THE INFLUENCE OF NBR WASTE MODIFIED WITH SiO_2/NOT MODIFIED ON PROCESSABILITY, PHYSICAL-MECHANICAL AND STRUCTURAL PROPERTIES OF PVC

MARIA SÖNMEZ, MIHAELA NITUICA (VILSAN), MIHAI GEORGESCU,
MARIA DANIELA STELESCU, LAURENTIA ALEXANDRESCU,
DENIS-ANDREI DRUSAN, ANA-MARIA CIOBANU, DANA GURAU, CIPRIAN CHELARU

The National Research & Development Institute for Textiles and Leather - Leather and Footwear Research Institute Division, Ion Minulescu St. 93, Bucharest, Romania, maria.sonmez@icpi.ro

The finished products made of PVC and NBR after the end of the life (waste) are considered harmful, because they do not degrade and thus remain for a long time in the environment. Therefore, there is intense research in order to recycle such materials and reintroduce them into the productive cycle in a new form, without compromising very much their mechanical properties. In the case of rubber recycling, there are currently several methods, from reducing the dimensions to expensive devulcanization processes in order to use them in different thermoplastic matrices. However, the simple reduction of the size of the vulcanized rubber and the mixing with PVC, leads to weak mechanical properties, due to the incompatibility and immiscibility between the phases. Such a composite material was obtained using recycled vulcanized NBR rubber particles (0.35 mm) unmodified/ modified with 10% PDMS, in virgin PVC matrix and waste PVC (50:50) and in the presence of the genioplast additive by the homogeneous mixing technique in the Brabender mixer. The materials experimented were analyzed structurally – FTIR, rheological (torque versus time), from the point of view of processability (flow index) but also mechanically. The analysis of the physico-mechanical values shows that the addition of 10% NBR in the PVC matrix reduces the tensile strength, the 100 and 300% modulus, the elongation at the break, the tear due to their agglomeration, reduce processability (based on the MFR obtained values) but improve the abrasion resistance, an important property of the materials used especially in the footwear industry. However, these types of materials can be used in other applications (automotive, agriculture, etc.) where very high resistances are not required.

Keywords: NBR waste, PVC, genioplast, recycling.

INTRODUCTION

The accentuated trend of widespread use of plastics and elastomers in a wide range of applications (automotive industry, packaging, toys, etc.) has led to the need to develop efficient and fast solutions / methods for their recycling (Fazli and Rodrigue, 2020). It is known that the decomposition of polymers is a long-term process causing harmful effects on the environment and health. Currently 1.5 billion tons of tires/year are decommissioned worldwide and discarded, with a content of up to 90% vulcanized rubber that is not easy to be reprocessed (recycled) due to its highly cross-linked structure (Medina *et al.*, 2018; Przydatek *et al.*, 2022). Other products that generate rubber waste are represented by discarded rubber pipes, shoe soles, belts, etc. Numerous studies have focused on rubber recycling, using different methods (size reduction, devulcanization, irradiation, etc.) to improve compatibility with other polymers (Dobrotă *et al.*, 2020; Fazli and Rodrigue, 2020; Rad *et al.*, 2019; Stelescu, 2013). The objective of this study was to bring added value to waste from different industries and especially PVC and NBR by making new composites, able to re-enter the productive circuit, without significant alteration of the properties of interest.

EXPERIMENTAL

Materials

Plasticized PVC granules (GST type) – Cardinal SRL, Romania; PVC technological waste from the processing of the soles injection; NBR powder obtained by cryogenic grinding (≤ 0.35 mm) of the materials left over from plate stamping to obtain the specimens

https://doi.org/10.24264/icams-2022.I.10

used in the mechanical tests; Genioplast®Pellet P Plus from Wacker-Germany; Poly (dimethylsiloxane) (PDMS), grade: analytical standard, density: 0.82 g/mL, molecular weight: 236.53 wt.%-Sigma Aldrich; Ethanol (96%) from Chemreactiv S.R.L., Romania.

Method

Surface Modification of the NBR Waste

The NBR waste was modified with PDMS by the hydrolysis-condensation method. In the first stage, 150g of NBR waste was weighed in a plastic Berzelius glass over which 600 mL of ethyl alcohol (96%) was added and stirred mechanically for 2 h. Afterwards, 15.4 mL of PDMS (10% relative to the amount of waste) was introduced in the form of fine drops and continued shaking for another 1h. In order for the hydrolysis of the silane to take place, 150 mL of distilled water was added and stirred for another 2h. The obtained powder was filtered, washed with abundant ethanol to remove the unreacted PDMS, and dried in the hot air oven at 70°C, 24 h.

Obtaining Mixtures Based on PVC and/ or NBR Waste

All variants of tested composites (presented in Table 1) were obtained by melt mixing technique using the Brabender plasticorder. During the experiments, the following parameters were recorded: the actual temperature of the mixture during processing and the torque versus time, in the form of a diagram called the plastogram (Figure 4).

Table 1. Composition of tested materials

Sample symbol/Raw material	Raw PVC	PVC waste	P0	P1A	5	6
Virgin PVC, g	350	-	175	175	175	175
PVC waste, g	-	350	175	175	175	175
Genioplast, g	-	-	-	3.5	3.5	3.5
NBR waste not functionalized, g	-	-	-	-	35	-
NBR waste / 10% PDMS, g	-	-	-	-	-	35
Total, g	350	350	350	353.5	388.5	388.5

All of the mixtures in Table 1 were processed under similar conditions in Brabender at 160°C, 30 rpm (2 minutes) and 100 rpm (5 minutes), respectively. After processing, the mixtures were removed from the chamber and used to obtain sheets (15x15 cm, and 2 mm thick, respectively 6 mm thick sheets – to determine the abrasion resistance) in a Fontijne electric press with the following parameters: electric heated plates – 170°C; preheating – 2 minutes; pressing – 5 minutes; cooling – 10 minutes; Force pressure – 300 kN. From the obtained sheets, after conditioning 24 h at room temperature, test specimens (dumbbell, trousers, and cylindrical shapes) are stamped to perform physico-mechanical tests.

RESULTS AND DISCUSSION

Primary Identification Process (FTIR Analysis)

The spectra obtained on the NBR and NBR waste/10% PDMS in relation to the virgin NBR rubber (Figure 1), highlight specific groups, namely: the bands from 2918, 2849 and 1450 cm^{-1} (stretching and deformation vibration of the -C-H bond), the band from 2238 cm^{-1} (stretching vibration of the -CN bond), the band from 1539 cm^{-1} (the stretching vibration of the -CN bond, from the additives added into the rubber). The band from 967 cm^{-1} comes from the -C=C- double bond (1.4 trans) (Liu *et al.*, 2020; Samantarai *et al.*,

https://doi.org/10.24264/icams-2022.I.10

2019). Additionally in the spectrum of NBR waste (not modified) intense bands at 1078 cm^{-1} originated from the Si-O-Si group (silicon dioxide) can be observed. The spectra obtained on the NBR/10%PDMS waste, highlights the groups originated from PDMS at 1260 cm^{-1} (symmetrical bending of the CH_3 bonds from the Si-CH_3 group), and the band from 800 cm^{-1} (rocking CH_3 bond from Si-CH_3 group) (Shi *et al*., 2016). Spectra obtained on raw PVC, PVC waste and P0 (Figure 2), highlight groups originated from PVC, plasticizer (dibutyl phthalate) and $CaCO_3$ (filler ingredient).

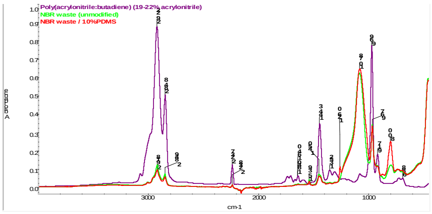

Figure 1. FTIR spectrum of waste: NBR unchanged and NBR / 10%PDMS

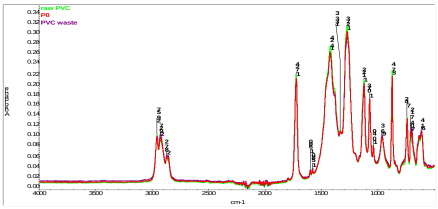

Figure 2. FTIR spectra of: raw PVC, PVC waste and P0 (50:50 raw PVC: PVC waste)

Thus, PVC bands can be observed at 2872 and 2927 cm^{-1} (stretch vibration of the -CH bond); The band from 1424 cm^{-1} (wagging of CH_2), 1333 cm^{-1} (deformation of CH_2 bond from CH-Cl group), the band from 1273 and 1073 cm^{-1} (the stretching vibration of the C-H bonds from the -CH-Cl group) and the one at 963 cm^{-1} (rocking of CH_2). The band at 614.27 cm^{-1} is associated with the C-Cl bond (Hashmi *et al*., 2022). The bands coming from dibutyl phthalate can be identified at 1724 cm^{-1} (the stretching vibration of the C=O ester group), at 1600 and 1580 cm^{-1} (stretching vibration of the aromatic ring structure) and those of 1122 and 1073 cm^{-1} are attributed to C-O stretching vibration (Kumari and Kaur, 2022). The bands at 874 and 712 cm^{-1} correspond to asymmetrical and symmetrical CO_3^{2-} bonds from $CaCO_3$. The $CaCO_3$ band from ~ 1413 cm^{-1} cannot be detected because it overlaps with the plasticizer bands (Bwatanglang *et al*., 2021). The FTIR spectrum of genioplast (Figure 3) highlights specific silicone rubber bands: 2958 cm^{-1} – stretching vibration of the CH_3 bonds; the bands from 1258 cm^{-1} (bending vibration of the Si-CH_3 bond) and those from 1080 and 1011 cm^{-1} (stretching vibration of the Si-O-Si bonds). The peak from 792 cm^{-1} is attributed to the coupling of the stretching vibration of Si-C bonds and the balance vibration of the -CH_3 bond (Salih *et al*., 2018). The band from 461 cm^{-1} is attributed to the presence of ultrafine silica (Li *et al*., 2014). In the case of samples 5 and 6, the presence of NBR waste can be clearly detected at ~ 800 cm^{-1}, with the highest intensity in sample 6 (besides Genioplast it also contains PDMS).

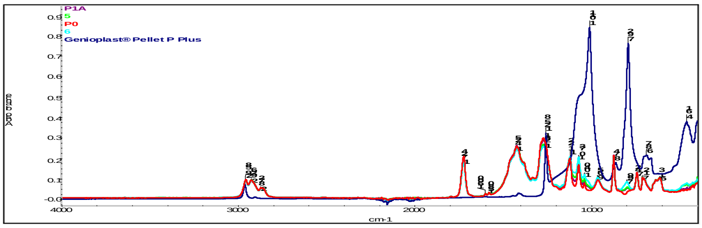

Figure 3. FTIR spectra of the obtained composites

Rheological Analysis

The torque-time recording shows the change in dynamics that took place in virgin PVC, waste PVC, polymer mixtures (samples P0, P1A) but also in the PVC/NBR waste composites, processed according to the so-called gelation process. In Figure 4 (A-F diagrams), a sudden torque increase in point A (the effect of loading the material, followed by a decrease in temperature inside the chamber) is observed in all mixtures. Then the torque dropped to a minimum at point B, exceeded the inflection point G and reached its maximum at point X. Such a curve at this stage indicated the coalescence of the particles. At the same time, the temperature of the mixtures increased slowly until reaching the set values, increasing even more near the G-X points. After passing the X-point, the torque decreased slightly then stabilized (point E), indicating the homogeneity of the mixture. The temperature of the material still increased slightly between X and E and the recording continued until the value of the torque stabilized. The following values were read from plastograms and compared in Table 2: the torque at the gelation point (Mx), the temperature at the gelation point (Tx), the torque (ME) and the temperature of the mixture (TE) at the end point and the gelling speed (Mirowski *et al*., 2021), respectively. The results (Table 2) show that the addition of 1% Genioplast (Sample P1A) and 10% NBR waste (Samples 5 and 6), respectively, increases the value of Mx and ME, as the filling is added, but also of Tx and TE. PVC gelling depends on the applied shear force (speed), temperature and composition. The action of shear tensions induces the disintegration of granules into smaller elements (agglomerated by primary particles). Subsequently, the heating determines the progressive plasticization and melting of these elements. These thermo-mechanical changes of the morphological structure of PVC grains involve the smallest elements, the so-called primary crystallites. It is assumed that the addition of a filler promotes the release of more heat, as a result of the friction between filler particles, against PVC grains, filler particles or PVC granules against chamber walls. Moreover, for the same weight of the batch, the volume of the mixture containing NBR waste is higher than that of PVC, which results in a higher shear effort. Due to these effects, the gelling of mixtures containing PVC/NBR waste functionalized/ unfunctionalized is faster than that of PVC (Bendjaouahdou and Aidaoui, 2021; Jubsilp *et al*., 2022; Mirowski *et al*., 2021).

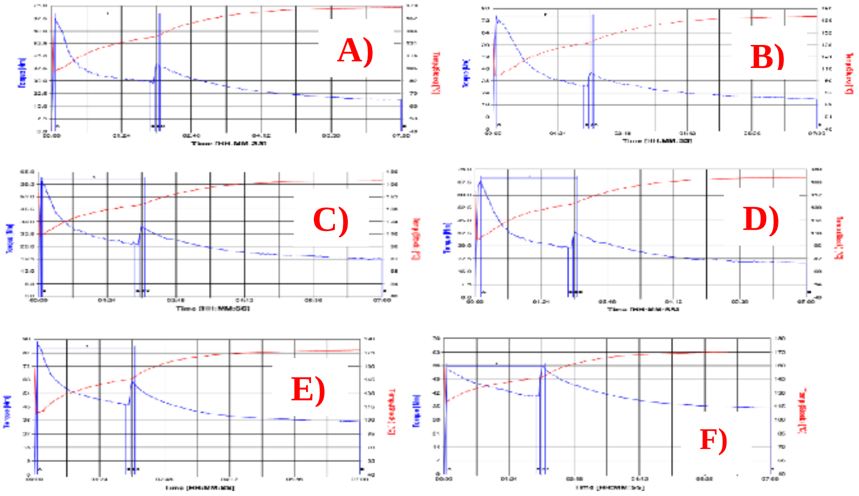

Figure 4. The plastograms obtained on virgin PVC (A), waste PVC (B), P0(C), P1A (D), Sample 5 (E) and 6 (F) with characteristic values related to the gelling process

Table 2. Analysis of values in plastograms

Features / Samples	M_X, Nm	T_X, °C	M_E, Nm	T_E, °C	Gelling rate, Nm
Virgin PVC	38.7	140	19.1	168	219.5
PVC waste	36.7	142	20.2	171	183.3
P0	35.3	145	19.5	170	181.2
P1A	37.1	144	20.4	171	165.5
5	59.9	149	35.1	178	273.8
6	54.4	149	34.1	176	233.6

Physico-Mechanical and Melt Flow Index Analysis

The properties were determined according to their standards: hardness (SR ISO 7619-1), modulus -100, 300%, elongation and tensile strength (SR ISO 37), tear strength (SR ISO 12771), MFR (SR ISO1133). Analyzing the values in Figure 5, it can be seen that PVC waste has tensile strength, modulus at 100 and 300%, elongation at break, and tear strength superior compared to raw PVC. This was also observed by Roman and Zattera (2014), that repeated reprocessing improve mechanical properties (especially due to the presence of $CaCO_3$ from PVC). In the case of samples 5 and 6, it can be observed the decrease of the tensile strength, modulus, elongation at break, and tear strength, due to the agglomerations and the reduced compatibility between phases (Stelescu, 2013; Subramanian *et al*., 2021). It has been found that recycled rubber particles (i.e. the cross-linked gel part) act as pressure concentration points, so that increasing the concentration of rubber (gel content) of mixtures increases the cross-linking density, lead to a lower tensile strength, elongation at break, and melt flow indices (MFR) (Fazli and Rodrigue, 2020). In the case of P1A mixture (50:50 PVC raw/PVC waste and 1% Genioplast) the highest values of tensile strength, modulus, and abrasion resistance (only 208.56 mm^3) are obtained, of all mixtures, but also good tear strength, elongation, and processability (MFR). These results prove that there is a very good compatibility between PVC and silicone rubber, respectively the ultrafine silica existing in Genioplast (Dobrotă *et al*., 2020).

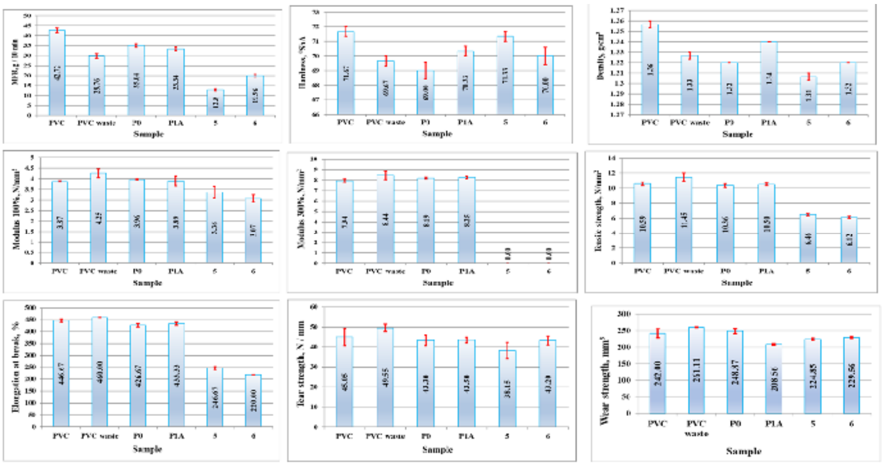

Figure 5. Values of the physico-mechanical characteristics and of the melt flow indices (MFR, g/10min)

https://doi.org/10.24264/icams-2022.I.10

CONCLUSIONS

The results obtained prove that the use of NBR waste in PVC matrix is possible, with the mention that the particle size must be more diminished.

Acknowledgment

This research was financed by MCI through PN 19 17 01 03/2019 project.

REFERENCES

Bendjaouahdou, C. and Aidaoui, K. (2021), "Synthesis and Characterization of Polyvinyl Chloride/Wood Flour/Organoclay Ternary Composites", *Polymers and Polymer Composites*, 29, 949-958, https://doi.org/10.1177/09673911211031139.

Bwatanglang, I.B., Magili, S.T. and Kaigamma, I. (2021), "Adsorption of Phenol over Bio-based Silica/Calcium Carbonate (CS-SiO_2/$CaCO_3$) Nanocomposite Synthesized from Waste Eggshells and Rice Husks", *PeerJ Physical Chemistry*, 3, 1-20, https://doi.org/10.7717/peerj-pchem.17.

Dobrotta, D., Petrescu, V., Dimulescu, C.S. and Oleksik, M. (2020), "Preparation and Characterization of Composites Materials with Rubber Matrix and with Polyvinyl Chloride Addition (PVC)", *Polymers*, 12(9), 1-27, https://doi.org/10.3390/polym12091978.

Fazli, A. and Rodrigue, D. (2020), "Waste Rubber Recycling: A Review on the Evolution and Properties of Thermoplastic Elastomers", *Materials (Basel)*, 13(3), 1-31, https://doi.org/10.3390/ma13030782.

Hashmi, S.U.M., Iqbal, M.A., Malik, M., Qamar, M.T., Khan, M., Zahid, A., Islam, M.R., Al-Bahrani, M., Morsy, K. and Lai, W.-C. (2022), "Synthesis and Characterization of Polyvinyl Chloride Matrix Composites with Modified Scrap Iron for Advanced Electronic", *Photonic and Optical Systems*, 12(18), 1-15, https://doi.org/10.3390/nano12183147.

Jubsilp, C., Asawakosinchai, A., Mora, P., Saramas, D. and Rimdusit, S. (2022), "Effects of Organic Based Heat Stabilizer on Properties of Polyvinyl Chloride for Pipe Applications: A Comparative Study with Pb and CaZn Systems", *Polymers*, 14(1), 1-16, https://doi.org/10.3390/polym14010133.

Kumari, A. and Kaur, R. (2022), "Uptake of a Plasticizer (di-n-butyl phthalate) Impacts the Biochemical and Physiological Responses of Barley", *PeerJ*, 10, 1-28, https://doi.org/10.7717/peerj.12859.

Li, K., Jiang, J.G., Tian, S.C., Chen, X.J. and Yan, F. (2014), "Influence of Silica Types on Synthesis and Performance of Amine-Silica Hybrid Materials Used for CO_2 Capture", *The Journal of Physical Chemistry C*, 118(5), 2454-2462, https://doi.org/10.1021/jp408354r.

Liu, J., Sun, J., Zhang, Z., Yang, H. and Nie, X. (2020), "One-step Synthesis of End-Functionalized Hydrogenated Nitrile-Butadiene Rubber by Combining the Functional Metathesis with Hydrogenation", *ChemistryOpen*, 9, 374-380, https://doi.org/10.1002/open.201900369.

Medina, N.F., Garcia, R., Hajirasouliha, I., Pilakoutas, K., Guadagnini, M. and Raffoul, S. (2018), "Composites with Recycled Rubber Aggregates: Properties and Opportunities in Construction", *Construction and Building Materials*, 188, 884–897, https://doi.org/10.1016/j.conbuildmat.2018.08.069.

Mirowski, J., Oliwa, R., Oleksy, M., Tomaszewska, J., Ryszkowska, J. and Budzik, G. (2021), "Poly(vinyl chloride) Composites with Raspberry Pomace Filler", *Polymers*, 13(7), 1-19, https://doi.org/10.3390/polym13071079.

Przydatek, G., Budzik, G. and Janik, M. (2022), "Effectiveness of Selected Issues Related to Used Tyre Management in Poland", *Environmental Science Pollution Research International*, 29(21), 31467-31475, https://doi.org/10.1007/s11356-022-18494-7.

Rad, A.S., Aali, E., Hallajian, S., Zangeneh, D., Tavakoli, M., Ayub, K. and Peyravi, M. (2019), "Enhancement in the Mechanical Property of NBR/PVC Nanocomposite by Using Sulfur and Electron Beam Curing in the Presence of Cloisite 30B Nanoclay", *Journal of Macromolecular Science, Part A*, 57, 1-8, https://doi.org/10.1080/10601325.2019.1673663.

Roman, C. and Zattera, A.J. (2014), "Study on the Recycling of Waste PVC Compounds from Electrical Wires", *AIP Conference Proceedings*, 52, 52-55, https://doi.org/10.1063/1.4873732.

Salih, S.I., Oleiwi, J.K. and Ali, H.M. (2018), "Study the Mechanical Properties of Polymeric Blends (SR/PMMA) Using for Maxillofacial Prosthesis Application", *IOP Conference Series: Materials Science and Engineering*, 454, 1-10, https://doi.org/10.1088/1757-899X/454/1/012086.

Samantarai, S., Nag, A., Singh, N., Dash, D., Basak, A., Nando, G.B. and Das, N.C. (2019), "Chemical Modification of Nitrile Rubber in the Latex Stage by Functionalizing Phosphorylated Cardanol Prepolymer: A Bio-based Plasticizer and a Renewable Resource", *Journal of Elastomers & Plastics*, 51(2), 99-129, https://doi.org/10.1177/0095244318768644.

Shi, D., Li, P. and Cao, B. (2016), "Preparation of PDMS/PVDF Composite Pervaporation Membrane Modified with Hydrophobic TiO_2 Nanoparticles for Separating Formaldehyde Solution", *Polymer Sciences*, 2(1), 1-7, https://doi.org/10.4172/2471-9935.100012.

Stelescu, M.D. (2013), "Polymer Composites Based on Plasticized PVC and Vulcanized Nitrile Rubber Waste Powder for Irrigation Pipes", *ISRN Materials Science*, 2013, 726121, 1-5, https://doi.org/10.1155/2013/726121.

Subramanian, N., Senthilvel, K. and Prabu, B. (2021), "Studies on the Morphology and Physico-Mechanical Properties of NBR/PVC Hybrid Nanocomposites", *Materials Today: Proceedings*, 38, Part 5, 2810-2816, https://doi.org/10.1016/j.matpr.2020.08.739.