

PAPER

INFLUENCE OF THERMODYNAMIC COMPATIBILITY ON THE PROPERTIES OF FOOTWEAR SOLE COMPOSITIONS BASED ON POLYOLEFIN DERIVATIVES

S.S. Musaev^{1,*}

¹Bukhara State Technical University, Uzbekistan

* ssmusaev@rambler.ru

Abstract

The article examines the influence of thermodynamic compatibility between various polymers on the deformation and strength properties of footwear sole compositions, with the aim of creating and developing a manufacturing technology for special-purpose shoe soles intended for use in dry and hot climates. Studies conducted on polymer blends indicate a significant impact of their thermodynamic compatibility on both the processing procedure and the properties of the resulting products.

Key words: Shoe sole materials, polymer composition, polymer compatibility, compatibility theory, polymer solubility parameter, compatibilizing agent, polymer melt viscosity.

Introduction

One of the ways to change the values of the properties of polymer compositions is the process of combining several polymers. By changing the composition and ratio of components, the mixture, using the advantages and reducing the disadvantages of individual polymers, it is possible to change the values of the properties of the polymer mixture within wide limits. The values of the properties of the polymer mixture are not always adequate to the composition of the polymers and vary significantly depending on the degree of

dispersity and interaction between the components.

For a long time, the problems of compatibility and technology for manufacturing footwear materials have been solved based on accumulated experience. Work conducted with polymer mixtures indicates a significant influence of their compatibility both on the processing process and on the values of the properties of the resulting products. It was considered that the condition for creating compositions with improved physical and mechanical properties is only their compatibility. At the same time, there are many examples that contradict this statement. This explains the great

Compiled on: February 3, 2026.

Copyright: ©2026 by the authors. Submitted to International Journal of Science and Technology for possible open access publication under the terms and conditions of the [Creative Commons Attribution \(CC BY\) 4.0 license](https://creativecommons.org/licenses/by/4.0/).

interest of researchers in the problems of polymer compatibility [1].

When considering the issue of improving the quality of polymer materials from a new perspective, it becomes clear that it is necessary to create multicomponent polymer systems formed by more than two polymers.

The main challenge in preparing polymer blends is the compatibility of different types of polymers [2,3].

Materials and methods

In this work, polymers with the closest cohesion energies were used, such as suspension polyvinyl chloride and ethylene vinyl acetate copolymer of domestic production.

Polymer compositions were obtained by "thermomechanical" and "thermodynamic" mixing methods under specific conditions in a PLV-651 model mixing chamber of the Brabender plasticorder (Germany).

The technological process and parameters for obtaining polymer blends of elastomer-thermoplastic by "thermomechanical" and "thermodynamic" mixing methods are the "know-how" of manufacturing companies. Therefore, at the exploratory experimental stage, the technology for producing polymer blends was determined.

The selection of these polymers as the primary research subject is attributed to their complex of valuable properties, the ability to produce thermoplastic polymer compositions based on them using "thermomechanical" and "thermodynamic" mixing methods, the possibility of processing them into products using high-performance injection molding equipment, a stable raw material base, and the relatively low cost of these polymers.

Results and discussion

Attempts have been made to establish polymer compatibility based on molecular weight, phase state, chemical structure, and other factors. However, until recently, the factors determining molecular compatibility have not been fully elucidated. This is due to the fact that when working with amorphous polymers, it is difficult to establish not only quantitative compatibility criteria but

also the very fact of compatibility itself. Crystalline polymers offer more opportunities in this regard, as their molecular compatibility should evidently lead to the formation of common crystals whose unit cells incorporate macromolecules of the mixed polymers [4].

It is believed [5] that compatibility is achievable if mutual solubility exists at the level of macromolecule segments of different components. If the phenomenon of mutual solubility is not observed and molecules of different polymers form separate phases, it is said that compatibility is absent.

For many years, the incompatibility of most polymers hindered the creation of useful polymer alloys. The collected experimental data on compatibility formed the basis of compatibility theory developed by Flory, Huggins, and Scott [6].

From the perspective of equilibrium system thermodynamics, the compatibility and incompatibility of a two-component system are determined by the contributions of mixing entropy (ΔS) and mixing enthalpy (ΔH) to the change in Gibbs free energy (ΔG) during mixing.

$$\Delta G = \Delta H - T \Delta S$$

where T is the absolute temperature.

According to the Florey–Hagens–Scott theory, ΔG can be expressed as follows:

$$\Delta G = RTV \left(\frac{V_1}{m_1} \ln V_1 + \frac{V_2}{m_2} \ln V_2 + X V_1 V_2 \right)$$

Where: V – molar volume of the mixed system;

R – gas constant;

V_1, V_2 – volume fractions of polymers 1 and 2;

m_1, m_2 – degrees of polymerization of polymers 1 and 2;

X – interaction parameter between different types of polymers.

For the polymer mixture to be compatible, the condition $\Delta G < 1$ must be met, and for this, ΔH must be a negative quantity, and ΔS must be a positive quantity. In the case of polymers, m_1 and m_2 are large and the term of the equation ΔS practically does not make a significant contribution. Therefore, to fulfill the condition $\Delta G < 1$, ΔH must be less than one.

In the Florey-Hagens-Scott theory, only the upper critical melting point was predicted. Subsequently, the existence of compatible polymer mixtures, as well as the lowest critical melting temperature, was confirmed, and theoretical limits were indicated [7].

The compatibility theory determines that the dominant quantity is the solubility parameter $[\delta]$. Comparing the solubility parameters of polymers allows for the selection of compatible polymer pairs (Table 1).

In the 1930s, Hildebrand [8] observed that the closer the solubility parameters of components are to each other, the higher the probability of their mutual compatibility, and the greater the compatibility of components, the higher the likelihood of obtaining compositions with high strength characteristics. The solubility parameters of polymers are one of the basic thermodynamic properties of substances in general and polymers in particular. Solubility parameters are used to assess the possibility of mutual solubility in multicomponent systems [9-10]. Evidently, knowledge of solubility parameters is of fundamental importance for solving various applied problems [11]. It is particularly noteworthy that expanding the range of polymer materials by blending known components is more cost-effective than the approach of synthesizing new polymers.

Table 1 presents the solubility parameter values of the studied polymers [1].

Polyethylene is a nonpolar polymer with a solubility parameter of $7.7-8.4$ $(\text{cal}/\text{cm}^3)^{1/2}$. Polyvinyl chloride is a polar polymer with a solubility parameter of $9.4-10.1$ $(\text{cal}/\text{cm}^3)^{1/2}$. The difference in solubility parameters between PVC and PE has a high value of $1.7-2.4$ $(\text{cal}/\text{cm}^3)^{1/2}$. Mixing these polymers with each other does not result in a polymer blend with satisfactory properties.

Table 1
Solubility parameter values for polymers

№ п/п	Name Polymer	Value of the solubility parameter δ [[kcal/cm ³] ^{1/2}]
1	Polyvinyl chloride	9.4 – 10.1
2	Polyethylene	7.7-8.4
5	Polyvinyl acetate	9.4 – 9.6
6	SEVA	8.7-9.4

Polyvinyl acetate is a polar polymer that is highly compatible with PVC: the difference in solubility parameters ranges from 0.05 to 0.5 $(\text{cal}/\text{cm}^3)^{1/2}$.

Ethylene-vinyl acetate copolymers with varying vinyl acetate content are obtained by polymerizing ethylene with vinyl acetate under high pressure in the presence of metallocene catalysts. Ethylene-vinyl acetate (EVA) is a copolymer containing 5 to 30 wt.% of vinyl acetate.

The vinyl acetate groups in the SEVA composition are statistically distributed along the length of the copolymer macromolecule, thereby increasing the compatibility of the PVC-SEVA mixture components. The difference in solubility parameters between PVC and SEVA is $0.4-0.7$ $(\text{cal}/\text{cm}^3)^{1/2}$.

By comparing the solubility parameters of polymers, a quantitative assessment of their compatibility was obtained (assuming similar mixing entropy values for all compared pairs).

For a substance with a known heat of vaporization, its solubility parameter was calculated using the formula:

$$\delta = \sqrt{(\Delta H_T - RT) V^{-1}}$$

where: T – experimental temperature;

ΔH_T – molar volume;

R – gas constant.

Small P.A. [6] published a table of molecular strain constants, which allows for the estimation of the solubility parameter based solely on the structural formula of a given compound and its density. Molecular strain constants are additive, meaning that the values of quantities corresponding to the whole object are equal to the sum of the values of quantities corresponding to its parts. Using the additivity method, it is possible to calculate the solubility parameter $[\delta^*]$ of compositions for a mixture of polymers and plasticizers (DOF, DBF, PM-T-1, IM-12A).

Hoy K.L. [13] obtained a set of similar group contributions that differ slightly from Small P.A.'s data [14]. We calculate the solubility parameter δ^* of the composition when introducing different amounts of plasticizer into EVA and PVC.

The calculation of solubility parameters for PVC and SEVA was conducted to theoretically assess the compatibility of PVC/SEVA polymer pairs.

For the polymer mixing process to occur and a homogeneous structure to be obtained, it is necessary that the value $\beta = (\delta_1 - \delta_2)^2$ be minimal,

ideally equal to 0, which can ensure high mechanical properties of the polymer composition.

We calculate β as the difference $(\delta_1 - \delta_2)^2$, where δ_1 is the solubility parameter of PVC; δ_2 is the solubility parameter of SEVA.

The solubility parameter values for the PVC/SEVA mixture and various types of plasticizers are presented in Table 2.

The polymer composition based on PVC and SEVA exhibits the best compatibility when DBP is introduced (the value of β is minimal).

Table 2

Values of parameter β		
П/П	Composition	Parameter β , J/cm ³
1	SEVA/PVC + DOP (according to Small)	0,49
2	SEVA/PVC + DBP (according to Small)	0,22
3	SEVA/PVC + PM-T-1 (according to Small)	0,70
4	SEVA/PVC + DOP (according to Hoy)	0,55
5	SEVA/PVC + DBP (according to Hoy)	0,21
5	SEVA/PVC + PM-T-1 (according to Hoy)	0,77

Having obtained the results of the solubility parameter calculation, it is possible to determine the optimal compatibility region for these polymers. Graphically, this region is represented in Figure 1 as a shaded quadrilateral (the area of best polymer solubility). Using the solubility region obtained, one can determine from the graph the numerical value of the plasticizer amount required for introduction into the PVC and SEVA mixture. This region falls within the range of 60 to 80 parts by weight of plasticizer.

Determining the optimal compatibility region for polymers has demonstrated the practicality of calculating solubility parameters. This is necessary to assess the possibility of mutual dissolution of polymers and, consequently, the potential for obtaining new shoe sole materials.

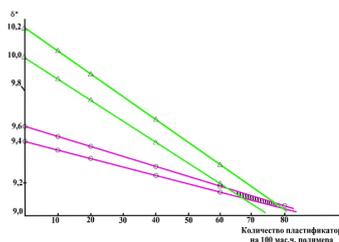


Figure 1. Compatibility region of PVC/SEVA mixture at different DOP content:

1 - solubility parameter of the PVC+DOP mixture according to Hoy;

2 - solubility parameter according to Small;

3 - solubility parameter of the PVC+DOP mixture according to Small;

4 - solubility parameter according to Hoy.

Analyzing the obtained results, the following conclusions can be drawn:

- The assessment of compatibility between the main components of the polymer mixture based on copolymer and thermoplastic with various plasticizers has proven that they are all well compatible. Consequently, all the studied plasticizers (DOF, DBF, PM-T-1) can be used in the production of sole compositions.

- When evaluating the influence of plasticizer quantity on the solubility parameter value, according to the degree of preference, the plasticizers are arranged in the following sequence: DBF, DOF, PM-T-1.

- Considering the high volatility of DBF during processing and its higher cost compared to DOF, we prefer DOF for obtaining polymer compositions.

- All the studied grades of suspension polyvinyl chloride can be used to a greater or lesser extent to obtain sole materials, but the PVC-S-6346M grade is closest to SEVA, while PVC-S-4700 is the most "questionable."

Conclusion

Thus, the study of thermodynamic compatibility's influence on the deformation and strength properties of shoe sole compositions allows for the development of scientific foundations for creating new polymer materials for special footwear soles designed for use in dry and hot climates with a predetermined set of properties. Comparing the solubility parameters of polymers enables the selection of compatible polymer pairs and facilitates the development of new polymer compositions for special-purpose footwear soles.

References

1. Schwartz A.G., Dinzbarg B.N. Combination of Rubbers with Plastics and Synthetic Resins. - Moscow: Khimiya, 2002, pp. 6-20.
2. Moiseev V.V. Thermoplastic Elastomers. - Moscow: Khimiya, 2015, p. 15.
3. Polymer Blends. Edited by D.R. Paul, S. Newman. /Translated from English// - Moscow: Mir, 2001,

- vol.1, p.5, vol.2, p.39.
4. Melnik L.A., Klimova L.V., Berdnik L.I. Determination of polymer compatibility in compositions based on PVC, styrene-butadiene and nitrile-butadiene rubbers. // "Plasticheskie massy," No. 4, 2011, pp. 11-13.
 5. Wu E., Barlow J., Paul D. Compatible blends of vinyl chloride-vinylidene chloride copolymer with poly (methyl acrylate) s. // Malcolm Dole Symposium, Waco, Texas, April 30 - May 1, 1982, "Journal of Polymer Science: Polymer Symposia," 2004, No. 71, pp. 137-150. Sci.: Polym.
 6. Flory P.J. Polymer Chemistry. - Moscow: Khimiya, 1984, Ch. 12-13.
 7. Tory P. New developments in the theory and practice of rubber mixing technology. Proceedings of the 10th Symposium on Rubber Technology. 2000.
 8. Hildebrand J.H. Solubility of Non-Electrolytes. Moscow: GONTI. 1988
 9. Krause S. In: Polymer Blends. Vol.1. Moscow: Mir. 1981. pp.26-144.
 10. Gerasimov V.K. Doctoral Dissertation in Chemical Sciences. Moscow: IPCE RAS. 2013.
 11. Sanchez I. In: Polymer Blends. Vol.1. Moscow: Mir. 1981. pp.145-171.
 12. Kuleznev V.N. Polymer Blends and Alloys (Lecture Notes). - St. Petersburg: Scientific Foundations and Technologies, 2013. - 216 p.
 13. Hoy K.I., Paint Technol., 42, 1979, 76 p.
 14. Small P.A., J. Appl. Chem. 3, 1953, 71
 15. MUSAYEV S. S., SAMIYEVA G. O. OPTIMIZATION OF VALUES OF TECHNOLOGICAL PARAMETERS FOR OBTAINING THERMOPLASTIC POLYMER COMPOSITION FOR BOTTOM SHOES //Leather & Footwear Journal/Revista de Pielarie Incaltaminte. - 2021. - T. 21. - №. 4.
 16. Musaev S., Samieva G. Study of the Resistance of Shoe Sole Compositions to various Aggressive Environments //International Journal. - 2023. - T. 11. - №. 4.
 17. Musaev S., Samiyeva G. Study of the morphology of shoe sole composites based on domestic suspension polyvinyl chloride and ethylene-vinyl acetate copolymer //E3S Web of Conferences. - EDP Sciences, 2023. - T. 390. - C. 05018.