



Butadiene-acrylonitrile elastomers as PVC modifiers

M. Rojek, J. Stabik*

Division of Metal and Polymer Materials Processing,
Institute of Engineering Materials and Biomaterials, Silesian University of Technology,
ul. Konarskiego 18a, 44-100 Gliwice, Poland

* Corresponding author: E-mail address: jozef.stabik@polsl.pl

Received 14.04.2006; accepted in revised form 25.01.2007

ABSTRACT

Purpose: The purpose of the paper is to present the results of research programme on influence of acrylonitrile-butadiene copolymers on plasticized polyvinylchloride compounds used as window gasket material.

Design/methodology/approach: Short review concerning application of modified plasticized PVC compounds as gasket material was presented. In experimental part two types of acrylonitrile-butadiene copolymers were used as elastomeric plasticizers for PVC. Formulations with fifteen different levels of elastomeric modifiers content (up to 25% by weight) were prepared and tested. As reference formulations three commercial compounds were additionally tested. Shore hardness, short-term and long-term elastic recovery, tensile strength, elongation at break and migration of plasticizers from gasket material to unplasticized PVC were searched.

Findings: Incorporation of acrylonitrile-butadiene copolymers into PVC enhanced many properties essential for its application as window gasket material. The most important changes occurred for long-term and short term elastic recovery, tensile strength and elongation at break. At the same time addition of these butadiene-acrylonitrile elastomers did not change migration of other plasticizers contained in gasket material into rigid PVC in being in contact with gasket. Obtained results showed that among tested compounds best properties as gasket material exhibited plasticized PVC with 23% of acrylonitrile-butadiene copolymer Chemigum P83. Reference commercial formulations exhibited worse performance properties than new compounds with this acrylonitrile-butadiene copolymer.

Practical implications: Research programme allowed to elaborate plasticized PVC compounds modified with acrylonitrile-butadiene copolymer that can be industrially applied for PVC window gaskets.

Originality/value: Obtained results are of scientific and practical value. Research programme allowed to investigate the influence of elastomeric modifiers on plasticized PVC properties. Research results are also of practical importance.

Keywords: Engineering polymers; PVC compounds; Mechanical properties; Window sealing

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Windows and doors with panes play very important role in a civil engineering as a barrier shielding building rooms from many harmful outside influences. One of the most widely applied design

solutions are double glazed windows with unplasticized PVC profiles as gaskets. To achieve the best barrier properties door and window designers apply more and more sophisticated window profile's cross-sections and panes with different inert gases inside and apply advanced materials for all components [1,2].

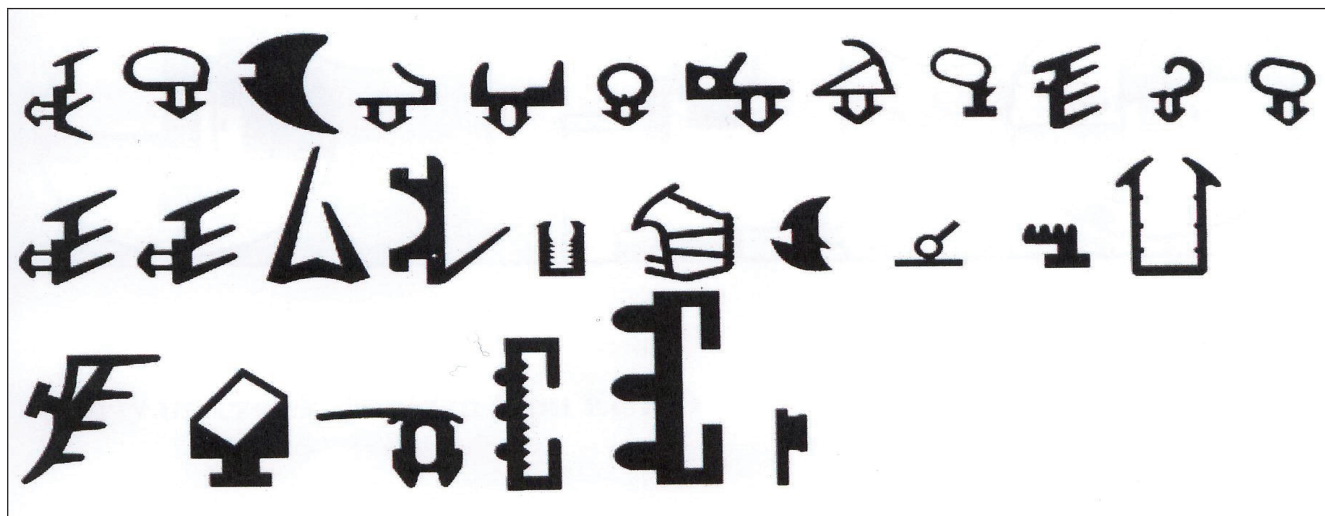


Fig. 1. Typical cross-sections of profiles for window gaskets [1]

But almost equally important for window performance are gaskets, which prevent penetration of cold or hot air, fine dust particles, water and water vapour and sounds into the building. Gaskets between panes and window profiles work in static conditions but gaskets between inner and outer window or door profiles work in more demanding dynamic conditions. Window and door gaskets are produced as profiles by extrusion technology. They possess many different and in many cases very complicated cross-sections and very narrow dimensional tolerances. To assure good sealing properties gasket's surface ought to be very smooth without any surface imperfections. Fig. 1 presents examples of cross-section of profiles for window gaskets [3]. To assure long-term exploitation of gaskets they should be applied in such a manner that they are not exposed or minimally exposed to direct influence of UV radiation, heat, freezing and ice. Fig. 2 shows cross-section of one of modern window profiles with arrows indicating gaskets.

Good window gaskets should fulfil many performance requirements. Among them the most important are:

- tightness under the wind pressure;
- tightness after many cycles of opening and closing of window;
- resistance to atmosphere in the temperature range from 243K to 333K (minus 30°C to plus 60°C);
- resistance to sunlight and ozone;
- resistance to detergents and other cleaning agents;
- good elastic recovery after long time of compression;
- very high elastic deformation,
- zero or low migration of plasticizers contained in gasket into profile.

Because of these criteria window gaskets are produced from different types of high performance elastomers. Most popular gasket materials applied for PVC windows include [4]:

a) vulcanized elastomers based on matrix materials such as:

- ethylene-propylene copolymer (EPDM);
- nitrile (NBR);
- neoprene;
- silicon;

b) thermoplastic compounds based on elastomers such as:

- ethylene-propylene copolymer (EPDM);
- nitrile (NBR);
- styrene-ethylene copolymer (SEBS);
- chlorinated polyethylene (CPE).

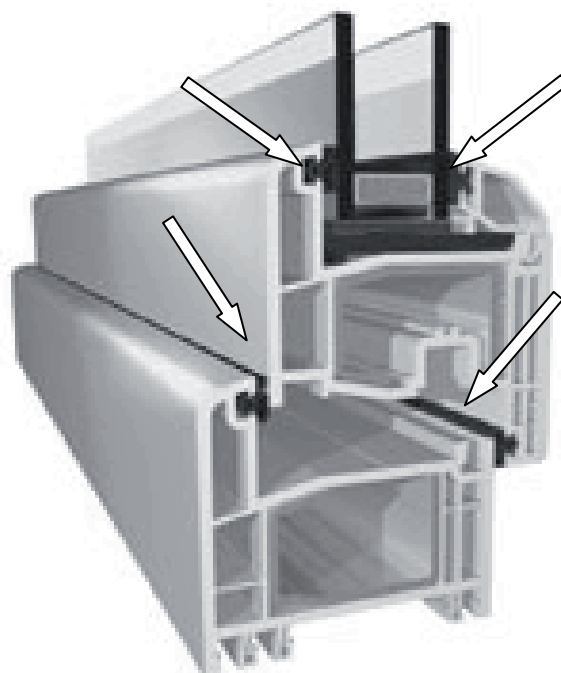


Fig. 2. Cross section of typical PVC window profiles. Arrows indicate elastomeric gaskets

These elastomers are very expensive and because of this new materials are extensively searched. Substitute materials have to be cheaper but their properties have to be very similar to mentioned

high performance materials and should fulfil all requirements stated by standards. Plasticized polyvinylchloride is more and more frequently applied as gasket's matrix material. To achieve better sealing properties polyvinylchloride is modified, apart from usually applied low-molecular-weight plasticizers, with elastomers and special plasticizers [5-11]. These modifiers cause the decrease of glass transition temperature enabling low temperature applications, increase elongation at break, elasticity in low temperatures, abrasion resistance, short-term and long-term elastic recovery, resistance to oils, fuels and many cleaning chemicals [7,12-14]. Plasticizers are frequently classified taking into account their effectiveness. Effectiveness is understood as amount of plasticizer needed to achieve assumed hardness, elasticity and strength change of PVC compound. Resistance to plate-out, oxidation, extraction and migration is understood as durability of plasticizer. Durability of plasticizer increases together with increasing molecular weight. Polymeric plasticizers are known as very resistant to migration and extraction. Polymeric plasticizers are non-volatile. But most of these plasticizer can be added to polyvinylchloride in limited amount. Among most interesting characteristics of polymeric plasticizers are essential enhance of mechanical properties of matrix, enhance resistance to organic solvents, oils and detergents. Polyvinylchloride applied for gaskets is frequently modified by polymeric plasticizers and among them butadiene-acrylonitrile and butadiene-acrylonitrile-styrene copolymers. Depending on molecular weight these plasticizers are of adhesive-like or elastomeric consistence [12]. Acrylonitrile is applied in this copolymer with content ranging from 15% to 50%. Higher acrylonitrile content provides improved solvent, oil and abrasive resistance and higher glass transition temperature. Butadiene provides rubbery nature in this copolymer. The most important is elastomeric nature of acrylonitrile-butadiene copolymers. Copolymers applied to plasticize polyvinylchloride possess about 36% of acrylonitrile and are absolutely non-volatile, exhibit very low migration and are resistant to extraction [12]. Also thermo-oxidative resistance of PVC gaskets can be improved by some polymeric modifiers [15].

In the present paper we demonstrate results of research on modification of plasticized PVC with butadiene-acrylonitrile copolymers as elastomeric modifiers.

2. Experimental

2.1. Materials

Plasticized polyvinylchloride in the form of dry blend prepared by AIB S.j. (Poland) and assigned as PVC-AIB was used as matrix to which modifiers were added. Two types of elastomers were used as PVC modifiers: pre-crosslinked copolymer of butadiene and acrylonitrile Chemigum P83 produced by Eliokem and copolymer of acrylonitrile and butadiene Nipol 1312 DL72 produced by Lehmann&Voss. Both elastomers were added to PVC with the following weight fractions: 6%, 7%, 8%, 9%, 10%, 11%, 12%, 13%, 15%, 17%, 19%, 21%, 23% and 25%. Additionally three ready commercial compounds were used as reference materials: plasticized PVC

compound (assigned as A1), elastomer modified PVC (assigned as A2), and second plasticized PVC compound (assigned as A3).

Modified formulations were prepared in the form of dry blend using PVC mixer, applying standard mixing procedure [16]. Test pieces for elastic recovery measurements were extruded using single-screw T60 (Metalchem – Gliwice, Poland) extruder. Tubes with outside diameter 11,0mm and inner diameter 8,0mm were extruded. Samples 25mm long were cut to testing. For tensile test, hardness measurements and migration test flat sheets were compression moulded using compounds in the form of granules. Before testing all samples were conditioned in temperature $293\text{K} \pm 3\text{K}$ ($20 \pm 3^\circ\text{C}$) during 24 hours.

2.2. Testing methods

Experimental programme was elaborated in such a manner that the most important performance properties of gasket materials were tested. The following tests were performed: Shore hardness, tensile test, short-term and long-term elastic recovery and plasticizer migration from gasket material into the unplasticized PVC.

Shore hardness was measured according to PN-EN ISO 868:2005 standard using Zwick 7206.H04 tester. "A" scale was used. Six measurements were done for every compound.

Tensile test was performed according to PN-EN ISO 527:1998 using Zwick 112025 tensile machine. Tensile velocity was 500 mm/min. 10 test pieces were tested for each compound.

Elastic recovery after compression was measured using special testing device designed and manufactured by AIB Poland. The device was designed and tests were performed according to BS 7412:1991. Two kinds of elastic recovery tests were performed. The short-term test was performed at temperature $296\text{K} \pm 2\text{K}$ ($23^\circ\text{C} \pm 2^\circ\text{C}$). Samples were deformed during 24 hours, elastic recovery was measured 5 minutes and 60 minutes after the end of deformation. The long-term test was performed at temperature $328\text{K} \pm 2\text{K}$ ($55^\circ\text{C} \pm 2^\circ\text{C}$). Test pieces were deformed during 336 hours, elastic recovery was measured 60 minutes after the end of deformation. During compression samples were deformed $50\% \pm 2\%$. Compressed samples were heated in temperature chamber with forced air circulation. Ten test pieces were applied for each measurement.

Migration test was performed to measure quantity of plasticizer migrating from gasket to unplasticized PVC adhering to gasket. The test is important because plasticizer migrating from gasket to window profile (usually made of unplasticized polyvinylchloride) can deteriorate mechanical properties of profile material and can cause profile swelling. Migration test was performed according to BS 7412:1991. Test was executed in $348\text{K} \pm 2\text{K}$ ($75^\circ\text{C} \pm 2^\circ\text{C}$) during 24 hours upon 5N compression loading. Between two unplasticized PVC plates with dimensions 10mm x 20mm x 1mm one plate with the same dimensions made of gasket material was inserted. Plates were placed in oven and compressed with 5N force. Samples were heated in temperature chamber with forced air circulation. Increase of weight of unplasticized PVC plates was measured. Six measurements were done for each compound.

3. Results and their analysis

3.1. Influence of copolymers content on PVC properties

Results of all test are presented in graphic form which enables easier results analysis. In all figures experimental results for reference compounds are presented as horizontal lines and assigned A1, A2 and A3. Results for compound without modifiers (PVC-AIB) are shown as results for formulations with zero modifiers content.

Because of results scatter no approximation procedure was performed and graphs are presented without approximation lines. Only mean values are shown.

Fig 3. shows influence of acrylonitrile- butadiene modifiers content on Shore °A hardness.

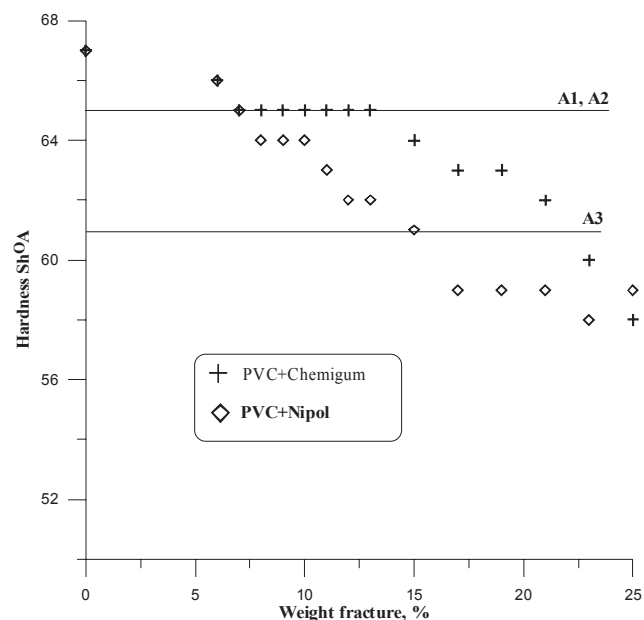


Fig. 3. Influence of weight fracture of modifiers in PVC on Shore A hardness of composites

Both types of copolymers caused hardness decrease. The higher modifier content the lower was Shore hardness. This result is typical for all types of plasticizers. As mentioned earlier both applied modifiers are butadiene-acrylonitrile copolymers but because of low polymerization level are in liquid form. The influence of Nipol 1312 DL72 butadiene-acrylonitrile copolymer on hardness was stronger than Chemigum P83. Experience show that best sealing properties posses gaskets with hardness in the range $60^{\circ}\text{Sh A} \pm 10^{\circ}\text{Sh A}$. Addition of both elastomers shifted hardness to the centre of this range.

Influence of weight fracture of acrylonitrile-butadiene copolymers in PVC on elastic recovery after 24 hours of deformation is present in Fig 4 (after 5 minutes of recovery) and in Fig.5 (after 60 minutes of recovery).

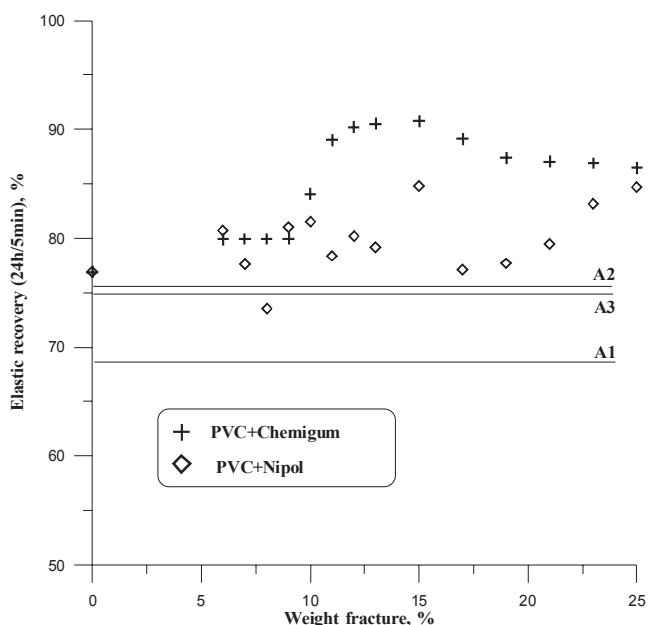


Fig. 4. Dependence of elastic recovery after 24 hours of deformation and 5 minutes of recovery on weight fracture of acrylonitrile – butadiene copolymers in PVC

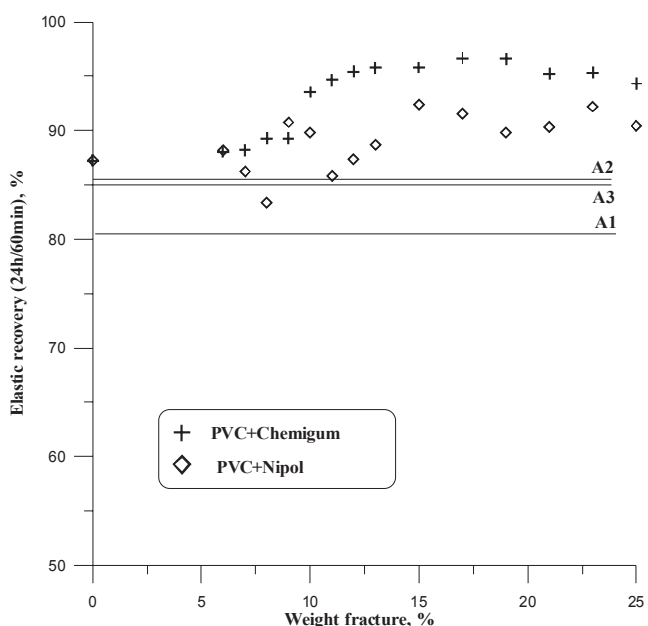


Fig. 5. Influence of weight fracture of acrylonitrile-butadiene copolymers in PVC on elastic recovery after 24 hours of deformation and 60 minutes of recovery

Addition of elastomeric modifiers enhanced elastic recovery of PVC compounds. The same tendencies were observed after 5 minutes of recovery and after 60 minutes of recovery. Such tendencies can be explained by polymeric and elastomeric nature of applied plasticizers. Also chemical interaction between PVC

and these plasticizers undergoing during processing play important role in elastic recovery enhancement [17]. Increase of elastic recovery was more pronounced after Chemigum P83 incorporation. It is the result of partial crosslinking of this copolymer. Comparing results presented in Fig. 3 and figures 4 and 5 one can see that Chemigum P83 copolymer softened PVC less than Nipol 1312 DL72 but its more pronounced elastomeric nature caused greater increase of elastic recovery. Increase of elastic recovery was especially pronounced at weight fracture lower than 15%.

According to BS 7412:1991 standard minimum elastic recovery of materials for window gaskets after 5 minutes of recovery is 60% and after 60 minutes of recovery is 75%. As can be seen from Fig. 4 and 5 all tested compounds fulfil these requirements. Compounds with acrylonitrile-butadiene copolymers exhibited higher elastic recovery than reference compounds A1, A2 and A3. It should be underlined that elastic recovery is one of most important properties essential for window gaskets.

Results of elastic recovery test for 336 hours of deformation in temperature 328K (55°C) and after 60 minutes of recovery are presented in Fig. 6.

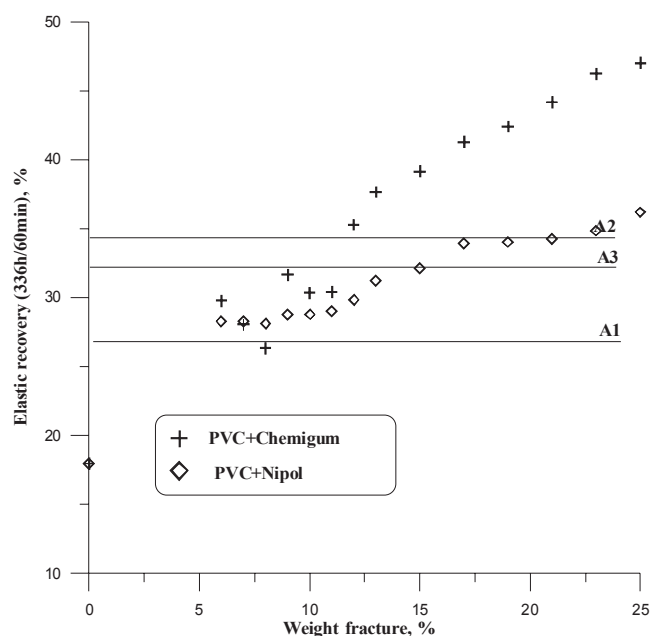


Fig. 6. Dependence of elastic recovery after 336 hours of deformation and 60 minutes of recovery on weight fracture of acrylonitrile-butadiene copolymers in PVC

It can be seen that acrylonitrile-butadiene plasticizers addition essentially influenced long-term elastic recovery. This property is even more important for window gaskets than short-term elastic recovery. According to BS 7412:1991 standard minimum long-term elastic recovery of materials for gaskets between PVC profile and glass panes is 25% and for gaskets between two PVC profiles is 40%. Compounds with 25% of Chemigum P83 exhibited 46% of elastic recovery and compounds with the same

content of Nipol 1312 DL72 exhibited 36% of long-term elastic recovery. Compounds with Chemigum P83 content higher than 12% obtained higher long-term elastic recovery than all reference formulations. Compounds with Nipol 1312 DL72 content higher than 15% exhibited long-term elastic recovery higher than reference formulations A1 and A3, compounds with 23% and 25% of Nipol 1312 DL72 exhibited long-term elastic recovery higher than all reference formulations.

Results of tensile test are presented in Fig. 7 and Fig. 8. In Fig. 7 dependence of tensile strength on copolymer content is presented and Fig.8. shows influence of copolymer content on elongation at break. As can be seen in Fig.7 addition of Chemigum P83 influenced weakly tensile strength. For all of this plasticizer content range tensile strength was between 11 MPa and 12 MPa. Addition of Nipol 1312 DL72 up to 10% by weight did not change essentially tensile strength but for higher concentration decrease of tensile strength was observed (up to 30% of initial value).

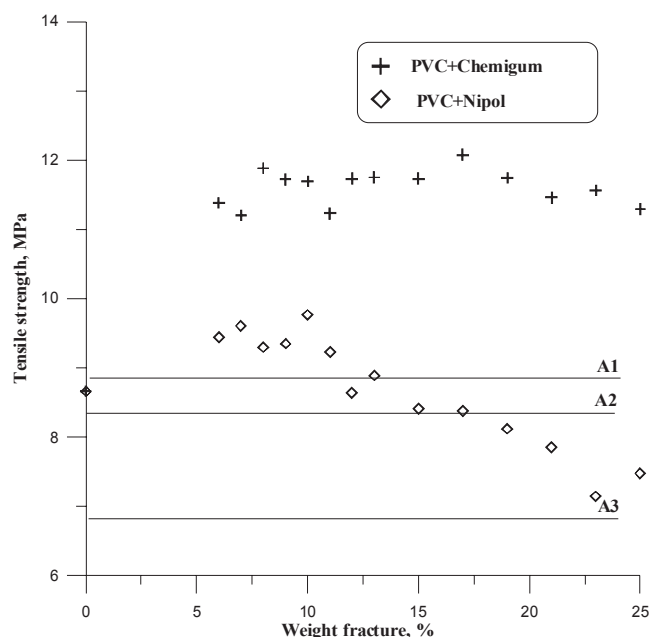


Fig. 7. Dependence of tensile strength on weight fracture of acrylonitrile-butadiene copolymers in PVC

Compounds modified with both types of acrylonitrile-butadiene copolymers shown essential increase of elongation at break. Better results were obtained for compounds with Chemigum P83. Elongation at break of compounds with Chemigum P83 addition increased from 249% to 410%, compounds with Nipol 1312 DL72 addition exhibited elongation at break increase from 249% to 270%. Additionally formulation with Chemigum P83 addition had much better strength properties (tensile strength and elongation at break) than reference formulations A1, A2 and A3.

Relation between migration of plasticizers from gasket to unplasticized PVC profile and nitrile butadiene copolymer content is shown in Fig. 9

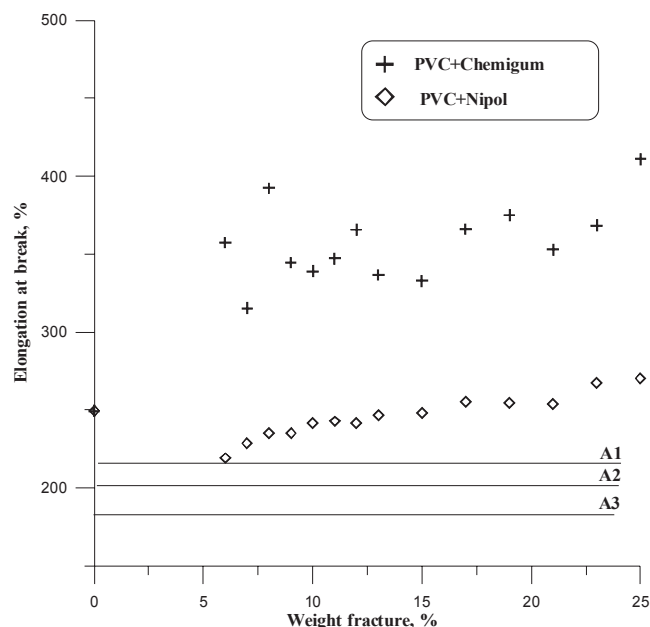


Fig. 8. Dependence of elongation at break on weight fracture of acrylonitrile-butadiene copolymers in PVC

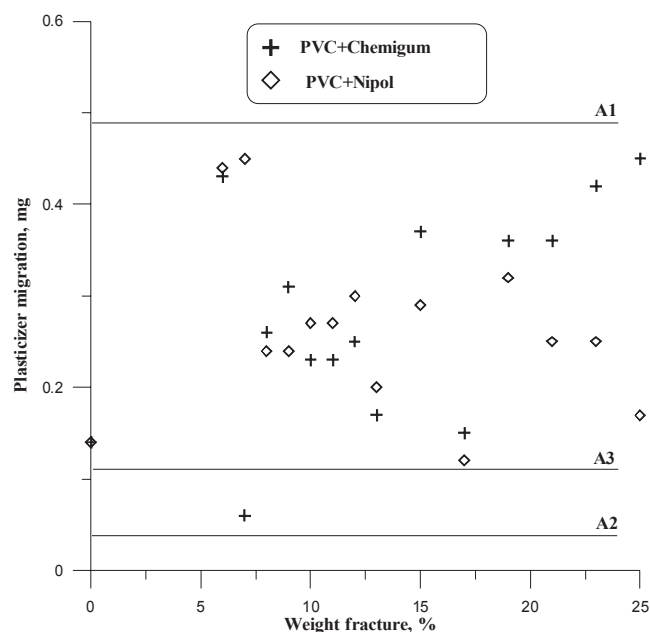


Fig. 9. Relation between migration of plasticizer from modified PVC to unplasticized PVC and weight fracture of acrylonitrile-butadiene copolymers

According to BS 7412:1991 standard maximum amount of plasticizers migrating from gasket material to unplasticized PVC in conditions mentioned earlier is 5 mg. As can be seen in Fig. 9 all researched formulations fulfil this requirement. Measured quantity of migrating plasticizer was between 0,40 mg to 0,45 mg.

Reference formulation A1 exhibited higher migration than other tested formulations but reference formulations A2 and A3 shown slower migration.

3.2. Influence of the type of elastomer

In order to compare influence of the type of copolymer addition, formulations with 25% of Chemigum P83 and with 25% of Nipol 1312 DL72 were taken into consideration. As reference formulations compound without elastomer (PVC-AIB) and commercial formulations A1, A2 and A3 were taken.

Comparison of results of hardness measurements are presented in Fig. 10.

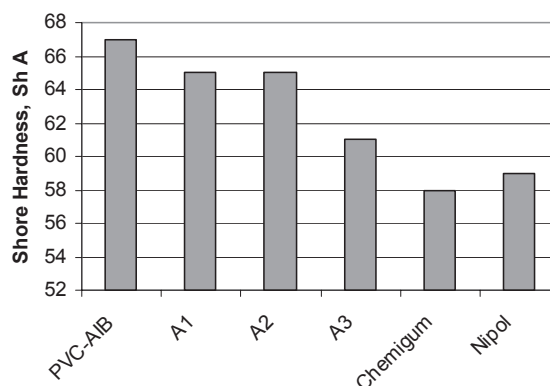


Fig. 10. Comparison of hardness of compounds with two types of elastomers and reference formulations

As can be seen compounds with acrylonitrile-butadiene addition exhibited hardness near 60° Sh A.

In Fig.11 short-term elastic recovery (24 hours of compression in 296K±2K (23°C±2°C), 60 minutes of recovery) is compared. Compound with Chemigum P83 achieved the highest short-time elastic recovery. At the same level but a little lower was short-term elastic recovery of PVC modified with 25% by weight of Nipol 1312 DL72. Compounds modified with elastomers were better in this field than PVC-AIB and all commercial formulations.

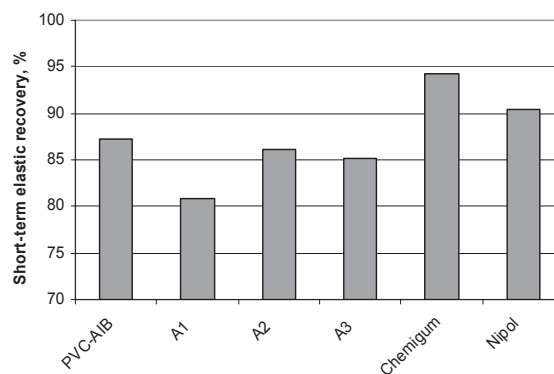


Fig. 11. Short-time elastic recovery of chosen compounds

Fig. 12 presents comparison of long-term elastic recovery (336 hours of compression in $328\text{K}\pm 2\text{K}$ ($55^\circ\text{C}\pm 2^\circ\text{C}$), 60 minutes of recovery) of the same compounds. Once more the best results were achieved for compound with 25% of Chemigum P83. About 23% lower long-term elastic recovery shown PVC with 25% of Niopol 1312 DL72. Commercial compounds exhibited long-term elastic recovery on the same level. The lowest result was achieved for plasticized PVC without copolymer addition.

Results of tensile strength are compared in Fig. 13.

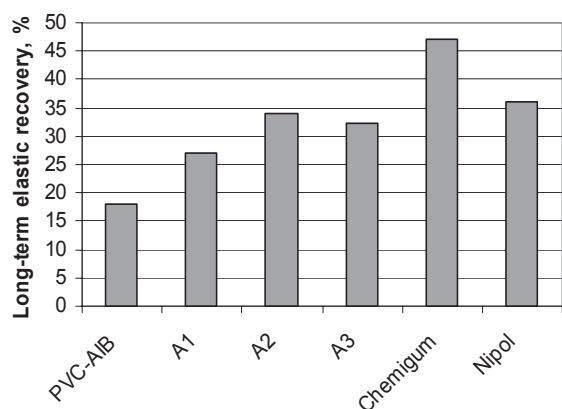


Fig. 12. Comparison of long-term elastic recovery results

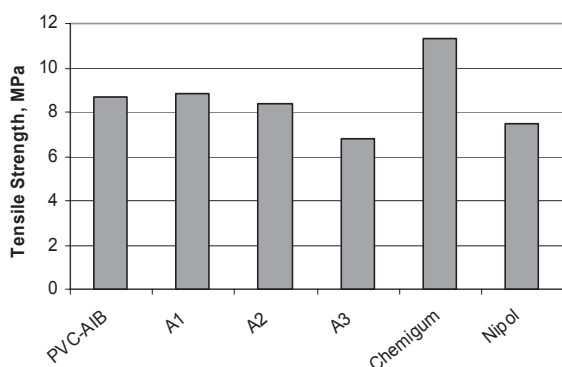


Fig. 13. Comparison of tensile strength of chosen compounds

Taking into account tensile strength once more the highest value was achieved for compound with 25% of Chemigum P83. The rest of investigated compounds achieved similar, but essentially lower, strength results.

Fig. 14 presents results of elongation at break measurements.

As for tensile strength the highest elongation at break value was measured for plasticized polyvinylchloride modified with 25% of Chemigum P83. Apart from elastic recovery it is the second important for window's gaskets characteristic. The highest value of elongation at break once more exhibited compound modified with Chemigum P83. About 34% lower elongation at break achieved compound modified with Niopol 1312 DL72. All reference formulations had elongation at level similar to compound modified with Niopol 1312 DL72.

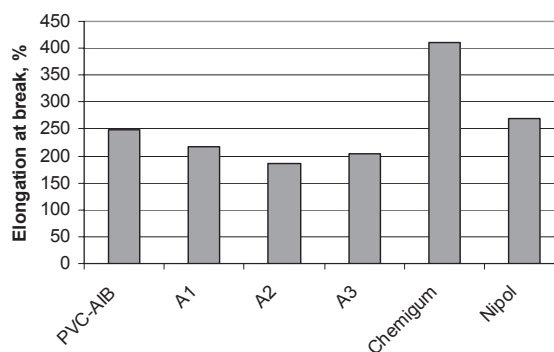


Fig. 14. Comparison of elongation At break results for tested and reference compounds

Comparing all characteristics of compounds modified by two applied acrylonitrile-butadiene copolymers it can be seen that almost all properties essential for window gaskets performance (long-term and short-term elastic recovery, tensile strength and elongation at break) were higher for compounds with partially cross-linked Chemigum P83. The best results were achieved for compounds with 25% weight fraction of this copolymer. Shore hardness and plasticizers migration were on the same level for compounds with both modifiers.

Compounds with Chemigum P83 content and some of compounds with Niopol 1312 DL72 content were better than reference formulations A1, A2 and A3.

4. Conclusions

Acrylonitrile-butadiene copolymers applied as PVC elastomeric modifier improved many properties. Among others increased such essential for window gaskets properties as long-term and short term elastic recovery, tensile strength and elongation at break. At the same time addition of these elastomers did not change or changed minimally other less essential properties as hardness and migration rate of other than acrylonitrile-butadiene elastomers plasticizers contained in gasket material from gasket to unplasticized PVC profile.

Obtained results indicate also that among tested compounds the best properties as gasket material exhibited plasticized PVC with 25% by weight of acrylonitrile-butadiene partially cross-linked copolymer Chemigum P83. The strongest chemical interaction between PVC and this plasticizer undergoing during processing is the probably reason.

Tested reference compounds: plasticized PVC compound (assigned as A1), elastomer modified PVC (assigned as A2), and second plasticized PVC compound (assigned as A3) and plasticized polyvinylchloride PVC-AIB, exhibited worse performance properties than compounds with Chemigum P83 and other elastomers addition.

Acknowledgements

Research programme was supported by P.P.P. AIB Sp.j. Knurów, Poland.

Additional information

The presentation connected with the subject matter of the paper was presented by the authors during the 14th International Scientific Conference on Achievements in Mechanical and Materials Engineering AMME'2006 in Gliwice-Wisła, Poland on 4th-8th June 2006

References

- [1] K. Flaga, Advances in materials applied in civil engineering, *Journal of Materials Processing Technology* 106 (2000) 173-183.
- [2] F. Kamisli, C. Turan, A study on usability of magnesium oxide with titanium dioxide in PVC door and window profiles, *Journal of Materials Processing Technology* 159 (2005) 40-47.
- [3] Technical catalogue of window gaskets, AIB, 2005, Knurów Poland (in Polish).
- [4] S. Ramakrishna, Z. Ming Huang, H.M. Yew, Development of a novel flexible composite material, *Journal of Materials Processing Technology* 89-90 (1999) 473-477.
- [5] J.R. Pena, M. Hidalgo, C. Mijangos, Plastification of poly(vinyl chloride) by polymer blending, *Journal of Applied Polymer Science* 75 (2000) 1303-1312.
- [6] D. Dickmann, Plasticizers, *Modern Plastics Encyclopedia'91* McGraw Hill, New York 1990, 202-208.
- [7] G. Wypych, *Handbook of Plasticizers*, ChemTec Publishing, 2004.
- [8] G. Wu, J. Zhao, H. Shi, H. Zhang, The influence of core-shell structured modifiers on the toughness of poly(vinyl chloride) grafted copolymer of polybutadiene and polymethyl methacrylate, *European Polymer Journal* 40 (2004) 2451-2456.
- [9] M. Rahman, C.S. Brazel, The plasticizer market an assessment of traditional plasticizers and research trends to meet new challenges, *Progress in Polymer Science* 29 (2004) 1223-1248.
- [10] A. Hassan, B. Hawotrh, Impast properties of acrylate rubber – modified PVC: Influence of temperature, *Journal of Materials Processing Technology* 172 (2006) 341-345.
- [11] M. Rojek, J. Stabik, Modification of PVC compounds with butadiene-acrylonitrile elastomers, *Journal Achievements in Materials and Manufacturing Engineering* 17 (2006) 141-144.
- [12] M. Oblój-Muzaj, B. Świerz-Motysia, B. Szablowska, Polyvinyl chloride, WNT, Warszawa 1997 (in Polish).
- [13] S.-H. Zhu, C.M. Chan, S. C. Wong, Y.W. Mai, Mechanical properties of PVC/SBR blends compatibilized by acrylonitrile-butadiene rubber and covulcanization, *Polymer Engineering Science*, 39 (1999) 1998-2006.
- [14] L. Zhou, X. Wang, Y. Lin, J. Yang, Q. Wu, Comparison of the toughening mechanisms of poly(vinyl chloride)/chlorinated polyethylene and poly(vinyl chloride)/acrylonitrile-butadiene-styrene copolymer blends, *Journal of Applied Polymer Science* 90 (2003) 916-924.
- [15] A. de Zarraga, S. Villanueva, M.E. Muñoz, R. Obeso, J.J. Peña, B. Pascual, A. Santamaría, Ternary Blends to Improve Heat Distortion Temperature and Rheological Properties of PVC, *Macromolecular Materials and Engineering* 289 (2004) 648-652.
- [16] B. Jurkowski, B. Jurkowska, Preparing of polymeric compounds WNT Warszawa 1995 (in Polish).
- [17] N.R. Manoj, P.P. De, An investigation of the chemical interactions in blends of poly(vinyl chloride) and nitrile rubber during processing, *Polymer* 39 (1998) 733-741.