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Enhancement of the Stiffness and Strength of Laminated Polyvinyl Chloride Synthetic Leather

S. M. Rahimian-Koloor, M. Zamani and M. M. Shokrieh*

Abstract

This research aims to improve the mechanical properties of laminated polyvinyl chloride (PVC) with polyurethane (PU) layers. The four samples were fabricated using the knife-coating technique and subjected to thermal and mechanical tests. The sample-1 included four plasticized PVC (P-PVC) layers. The sample-2 and sample-3 specimens involved the suspension PVC (S-PVC) layers with different volume fractions among P-PVC layers, and sample-4 included three PU layers between P-PVC layers. The results indicated that at high temperatures, the plasticizer penetrates from P-PVC layers to S-PVC layers in sample-2 and sample-3, creating an anti-plasticization phenomenon at their interphase. Sample 2 showed a 39% increase in rupture strain, a 23% increase in elastic modulus, and a 29% increase in ultimate tensile strength compared to sample 1. These three parameters of sample-3 improved up to 11%, 63%, and 48%, respectively, while the initial glass transition temperature range (Tg) increased by 1.34 ℃ compared to sample-1. Although the sample-4 showed a 20% reduction in rupture strain compared to the sample-1, it exhibited a significant increase in the other properties. Specifically, the elastic modulus increased by 63%, ultimate tensile strength by 47%, and initial range of Tg by 2.87 ℃.

Keywords: Laminated polyvinyl chloride; Knife-coating technique; Plasticized PVC; Suspension PVC; Polyurethane.

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1. Introduction

Polyvinyl chloride (PVC) is one of the most commonly used polymers worldwide. It is widely used in various industries owing to its desirable electrical properties, chemical resistance, minor flammability, and low manufacturing cost.[1–3] Different industrial sectors, including synthetic leather production, toys market, medical applications, construction, and coating of electric wires, are the primary users of PVC.[4-7]

Nowadays, many studies have been conducted in the field of enhancing the physical and mechanical properties of composites with the help of fillers,[8] bio-fillers,[9] fibers,[10] and new fabrication methods.[11,12] Improving and modifying PVC properties through various additives such as organic and inorganic fillers, plasticizers, heat stabilizers, and lubricants have been extensively investigated.[13,14] The effect of fillers on the properties of PVC resin depends on various factors, including shape, particle content, particle size, aggregate size, surface characteristics, and degree of dispersion in the PVC matrix.[13,15,16] The most common filler used in PVC is calcium carbonate, whose global consumption in polymers exceeds ten million tons per year.[17] Chen *et al*.[18] studied the effect of micro-calcium carbonate particles on PVC. They showed that adding micro-calcium carbonate up at 15 PHR increased the tensile strength and yield stress of PVC composites while adding them at 10 PHR increased its elongation at break.

In an experiment by Chen *et al*.[16], different quantities of nano-calcium carbonate at 35 and 45 nm were added to the rigid PVC matrix. The results indicated that adding 7% nano-calcium carbonate could increase the tensile strength by up to 15% and the elongation by up to four times. Furthermore, adding more than 7% nano-calcium carbonate to the rigid PVC caused the tensile strength and elongation to decrease.[16] Other researchers have also investigated the effect of nano-calcium carbonate on the mechanical, thermal, and rheological properties of PVC resin, demonstrating that increasing the amount of nano-calcium carbonate can increase the flexural modulus and glass transition temperature (Tg).[2,18-21]

To elevate the mechanical properties of PVC, researchers have also investigated the impact of adding glass beads,[6] fly ash,[22-25] silicon dioxide,[7,26,27] montmorillonite,[28,29] talc,[30,31]

Composite Research Laboratory, Center of Excellence in Experimental Solid Mechanics and Dynamics, School of Mechanical Engineering, Iran University of Science and Technology, Tehran, 16846-13114, Iran

**Email:* Shokrieh@iust.ac.ir (M. M. Shokrieh)

and carbon blackto PVC resin.[32-34] Ermis *et al*.[6] examined the effect of glass beads at 5, 10, and 20 wt.% on the mechanical properties and tribology of P-PVC cables used in vehicles. They showed that increasing the number of glass beads in the P-PVC composite causes an increase in the elastic modulus and hardness and a decrease in the tensile strength, rupture strain, coefficient of friction, and wear rate values.

Gohatre *et al*.[22,23] studied the effect of silane-treated fly ash fillers on the mechanical, thermal, and morphological properties of recycled PVC (R-PVC) composites. Results indicated that adding fly ash at 20 wt.% to R-PVC increased the tensile strength and elongation at break. In contrast, adding more than 20 wt.% fly ash reduced the tensile strength and elongation. In addition, increasing the number of fly ash fillers augmented the tensile modulus and hardness of R-PVC composites. Along similar lines, the impact of fly ash particle size on the interfacial interaction and the mechanical properties of fly ash/PVC composite was tested by Khoshnoud and Abu-Zahra.[24] Their findings showed that small-size fly ash particles resulted in better interaction and thus improved the mechanical properties of PVC composite. In a study by Joshi *et al*.[22] the effect of fly ash on the mechanical properties of PVCs was examined. They demonstrated that fly ash fillers do not considerably change the impact resistance of rigid PVCs. Another PVC additive is a plasticizer that adjusts PVCs' mechanical and thermal properties. Plasticizers reduce the interaction and adhesion between PVC chains. Adding a large amount of plasticizer can decrease the elastic modulus and Tg.[5,35-37] P-PVC is generally flexible, and its flexibility significantly depends on the type and the quantity of plasticizer. Some of the common plasticizers used in PVC-related industries are phthalate, trimellitate, adipate, soybean oil, and tertiary fatty amide.[6,38-41]

PVC has paved the way for using plasticizers in polymers and enabled the production of the first thermoplastic-elastomer.[42,43] Some studies have examined the effect of different percentages of plasticizers on the mechanical, thermal, and electrical properties of PVC composites.[44] In some studies, using plasticizers in low quantity yielded an uncommon phenomenon called anti-plasticization.[5,44,45] During this process, small amounts of plasticizer molecules penetrate the PVC chains and reduce the possibility of vibrations and molecular motions of the polymer, thus increasing mechanical properties, including the ultimate strength.[45] The knife-coating technique (KCT) places layers on each other to make PVC-based synthetic leather. However, laminated synthetic leather produced by this method does not have good mechanical properties.

The present study is focused on improving the mechanical properties of PVC-based laminated synthetic leather through a multilayer hybrid system that takes advantage of suspension PVC (S-PVC) and polyurethane (PU). Owing to the suitable interaction between S-PVC and P-PVC and the satisfactory adhesion of PU with P-PVC, this research used S-PVC and PU between P-PVC layers to enhance the mechanical properties of the laminated synthetic leather. The results show that the method presented in this research significantly improves the mechanical properties of laminated synthetic leather. These results are due to the penetration of the plasticizer in the P-PVC layers and the formation of interphase properties between the layers. Also, the interface interaction between PU functional groups and P-PVC chains causes a noticeable increase in elastic modulus and ultimate tensile strength of the synthetic leather. In addition, the DSC test results indicated that using S-PVC and PU layers between P-PVC layers in the described synthetic leathers does not lead to an evident change in the thermal properties, especially Tg.

2. Test method

2.1 Materials and manufacturing method

The present research used PU, S-PVC, and emulsion PVC (E-PVC) to fabricate samples. S-PVC and E-PVC are synthesized as powders with K-values of 65 and 68. The utilized PVC was purchased from Arvand Petrochemical Co., Iran. Also, the PU was obtained as a solution from IMA srl company with the commercial code 1880/25, whose properties are listed in Table 1.[46]

To make P-PVC plastisol, a certain amount of plasticizer (DOP), thermal stabilizer (barium/cadmium/zinc), and internal lubricant were added to E-PVC powder (E-PVC6834). According to Table 2, the PVC resin and additives were weighed using a high-precision balance. The components were mixed at ambient conditions for 10 minutes by a high-shear mechanical mixer at 2000 rpm. The plastisol was passed through a filter to agglomerate particles and separate impurities in the next step. After the filtration stage, the plastisol was vacuumed for one hour at 0.3 bar to remove the air bubbles.

Table 1: Mechanical properties of PU 1880/25 material.

Material	Ultimate tensile strength (MPa)	Rupture strain (%)	Elastic modulus (MPa)
PU 1880/25	32.36	210	19.61

Table 2: Formulation of P-PVC plastisol.

	E-PVC 6834	DOP	Lubricant	Heat stabilizer
Weight ratio (PHR)	100	60	20	5

Table 3: Specifications of specimens.

Specimen name	Description
S-PVC	Suspension PVC with a thickness of 1 mm
Laminate-1	Four layers of P-PVC with a thickness of 0.3 mm in each layer
Laminate-2	Seven-layer composites with four layers of P-PVC with a thickness of 0.3 mm and three layers of S-PVC with a thickness of 0.1 mm (evenly distributed layers)
Laminate-3	Seven-layer composites with four layers of P-PVC with a thickness of 0.2 mm and three layers of S-PVC with a thickness of 0.1 mm (evenly distributed layers)
Laminate-4	Seven-layer composites with four layers of P-PVC with a thickness of 0.2 mm and three layers of PU with a thickness of 0.1 mm (evenly distributed layers)

To prepare the S-PVC solution, the powder (at 25 wt.%) was gradually added to the cyclohexanone solvent.[47] It was then placed under a vacuum for one hour. The next step involved determining the mechanical properties of pure S-PVC. To this end, dumbbell samples (Fig. 1) were prepared for tensile testing. After pouring the S-PVC solution into the mold, the pieces were placed in ambient conditions for 15 days to allow the cyclohexanone solvent to evaporate.

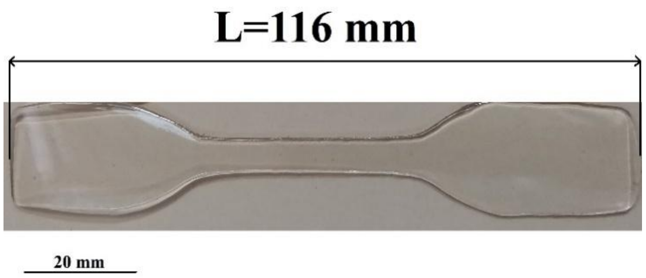

Fig. 1: The dumbbell-shaped specimens of S-PVC.

As shown in Table 3, five different types of samples were fabricated with different stacking sequences. The layers are consecutively placed on each other using KCT. Fig. 2 shows a schematic of the Laminate-1 sample. In its preparation process, the first layer was located as a P-PVC plastisol film on the released paper and left at 140 °C for one minute. Similar to the first layer, the subsequent layers were laid on the previous ones using KCT, and each time, the specimen was placed at 140 °C for one minute. To complete the process of fusion and gelation, the four-layer film with a thickness of 1.2 mm was set in an oven at 190 °C for 10 minutes.

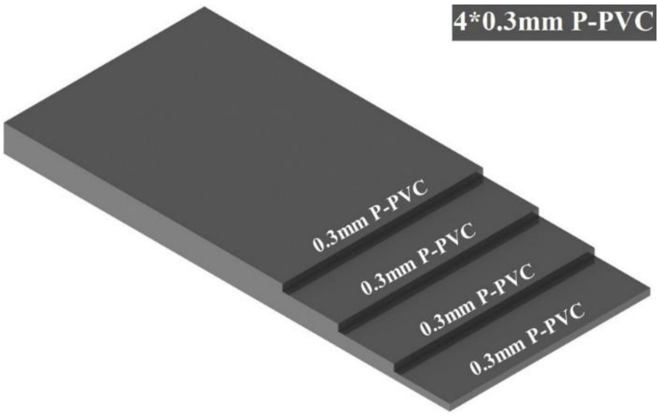

Fig. 2: Schematic of Laminate-1.

Fig. 3 shows a schematic of the Laminate-2 sample. In the first step of preparing Laminate-2, a P-PVC plastisol film with a thickness of 0.3 mm was positioned as the first layer on the released paper using KCT and then heated at 140 °C for one minute. Afterward, a layer of S-PVC solution with a thickness of 0.1 mm was positioned as the second layer on the P-PVC layer (*i.e.*, the first layer). For evaporating the solvent from the S-PVC layer, the sample was placed at a temperature of 80 °C for 30 minutes. Then, the following layers were added to obtain a sample of 7 layers, including three S-PVC layers among four P-PVC layers. Finally, similar to the Laminate-1 sample, the specimen was placed at 190 °C for 10 minutes to complete the fusion and gelation process (Fig. 4).

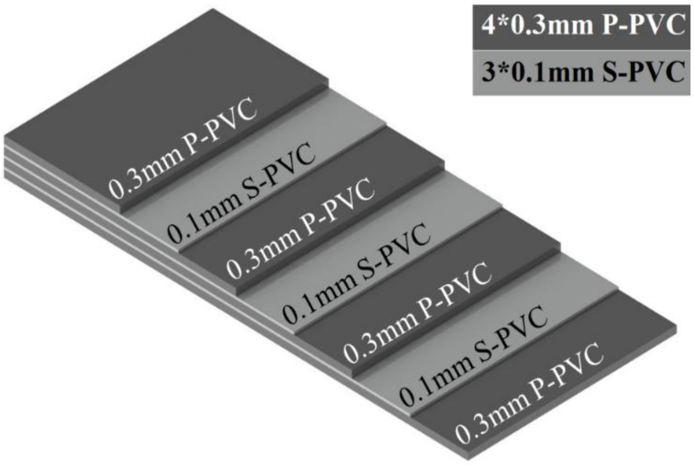

Fig. 3: Schematic of Laminate-2.

The fabrication procedures for Laminate-3 and Laminate-4 samples are similar to that of Laminate-2. To investigate the effect of the S-PVC volume fraction in laminated synthetic leather, the thickness of P-PVC layers in the Laminate-3 sample was set at 0.2 mm. The laminate-4 specimen consisted of 7 layers, including 3 PU layers with a thickness of 0.1 mm, among four layers of P-PVC with a thickness of 0.2 mm. The method of adding PU layers to the Laminate-4 sample is the same as adding S-PVC layers to Laminate-2 and Laminate-3 specimens. After adding each PU layer, the sample was kept at 80 °C for 30 minutes for the PU solvent to evaporate completely. In the last step, all specimens were prepared for the tensile test by cutting them from the laminated synthetic leather with a dumbell-shaped cutting die.

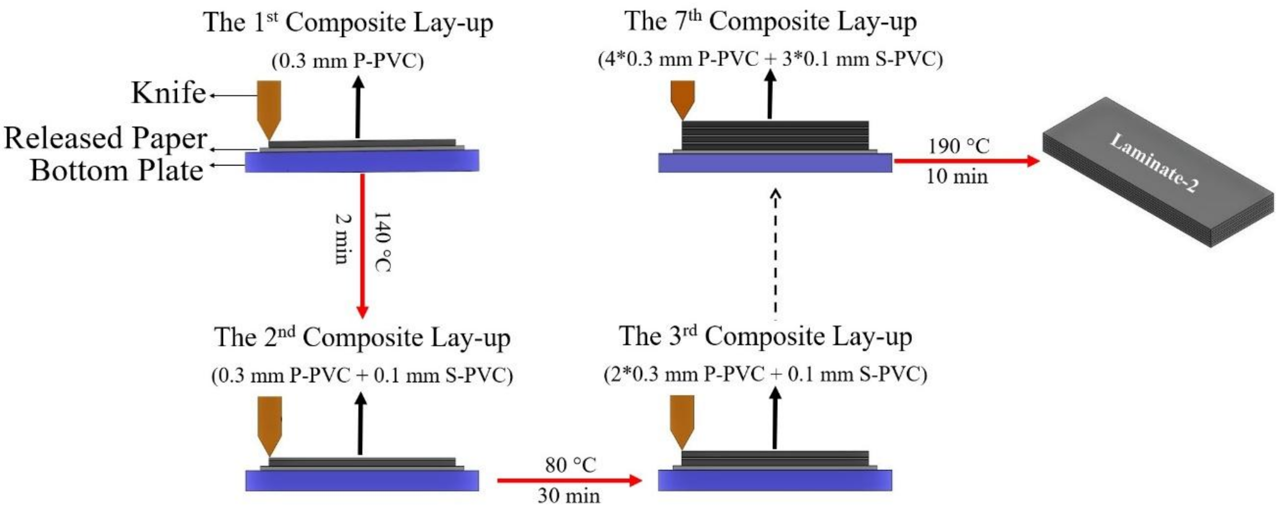

Fig.4: The schematic of the fabrication process.

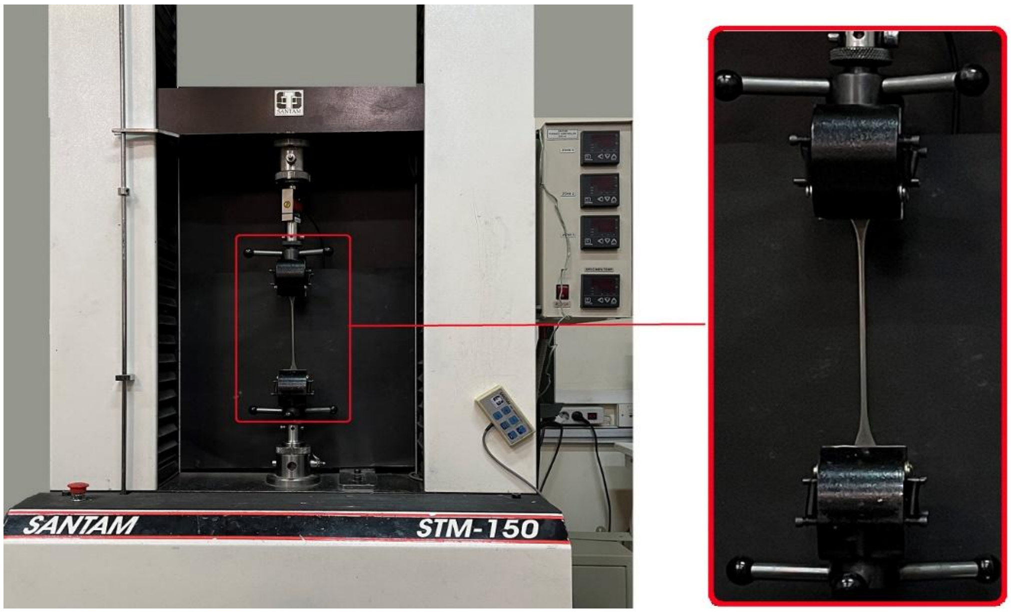

Fig. 5: The tensile testing of a specimen.

2.2 Tests

Tensile test samples were prepared according to the ASTM D638 standard.[48] A Santam STM-150 universal testing machine with a 50 kgf load cell was used for mechanical measurements. As shown in Fig. 5, tensile tests were performed at 50 mm/min speed under ambient conditions and 20% relative humidity. The elastic modulus at 20% strain, ultimate tensile strength, and rupture strain were obtained during these experiments.

Thermal characterization was carried out by differential scanning calorimetry (DSC) with an STD-Q600 DSC machine. According to ASTM E 1640,[49] Laminate-1, Laminate-3, and Laminate-4 samples were prepared, and their temperature reached from 25 °C to 190 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1 Mechanical properties

It is crucial to prevent layers from delamination to improve the strength of laminates. The functional groups in the polymer chains enhance the van der Waals interaction at the layers' interface. Furthermore, the effective interactions between the chains can form reinforced interphase. The interphase formation can decrease the delamination phenomenon and improve the mechanical properties of laminates.[50] Accordingly, in the present study, S-PVC and PU solutions, which interact well with P-PVC, were used between synthetic leather layers. The stress-strain behavior of the samples during the tensile test was measured, as shown in Fig. 6, to determine the specimens' elastic modulus, rupture strain, and ultimate tensile strength.

Table 4 lists important mechanical properties of S-PVC, PU, and laminated composites, such as elastic modulus, rupture strain, and ultimate tensile strength. Fig. 7 shows a cross-section of the Laminate-2 sample.

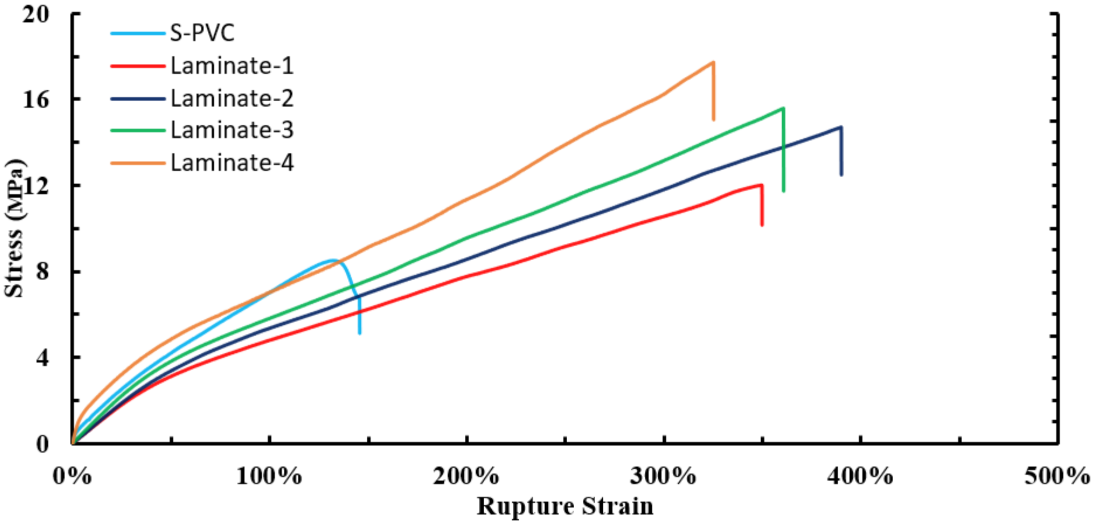

Fig. 6: The stress-strain diagram of dumbbell-shaped specimens under the tensile test.

Table 4: The mechanical properties of samples.

Material	Elastic modulus (MPa)	Rupture strain (%)	Ultimate tensile strength (MPa)	Standard deviation (Elastic modulus/ Rupture strain/ Ultimate tensile strength)
S-PVC	12.17	146%	8.50	(0.09/0.07/0.36)
PU	19.61	210%	32.36	-
Laminate-1	7.25	350%	12.00	(0.19/0.08/0.13)
Laminate-2	7.92	389%	14.71	(0.24/0.14/0.19)
Laminate-3	8.99	361%	15.52	(0.12/0.07/0.10)
Laminate-4	11.82	330%	17.72	(0.17/0.01/0.07)

Fig. 7: The cross-section view of Laminate-2.

According to Table 3, the volume fraction of S-PVC in Laminate-2 and Laminate-3 samples is 0.2 and 0.27, respectively. Moreover, the volume fraction of PU in the Laminate-4 sample equals 0.27. Fig. 8 offers a comparison of the elastic modulus and ultimate tensile strength of the specimens. Compared to Laminate-1, the Laminate-2 sample showed a 9% increase in elastic modulus and a 23% increase in ultimate tensile strength. Compared to Laminate-1, Laminate-3 showed a 24% increase in elastic modulus and a 29% increase in ultimate tensile strength. According to the results, compared to the Laminate-1 sample, the addition of three layers of PU with a volume fraction of 0.27 among the four layers of P-PVC (Laminate-4) increased the elastic modulus and ultimate tensile strength by 63% and 48%, respectively.

Fig. 9 shows the rupture strain for all specimens. The rupture strain for the Laminate-1 sample is 350%. In samples of Laminate-2 and Laminate-3, using S-PVC layers between synthetic leather layers with different volume fractions resulted in a 389% and 361% increase in rupture strain, respectively. Based on the rupture strain values for PU1880 (Table 1), using three PU layers among four P-PVC layers reduced the rupture strain in the Laminate-4 sample by 330%.

According to the results, the plasticizer in P-PVC layers can improve the mechanical properties of Laminate-2 and Laminate-3 samples compared to the Laminate-1 sample. The plastisol in P-PVC layers contains 60 PHR plasticizers, which can migrate from P-PVC layers to S-PVC layers. In the final stage of the fusion and gelation process, when the sample is placed at 190°C, the molecular motion of the particles increases, and small amounts of plasticizer can penetrate from the P-PVC layers to the S-PVC layers. This mechanism is such that a small amount of plasticizer penetrates a portion of the S-PVC layers, forming the interphase region. The anti-plasticization phenomenon occurs in this area due to the small amount of plasticizer used. Two essential factors explain this phenomenon. From a chemical point of view, the presence of plasticizers in small amounts increases the mobility of polymer chains so that the chains possess a more stable chemical structure in van der Waals interactions. The stability

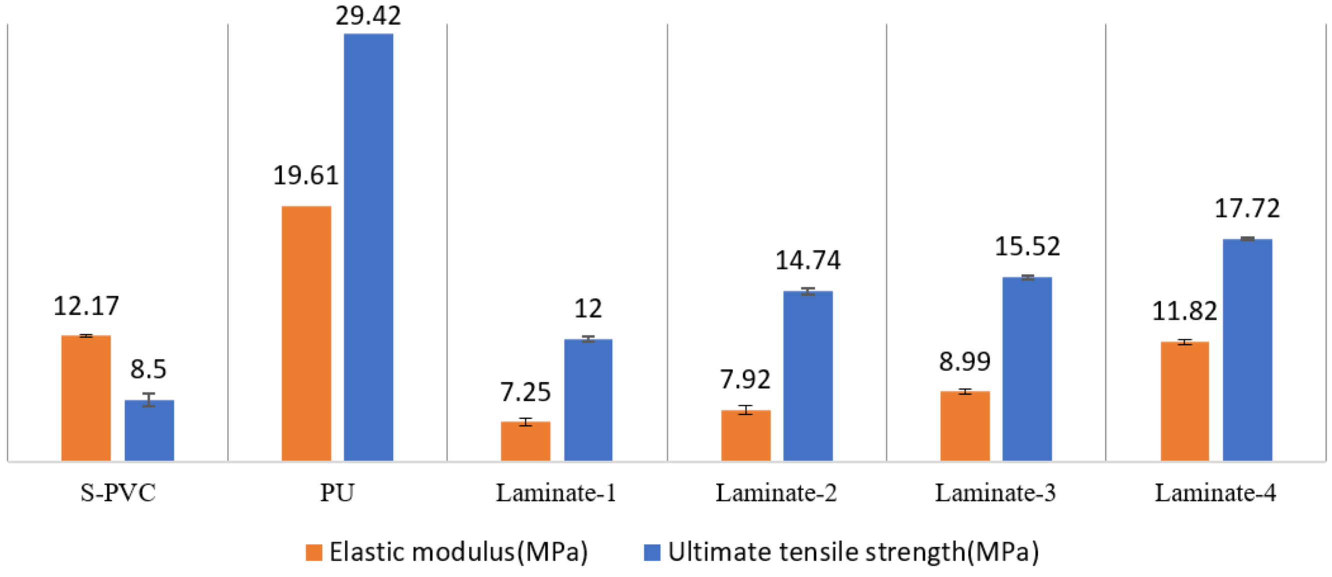

Fig. 8: A comparison of the ultimate tensile strength and elastic modulus properties.

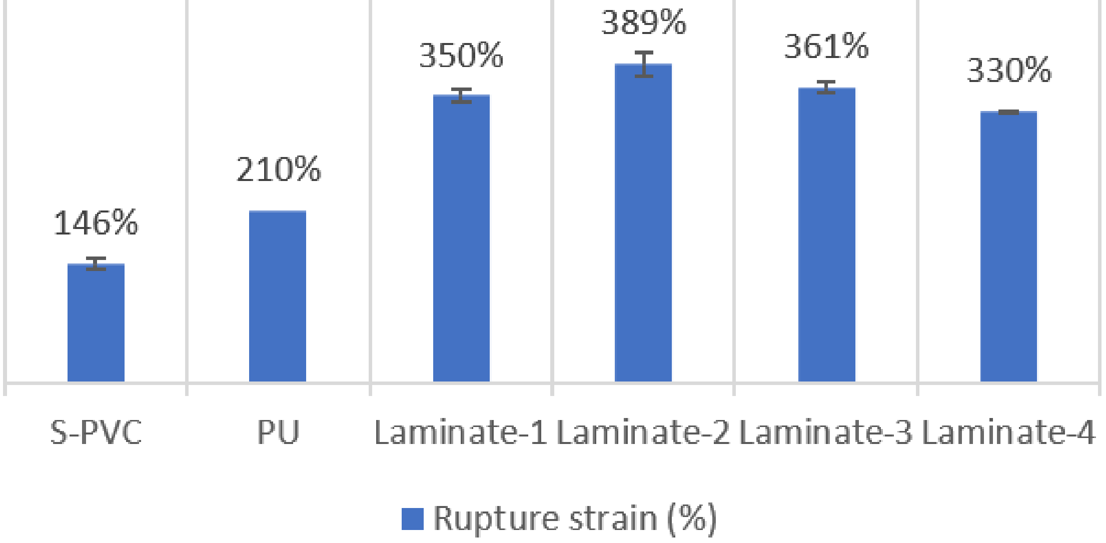

Fig. 9: A comparison of the rupture strain of specimens.

of the chemical structure of the chains reduces the residual stress in the interphase region. It ultimately enhances the mechanical properties of laminated synthetic leather. In addition, small plasticizer molecules reduce the free volume between PVC chains. It thus lowers the possibility of the polymer's vibration and molecular motion, increasing the interphase region's mechanical properties.

The presence of active functional groups in the PU polymer chain leads to a proper interaction between PU and P-PVC layers in the Laminate-4 sample. The interface interaction between PU and P-PVC layers reduces the probability of the delamination phenomenon. In contrast to Laminate-2 and Laminate-3 samples, the plasticizer's penetration and the interphase area's formation do not occur in the Laminate-4 specimen. Since the PU material has a higher elastic modulus, ultimate tensile strength, and lower rupture strain compared to the Laminate-1 sample, the decrease in rupture strain and an increase in elastic modulus and ultimate tensile strength in the Laminate-4 specimen were predictable.

3.2 Differential scanning calorimetry (DSC) analysis

DSC analysis was employed to investigate the effect of S-PVC and PU layers on the thermal properties of laminated synthetic leather. The thermal properties of three types of samples (*i.e.*, Laminate-1, Laminate-3, and Laminate-4) were measured using DSC. Fig. 10 shows the DSC plots of these samples. Moreover, the dashed line on the graph offers the range of Tg in the curves.

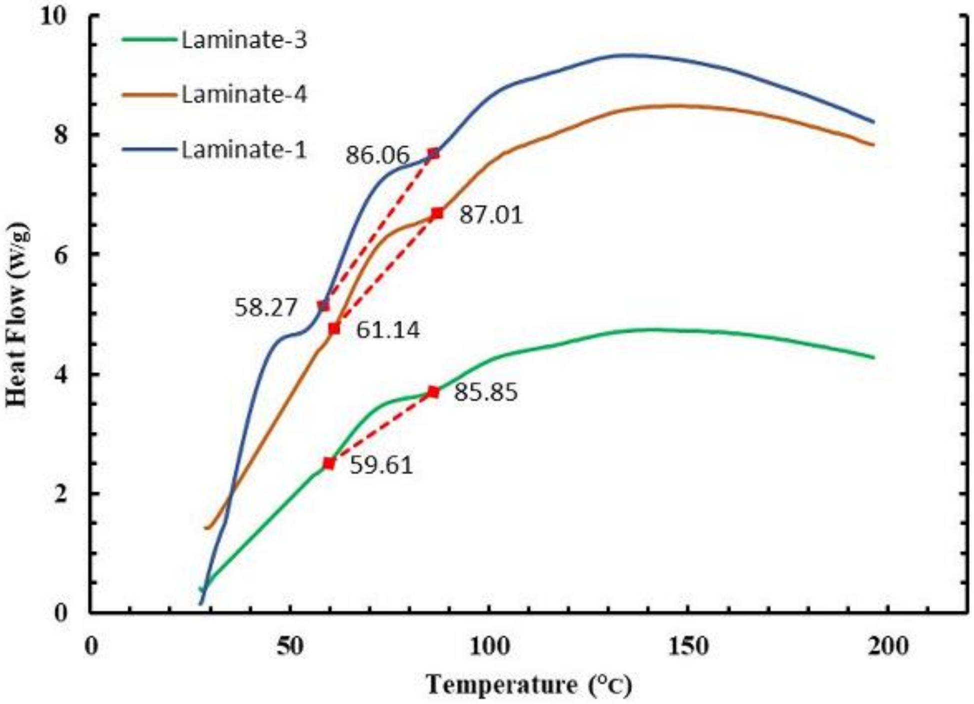

Fig. 10: DSC curves of laminated synthetic leather samples.

Table 5: The initial range of Tg and the Tg of laminated synthetic leather samples.

Material	Initial range of Tg (°C)	Tg (°C)
Laminate-1	58.27	71.52
Laminate-3	59.61	71.90
Laminate-4	61.14	72.36

The plasticizer in the P-PVC composite increases the motion and flexibility of the polymer chains, hence decreasing Tg.[5] On the other hand, due to the absence of a plasticizer and lower mobility and flexibility in S-PVC and PU polymer chains, the Laminate-3 and Laminate-4 samples had a slight increase in Tg values and initial Tg range compared to the Laminate-1 sample. Table 5 shows the Tg values and initial Tg range for the Laminate-1, Laminate-3, and Laminate-4 samples.

4. Conclusion

Producing laminated synthetic leather made of P-PVC and improving its mechanical properties using the KCT may raise numerous challenges. Considering some problems, such as limitations in the selection of additives to achieve desirable mechanical properties in the synthetic leather industry, the present study offered a novel idea to improve the mechanical properties of laminated synthetic leather using PU and S-PVC layers.

To this end, tensile and DSC tests were conducted to investigate the mechanical and thermal behavior of a laminated synthetic leather reinforced with some intermediate layers of PU and S-PVC compared to its P-PVC-laminated counterpart. The interaction between the layers beneficially affects the mechanical behavior of multilayer samples. Therefore, in the current research, S-PVC and PU layers, whose types of interaction with P-PVC are different, were used to boost the mechanical properties of laminated synthetic leather. The main results are summarized as follows:

This study showed that a small amount of plasticizer in PVC chains causes anti-plasticization. At 190°C, the plasticizer can migrate from P-PVC layers to S-PVC layers due to increased molecular motion. The migration of a small quantity of plasticizer from P-PVC to S-PVC layers improves interphase properties between the layers. The interphase formed causes a better binding of the layers and the superiority of the mechanical properties of laminated synthetic leather with the S-PVC intermediate layers compared to that of S-PVC material and P-PVC laminates.

The weight percentage of S-PVC in the Laminate-3 sample is higher than that in the Laminate-2 specimen. The experimental results showed that the Laminate-3 sample has a higher elastic modulus and ultimate tensile strength than the Laminate-2 sample. This difference is attributed to the larger size and effect of the interphase area in the Laminate-3 sample compared to the Laminate-2 specimen.

In the Laminate-4 sample with PU intermediate layer, as opposed to Laminate-2 and Laminate-3 samples, the plasticizer migration from P-PVC layers does not happen. In this laminate, the delamination is reduced due to active functional groups in the PU polymer chain and the interfacial interaction of the layers.

By comparing the mechanical properties of the Laminate-4 sample with those of the Laminate-1 specimen, one concludes that using PU1880 layers between the layers of the synthetic leather can significantly increase its elastic modulus and tensile strength. Also, owing to the lower rupture strain of PU1880 compared to that of P-PVC, the Laminate-4 sample had a lower rupture strain than Laminate-1.

DSC test results showed that implementing S-PVC and PU layers among P-PVC layers in laminated synthetic leathers does not significantly modify their thermal properties, especially Tg.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] L. Madaleno, J. Schjødt-Thomsen, J. C. Pinto, Morphology, thermal and mechanical properties of PVC/MMT nanocomposites prepared by solution blending and solution blending+melt compounding, *Composites Science and Technology*, 2010, **70**, 804-814, doi: 10.1016/j.compscitech.2010.01.016.

[2] I. Bonadies, M. Avella, R. Avolio, C. Carfagna, M. E. Errico, G. Gentile, Poly(vinyl chloride)/$CaCO_3$ nanocomposites: Influence of surface treatments on the properties, *Journal of Applied Polymer Science*, 2011, **122**, 3590-3598, doi: 10.1002/app.34770.

[3] I. Janajreh, M. Alshrah, S. Zamzam, Mechanical recycling of PVC plastic waste streams from cable industry: A case study, *Sustainable Cities and Society*, 2015, **18**, 13-20, doi: 10.1016/j.scs.2015.05.003.

[4] B. Liu, A. S. Desai, X. Sun, J. Ren, H. M. Pathan, V. Dabir, N. Bhagat, An overview of sustainable biopolymer composites in sensor manufacturing and smart cities, *Advanced Composites and Hybrid Materials*, 2024, **7**, 146.

[5] B. L. Shah, V. V. Shertukde, Effect of plasticizers on mechanical, electrical, permanence, and thermal properties of poly(vinyl chloride), *Journal of Applied Polymer Science*, 2003, **90**, 3278-3284, doi: 10.1002/app.13049.

[6] K. Ermis, H. Unal, M. Gunay, Glass bead effects on tribological and mechanical properties of plasticized polyvinyl chloride cable used in vehicles as a filler, *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 2021, **235**, 2432-2439, doi: 10.1177/13506501211001155.

[7] M. Syabani, I. N. A. Amaliyana, I. Hermiyati and Y. I. Supriyatna, Silica from geothermal waste as reinforcing filler in artificial leather, *Key Engineering Materials*, 2020, **849**, 78-83, doi: 10.4028/www.scientific.net/KEM.849.78.

[8] H. Zhu, X. Liu, H. Bai, T. Yang, Antiferroelectric nano-heterostructures filler for improving energy storage performance of PVDF-based composite films, *Chemical Engineering Journal*, 2024, **479**, 147572, doi: 10.1016/j.cej.2023.147572.

[9] S. Kowshik, U. S. Rao, S. Sharma, P. Hiremath, R. Prasad K. S., N. Naik, R. Bhat, K. Kasipandian, Mechanical properties of eggshell filled non-post-cured and post-cured GFRP composites: a comparative study, *ES Materials & Manufacturing*, 2023, **22**, 1043, doi: 10.30919/esmm1043.

[10] S. R. Koloor, A. Karimzadeh, M. R. Abdullah, M. Petrů, N. Yidris, S. M. Sapuan, M. N. Tamin, Linear-nonlinear stiffness responses of carbon fiber-reinforced polymer composite materials and structures: a numerical study, *Polymers*, 2021, **13**, 344, doi: 10.3390/polym13030344.

[11] J. Mlýnek, S. S. Rahimian Koloor, T. Martinec, M. Petrů, Fabrication of high-quality straight-line polymer composite frame with different radius parts using fiber winding process, *Polymers*, 2021, **13**, 497, doi: 10.3390/polym13040497.

[12] S. P. Parida, D. Mishra, R. L. Padhy, P. C. Jena, S. R. Das, A. A. Basem, D. Dhupal, A. Elsheikh, Effect of alkali treatment on mechanical and buckling behaviour of natural fiber reinforced composite cylinder, *ES Materials & Manufacturing*, 2024, **24**, 1161, doi: 10.30919/esmm1161.

[13] X. Xie, Q. Liu, R. K. Li, X. Zhou, Q. Zhang, Z. Yu, Y. Mai, Rheological and mechanical properties of PVC/$CaCO_3$ nanocomposites prepared by *in situ* polymerization, *Polymer*, 2004, **45**, 6665-6673, doi: 10.1016/j.polymer.2004.07.045.

[14] W. H. Awad, G. Beyer, D. Benderly, W. L. Ijdo, P. Songtipya, M. del Mar Jimenez-Gasco, E. Manias, C. A. Wilkie, Material properties of nanoclay PVC composites, *Polymer*, 2009, **50**, 1857-1867, doi: 10.1016/j.polymer.2009.02.007.

[15] N. Yarahmadi, I. Jakubowicz, T. Hjertberg, The effects of heat treatment and ageing on the mechanical properties of rigid PVC, *Polymer Degradation and Stability*, 2003, **82**, 59-72, doi: 10.1016/S0141-3910(03)00163-0.

[16] N. Chen, C. Wan, Y. Zhang, Y. Zhang, Effect of nano-$CaCO_3$ on mechanical properties of PVC and PVC/Blendex blend, *Polymer Testing*, 2004, **23**, 169-174, doi: 10.1016/S0142-9418(03)00076-X.

[17] Y. He, Z. Han, J. Ren, H. Hou, D. Pan, An overview of flexible sensing nanocomposites, *Advanced Composites and Hybrid Materials*, 2024, **7**, 142, doi: 10.1007/s42114-024-00954-y.

[18] C. H. Chen, C. C. Teng, S. F. Su, W. C. Wu, C. H. Yang, Effects of microscale calcium carbonate and nanoscale calcium carbonate on the fusion, thermal, and mechanical characterizations of rigid poly(vinyl chloride)/calcium carbonate composites, *Journal of Polymer Science Part B: Polymer*

Physics, 2006, **44**, 451-460, doi: 10.1002/polb.20721.

[19] X. Zeng, J. Chen, G. Wang, Study on the toughened pvc blends with nano-$CaCO_3$ particles and elastic cpe particles, *Acta Polymerica Sinica*, 2002, **33**, 738-741.

[20] D. Wu, X. Wang, Y. Song, R. Jin, Nanocomposites of poly(vinyl chloride) and nanometric calcium carbonate particles: Effects of chlorinated polyethylene on mechanical properties, morphology, and rheology, *Journal of Applied Polymer Science*, 2004, **92**, 2714-2723, doi: 10.1002/app.20295.

[21] S. Sun, C. Li, L. Zhang, H. L. Du, J. S. Burnell-Gray, Interfacial structures and mechanical properties of PVC composites reinforced by $CaCO_3$ with different particle sizes and surface treatments, *Polymer International*, 2006, **55**, 158-164, doi: 10.1002/pi.1932.

[22] O. K. Gohatre, M. Biswal, S. Mohanty, S. K. Nayak, Effect of silane treated fly ash on physico-mechanical, morphological, and thermal properties of recycled poly(vinyl chloride) composites, *Journal of Applied Polymer Science*, 2021, **138**, 50387, doi: 10.1002/app.50387.

[23] O. K. Gohatre, M. Biswal, S. Mohanty, S. K. Nayak, Study on thermal, mechanical and morphological properties of recycled poly(vinyl chloride)/fly ash composites, *Polymer International*, 2020, **69**, 552-563, doi: 10.1002/pi.5988.

[24] P. Khoshnoud, N. Abu-Zahra, The effect of particle size of fly ash (FA) on the interfacial interaction and performance of PVC/FA composites, *Journal of Vinyl and Additive Technology*, 2019, **25**, 134-143, doi: 10.1002/vnl.21633.

[25] P. S. Joshi, D. S. Marathe, Experimental investigation of mechanical properties of impact modified polyvinyl chloride-fly ash composites, *Journal of Minerals and Materials Characterization and Engineering*, 2019, **7**, 34-47, doi: 10.4236/jmmce.2019.71003.

[26] D. Edison Selvaraj, R. Vijayaraj, U. Satheeshwaran, J. Nancy, C. Pugazhendhi Sugumaran, M. Raj Kumar, J. Ganesan, S. Geethadevi, S. Dinesh Kumar, Experimental investigation on electrical and mechanical characteristics of PVC cable insulation with silica nano filler, *Applied Mechanics and Materials*, 2015, **749**, 159-163, doi: 10.4028/www.scientific.net/amm.749.159.

[27] M. Conradi, A. Kocijan, M. Zorko, I. Jerman, Effect of silica/PVC composite coatings on steel-substrate corrosion protection, *Progress in Organic Coatings*, 2012, **75**, 392-397, doi: 10.1016/j.porgcoat.2012.07.008.

[28] N. Yarahmadi, I. Jakubowicz, T. Hjertberg, Development of poly(vinyl chloride)/montmorillonite nanocomposites using chelating agents, *Polymer Degradation and Stability*, 2010, **95**, 132-137, doi: 10.1016/j.polymdegradstab.2009.11.043.

[29] H. Petersen, Plasticized PVC Nanocomposites–the Effect of Montmorillonite Treatment and Processing Conditions on Material Properties, Chalmers Tekniska Hogskola (Sweden), 2017.

[30] D. Lee, S. Kim, B. J. Kim, S. J. Chun, Q. Wu, Effect of nano-CaCO 3 and talc on property and weathering performance of PP composites, *International Journal of Polymer Science*, 2017, **2017**, 1-9, doi: 10.1155/2017/4512378.

[31] B. S. Tuen, A. Hassan, A. Abu Bakar, Mechanical properties of talc- and (calcium carbonate)-filled poly(vinyl chloride) hybrid composites, *Journal of Vinyl and Additive Technology*, 2012, **18**, 76-86, doi: 10.1002/vnl.20280.

[32] C. H. Chen, H. C. Li, C. C. Teng, C. H. Yang, Fusion, electrical conductivity, thermal, and mechanical properties of rigid poly(vinyl chloride) (PVC)/carbon black (CB) composites, *Journal of Applied Polymer Science*, 2006, **99**, 2167-2173, doi: 10.1002/app.22656.

[33] A. L. G. Saad, H. A. Aziz, O. I. H. Dimitry, Studies of electrical and mechanical properties of poly(vinyl chloride) mixed with electrically conductive additives, *Journal of Applied Polymer Science*, 2004, **91**, 1590-1598, doi: 10.1002/app.13239.

[34] I. Islam, S. Sultana, S. Kumer Ray, H. Parvin Nur, M. T. Hossain, W. Md. Ajmotgir, Electrical and tensile properties of carbon black reinforced polyvinyl chloride conductive composites, *C*, 2018, **4**, 15, doi: 10.3390/c4010015.

[35] H. B. Pyeon, J. E. Park, D. H. Suh, Non-phthalate plasticizer from camphor for flexible PVC with a wide range of available temperature, *Polymer Testing*, 2017, **63**, 375-381, doi: 10.1016/j.polymertesting.2017.08.029.

[36] M. A. Mohamed, A. S. Ammar, Quantitative analysis of phthalates plasticizers in traditional Egyptian foods (koushary and foul medams), black tea, instant coffee and bottled waters by solid phase extraction-capillary gas chromatography-mass spectroscopy, *American Journal of Food Technology*, 2008, **3**, 341-346, doi: 10.3923/ajft.2008.341.346.

[37] J. Liu, Y. Tao, K. Zhou, Y. Shi, X. Feng, G. Jie, R. K. K. Yuen, Y. Hu, The influence of typical layered inorganic compounds on the improved thermal stability and fire resistance properties of polystyrene nanocomposites, *Polymer Composites*, 2017, **38**, 23792, doi: 10.1002/pc.23792.

[38] S. Rogalsky, O. Tarasyuk, A. Vashchuk, V. Davydenko, O. Dzhuzha, S. Motrunich, T. Cherniavska, Oleksii Papeikin, L. Bodachivska, J. F. Bardeau, Synthesis and evaluation of N, N-dibutylundecenamide as new eco-friendly plasticizer for polyvinyl chloride, *Journal of Materials Science*, 2022, **57**, 6102-6114, doi: 10.1007/s10853-022-07006-0.

[39] H. Hosney, B. Nadiem, I. Ashour, I. Mustafa, A. El-Shibiny, Epoxidized vegetable oil and bio-based materials as PVC plasticizer, *Journal of Applied Polymer Science*, 2018, **135**, 46270, doi: 10.1002/app.46270.

[40] G. Malarvannan, M. Onghena, S. Verstraete, E. van Puffelen, A. Jacobs, I. Vanhorebeek, S. C. A. T. Verbruggen, K. F. M. Joosten, G. Van den Berghe, P. G. Jorens, A. Covaci, Phthalate and alternative plasticizers in indwelling medical devices in pediatric intensive care units, *Journal of Hazardous Materials*, 2019, **363**, 64-72, doi: 10.1016/j.jhazmat.2018.09.087.

[41] F. Chiellini, M. Ferri, A. Morelli, L. Dipaola, G. Latini, Perspectives on alternatives to phthalate plasticized poly(vinyl chloride) in medical devices applications, *Progress in Polymer Science*, 2013, **38**, 1067-1088, doi: 10.1016/j.progpolymsci.2013.03.001.

[42] N. Kinjo, T. Nakagawa, Antiplasticization in the slightly plasticized poly(vinyl chloride), *Polymer Journal*, 1973, **4**, 143-

153, doi: 10.1295/polymj.4.143.

[43] S. L. Brous, W. L. Semon, Koroseal A new plastic some properties and uses, *Industrial & Engineering Chemistry*, 1935, **27**, 667-672, doi: 10.1021/ie50306a016.

[44] A. I. Al-Mosawi, K. Marossy, C. Kónya, Effect of plasticizer percentage on thermal properties of plasticised PVC, *Elixir International Journal*, 2018, **117**, 50509-50511, doi: 10.6084/m9.figshare.12567878.

[45] L. Mascia, Y. Kouparitsas, D. Nocita, X. Bao, Antiplasticization of polymer materials: structural aspects and effects on mechanical and diffusion-controlled properties, *Polymers*, 2020, **12**, 769, doi: 10.3390/polym12040769.

[46] A. Piccirilli, Ottimizzazione del processo di gestione delle modifiche della distinta base prodotto il caso IMA SpA, 2022.

[47] N. Gizli, Ç. Sanem, M. Demircioğlu, Characterization of poly(vinylchloride) (PVC) based cation exchange membranes prepared with ionic liquid, *Separation and Purification Technology*, 2012, **97**, 96-107, doi: 10.1016/j.seppur.2012.02.028.

[48] A. International, Standard test method for tensile properties of plastics, ASTM International, 2014.

[49] A. International, Standard test method for the glass transition temperature by dynamic mechanical analysis. ASTM International, 2013.

[50] S. R. Koloor, S. M. Rahimian-Koloor, A. Karimzadeh, M. Hamdi, M. Petrů, M. N. Tamin, Nano-level damage characterization of graphene/polymer cohesive interface under tensile separation, *Polymers*, 2019, **11**, 1435, doi: 10.3390/polym11091435.

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