzed by the parameters σ_f , ϵ_b and E for a wide range of compositions of the PVC / PE polymer mixture. For compositions with a polyethylene matrix, the special role of compatibilizers introduced from the outside and the formed grafted copolymer of PVC with PE in the process of dehydrochlorination of PVC and introduced chlorinated polyethylene, which enhance the interfacial adhesion, is revealed. This effect is confirmed by the presence of all three strain zones on the $\sigma - \epsilon$ curves. The introduction of two types of compatibilizers from the outside leads to an additional enhancement of interfacial adhesion. Due to the optimal localization at the phase boundary, the grafted PE / PVC copolymer exhibits the best effect of compatibilization. Compositions with a PVC matrix in the entire range of the content of PE as a dispersed phase, due to the enhancement

of interfacial adhesion by the introduction of CPE, have high values of the elastic modulus of mixtures. A positive deviation of the elastic modulus at low PE contents (5–20 wt%) from the additive curve is associated with optimal compatibilization of the mixture and, apparently, partial capture of PVC plasticizer (DOP) by PE macroradicals.

5 ACKNOWLEDGMENT

The authors would like to thank B. Allambergenov, the head of the central laboratory of JV «UZ-KOR GAS CHEMICAL» and his staff for their conducting the physical and mechanical tests of samples.

6 REFERENCES

- [1] T. Hjertberg, & E. M. Sorvik, In Degradation and Stabilization of PVC, ed. E. D. Owen. Elsevier Applied Science Publishers Ltd, London, 1984.
- [2] D. Braun, In Degradation and Stabilisation of Polymers, ed. G. Geuskens. Applied Science Publishers, London, 1975, Ch. 2.
- [3] S.G. Patrick Practical guide to polyvinylchloride. - Rapra Technology Limited, -United Kingdom, 2005. - 164 p.
- [4] J. Wypych, Polyvinyl Chloride Degradation, Elsevier, Amsterdam, 1985.
- [5] K. S. Minsker, S. V. Kolesov, & G. E. Zaikov, Degradation and Stabilization of Vinyl Chloride based Polymers. Pergamon Press, Oxford, 1988.
- [6] D. R. Paul and S. Newman, In Polymer Blends, Ed.Vol. 1, Academic Press, New York (1978).
- [7] P. Bataille, C. Jolicoeur, and H. P. Schreiber, Journal of vinyl technology, 1980, V. 2, №. 4., 218-221.
- [8] J. Prachayawarakorn, J. Khamsri, K. Chaochanchaikul, and N. Sombatsompop, J. Appl. Polym. Sci., 102, 598 (2006).
- [9] S.Maou, A.Meghezzi, N.Nebbache and Y.Meftah, J.Vinyl Addit. Technol., 25, 8(2019).
- [10] C.Thongpin and O. Santavitee, J. Vinyl Addit. Technol., 12, 115 (2006).
- [11] J. C. Arnold and B. Maund, Polym. Eng. Sci., 39, 1242(1999)
- [12] N. Sombatsompop, K. Sungsanit, and C. Thongpin, Polym.Eng. Sci., 44, 487 (2004).
- [13] Zhengping Fang, Guowei Ma, Chao Liu, Chengwei Xu, Journal of Applied Polymer Science., 91, 772 (2004).
- [14] E. O. Khakberdiev, N. Sh. Ashurov, Sh. G. Sadykov, N. R. Ashurov, American journal of research., 6, 215 (2019).
- [15] C. Harrats, T. Benabdallah, G. Groeninckx, R. Jerome, Journal of Polymer Science: Part B: Polymer Physics., 43, 34 (2005).
- [16] K. S. Minsker, Polym. Sci. Ser., B42, 44 (2000).