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Waste Tire Rubber-based Refrigerants for Solid-state Cooling Devices

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Electronic Supplementary Information

Abstract Management of discarded tires is a compelling environmental issue worldwide. Although there are several approaches developed to recycle waste tire rubbers, their application in solid-state cooling is still unexplored. Considering the high barocaloric potential verified for elastomers, the use of waste tire rubber (WTR) as a refrigerant in solid-state cooling devices is very promising. Herein, we investigated the barocaloric effects in WTR and polymer blends made of vulcanized natural rubber (VNR) and WTR, to evaluate its feasibility for solid-state cooling technologies. The adiabatic temperature changes and the isothermal entropy changes reach giant values, as well as the performance parameters, being comparable or even better than most barocaloric materials in literature. Moreover, pure WTR and WTR-based samples also present a faster thermal exchange than VNR, consisting of an additional advantage of using these discarded materials. Thus, the present findings evidence the encouraging perspectives of employing waste rubbers in solid-state cooling based on barocaloric effects, contributing to both the recycling of polymers and the sustainable energy technology field.

Keywords Waste tire rubber; Solid-state cooling; Barocaloric effect; Tire recycling; Sustainable energy

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INTRODUCTION

Polymers are widespread in our everyday life, with applications in practically all branches of science and technology. For this reason, the term “Plastic Age” is sometimes used to refer to the recent period. This increasing amount of plastics in industrial products creates a serious ecological issue: without proper management of wastes, the long durability of these materials results in their accumulation in nature. Besides, the microplastic particles released by the polymer decomposition are also environmentally harmful.^[1] Most of this polymeric material worldwide is used in automobile tires: estimates indicate that 1.5 billion of tires are manufactured each year,^[2,3] 800 million of them are discarded and this number is expected to grow 2% annually.^[4] A tire is a complex engineering product, mainly composed of elastomers, also containing textiles and metals.^[5] The production of crosslinked elastomers involves the vulcanization process, which prevents this class of polymers

from being completely recycled or reprocessed, on the contrary of thermoplastics.^[6] Considering the growing environmental awareness and the possibility of reusing the valuable raw materials contained in tires, end-of-life strategies for the management of used tires are highly demanding.

The classified methods for waste tire management of rubbery materials are: landfill, energy recovery, recycling, re-use, and prevention,^[7] following the European Union (EU) hierarchy,^[8] from the least to the most desirable. Although landfilling is the easiest way to discard used tires, the hazardous character of rubber waste makes this practice unacceptable given the current ecological requirements, justifying its ban by the EU since 1999.^[9] Energy recovery is the second method for rubber waste management, since tires present a calorific value equivalent to or higher than coal.^[10] Re-use of scrap tires by retreading is the most economically viable method for waste tire utilization, but its market is still scarce.^[10,11] Recycling is the most used approach for old tire management, and should be preferred to recovery, since only 30%–38% of the energy contained in a new tire can be recovered.^[12,13] To date, several recycling methods are being employed,^[6] most of them related to the grinding of rubber waste in a powder.^[14,15] Grinding rubber waste for recycling purposes

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was first proposed by Goodyear in 1853.^[16]

Among waste tire rubber (WTR) recycling approaches, blending the rubber waste particles with polymers is very effective, allowing to reduce the costs of the derived products.^[4,17] WTR polymer blends were already produced with the three families of polymers: elastomers, thermosets, and thermoplastics. In all cases, a final product with good mechanical characteristics is obtained, which can be further improved by the reduction of the particle size of rubber granulates^[18,19] or enhancing the compatibilization between the blend matrix and WTR powder.^[20–23] Despite this promising potential for recycling verified in WTR-based polymer blends, their solid-state cooling properties are still unexplored.

The current refrigeration technology is based on vapor-compression cycles employing hazardous gases as refrigerants, which may present global warming potentials up to 2000 times that of CO₂.^[24] Besides, the energetic efficiency of these machines is quite low, reaching only 30% of the Carnot efficiency.^[25] Solid-state cooling based on *i*-caloric materials is considered the most promising approach to replace conventional cooling systems due to the use of eco-friendly materials with higher energy efficiencies.^[25–29] *i*-Caloric effects are characterized by temperature and entropy changes induced by the application of external fields on a material, where *i* stands for intensive variables. Very recently, giant barocaloric effects, driven by the application of isostatic pressure, were observed in distinct elastomers: vulcanized natural rubber (VNR),^[30,31] PDMS,^[32] and acetoxy silicone rubber.^[33] In all these cases, barocaloric effect values are higher than those observed in other classes of materials, such as intermetallics. Besides revealing the high barocaloric potential of the elastomers, these results also open an encouraging perspective for using waste tire rubber in such applications, since elastomeric materials are the dominant components of a typical tire.^[5] Moreover, combining a novel recycling method with an energy-saving technology—represented by solid-state cooling—is particularly appealing from the sustainability standpoint.

In the present study, we systematically investigated the barocaloric effects in WTR and polymer blends made of WTR and VNR. We performed the experiments in a customized experimental apparatus developed by our group.^[34] The results show the barocaloric effects (adiabatic temperature change and isothermal entropy change) and the performance parameters in WTR-based samples are comparable to those values obtained from pure VNR. Moreover, the thermal exchange is significantly faster in WTR than in VNR, constituting an additional gain in using waste rubbers.

EXPERIMENTAL

Samples

We prepared the VNR samples using commercial pre-vulcanized latex (purchased from Siquiplas). The 8-mm-diameter VNR cylinders were cast into a plaster mold with a latex feed to prevent the formation of cavities in the drying process. The density of the samples is 902(7) kg·m⁻³, checked by a pycnometer.

UTEP Company supplied the WTR powder used in the blends. The diameters of the granules are distributed from

~10 μm to ~3 mm, with the highest concentration within the 0–100 μm range (~56%), as displayed in Table S1 (in the electronic supplementary information, ESI).

Polymer blend samples were prepared by mixing ~33% of WTR powder to 67% of latex into a cylindrical steel mold. The material was pressed by a piston to remove part of the latex. We roughly controlled how much of the latex was removed by the height of the piston inside the mold, neglecting the WTR powder going out with the liquid phase. In the final step, the blend was allowed to dry naturally for 3 days inside the mold and 7 days in the air. We indirectly determined the percentage of WTR in these 8-mm-diameter cylinders by the calculation of the difference between the weights before and after the whole process.

We also sintered WTR powder into an 8-mm-diameter cylinder under pressure of 40 MPa for 30 min at a high temperature of 453 K. We only used this sample for DSC measurement.

Fourier-transform Infrared Spectroscopy

We performed Fourier transform infrared spectroscopy (FTIR) characterizations within the 500 cm⁻¹ to 4000 cm⁻¹ range (fixed step of 2 cm⁻¹) using an FTIR spectrometer from Perkin Elmer® (model Spectrum Two).

Fig. S1 (in ESI) displays the FTIR spectra for VNR, pure WTR, and WTR 88 wt% blend. The bands between 3100 and 2800 cm⁻¹, observed in all spectra, are attributed to C—H stretching vibration and are typical for VNR,^[35] but are also verified in styrene-butadiene rubber compounds.^[36] The band at 1537 cm⁻¹, which appears only in the WTR-based samples, corresponds to the stretching vibration of double bonds in CH=CH groups and may indicate a partial devulcanization of the tire rubber.^[37] The presence of the band at 1710 cm⁻¹, assigned to the absorption of carbonyl groups (C=O), results from the milling process.^[37]

X-ray Diffraction

X-ray diffraction (XRD) data were obtained at the XRD1 beamline^[38,39] in the Brazilian Synchrotron Light Laboratory (LNLS). The beam energy used in XRD1 was 12 keV.

The XRD profile in Fig. S2 (in ESI), corresponding to the pure WTR powder, displays the typical amorphous components, assigned to elastomers usually contained in tires (natural and synthetic rubber, carbon black). Also, it exhibits various crystalline peaks. It is worth mentioning WTR powder is formed by tires from different producers, which may lead to a considerable variation in the compositional materials. Though, the presence of zinc compounds is expected, since zinc oxide (ZnO) is commonly used as an activator for the vulcanization reaction.^[40] We also identify the presence of common rubber fillers such as calcium carbonate (CaCO₃) and silicon dioxide (SiO₂).

Experiments under Pressure

We performed the compression-decompression experiments in a piston-cylinder carbon-steel chamber surrounded by a copper coil, which enables the use of cooling/heating fluids (such as water and liquid nitrogen). We used a thermostatic bath (TE 184, Tecnal) to reach temperatures above 280 K, by pumping water into the copper coil. Below 280 K, we used nitrogen to cool down the chamber. In both cases, two tubular heating elements (NP 38899, HG Resistências) were

used to provide thermal stability to the system. We used a manual 15,000-kgf hydraulic press (P15500, Bonevau) to apply the uniaxial load. A load cell (3101C, ALFA Instrumentos) measured the contact force. A cryogenic temperature controller (Model 335, Lake Shore Cryotronic) carried out the temperature acquisition and control. More details about the apparatus are found in Bom's report.^[34]

We performed the direct measurements of barocaloric adiabatic temperature changes in a four-step procedure: (i) the sample was compressed quasi-adiabatically, causing a fast increase in temperature; (ii) the sample was cooled down to the initial temperature while the load was kept constant; (iii) adiabatic decompression was applied to the sample, causing an abrupt decrease in temperature; (iv) sample temperature was returned to the initial value. We performed these cycles only after temperature stabilization.

Specific Heat from Differential Scanning Calorimetry

We determined the specific heat (c_p) as a function of temperature for the VNR, sintered WTR and the polymer blend samples (57 wt%, 73 wt%, and 88 wt%) using differential scanning calorimetry (DSC) data. The DSC measurements were carried out under ambient pressure, with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ from $\sim 180 \text{ K}$ to $\sim 350 \text{ K}$.

Calculation of Time Constant of Temperature versus Time Curves

We used the following relationship, describing the variation of the temperature as a function of time, to fit the decompression behavior of our experimental curves:^[41]

$$T(t) = T_0 + (T_1 - T_0) e^{-\frac{(t - t_1)}{\tau}} \quad (1)$$

where τ corresponds to the time constant; T_0 and T_1 are the initial and final temperatures, respectively; t is the time parameter and t_1 is the final time (when $T = T_1$). This model was fitted at the decompression region of temperature versus time curves within the 333–233 K range (examples in Fig. S3 in ESI). T_0 was defined as the inflection point of the exponential increase of temperature $\left(T_0 = T \left(\frac{d^2T}{dt^2} = 0 \right) \right)$, and T_1 was taken at

the beginning of the temperature plateau. We did not include the data for 223 K due to phase transitions occurring at this temperature, precluding the fitting. The values obtained from this procedure are listed in Table S2 (in ESI).

RESULTS AND DISCUSSION

Barocaloric Effects

Fig. 1 shows the adiabatic temperature change (ΔT_S) values obtained from decompression step of the barocaloric experiments, as a function of the distinct percentages of WTR, including pure VNR (0 wt%). We performed these experiments at the initial temperatures of 333, 293, and 243 K (Figs. 1a, 1b, and 1c, respectively), for pressure changes (Δp) of 173(3), 260(8), and 390(12) MPa. One can verify a similar pattern in all experimental conditions, where $|\Delta T_S|$ consistently decreases as WTR content is increased. The large values of temperature change are mainly due to the natural rubber content. As the WTR content increases, the natural rubber content decreases giving place to other non-rubbery elements also present in the

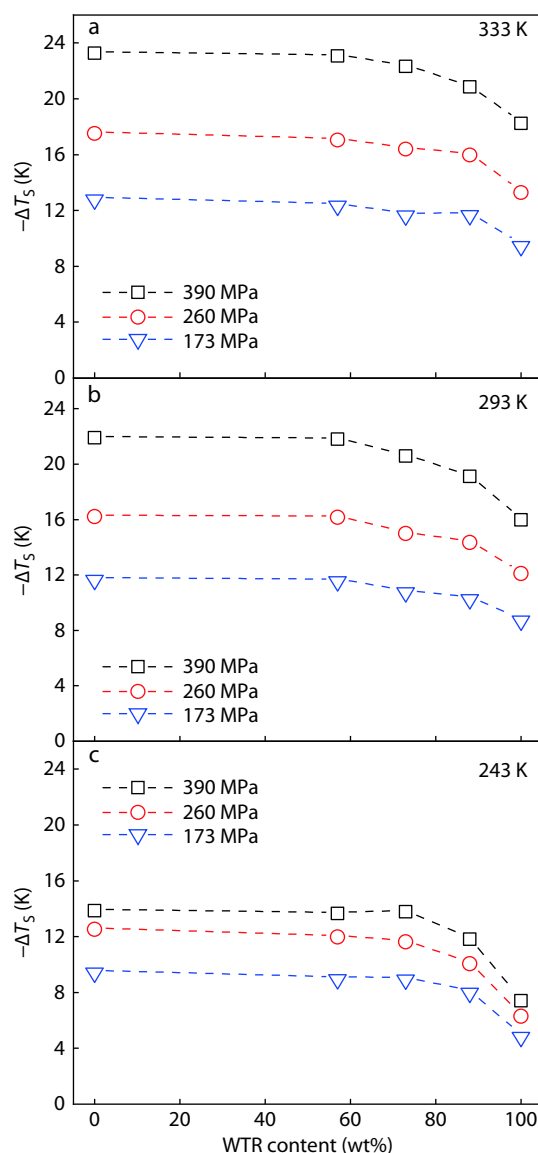


Fig. 1 Direct measurements of ΔT_S in decompression as a function of WTR weight percentages within the samples. The experiments were performed at the initial temperatures of 333 K (a), 293 K (b), and 243 K (c), for pressure changes of 173(3), 260(8), and 390(12) MPa. We estimate an error of 3% for pressure.

WTR, like oxides and other fillers (e.g. carbon black, fibers). In the case of oxide fillers (SiO_2 , CaCO_3 , and ZnO), we expect they give a slight contribution to the barocaloric effects due to the absence of structural phase transitions in these compounds within the pressure and temperature ranges of our experiments. Besides, the coexistence of other rubber materials in the WTR, especially from the butadiene group, possibly leads to lower barocaloric responses to the applied stress compared to VNR. Therefore, the barocaloric temperature and entropy changes tend to reduce at higher WTR percentages. Nevertheless, the rate of decrease is quite low, even for samples with pure WTR powder (100 wt%). The maximum $|\Delta T_S|$ reduction in comparison with pure VNR is 25%, obtained at 243 K for $\Delta p = 260 \text{ MPa}$; the average $|\Delta T_S|$ loss for the entire set of samples is $\sim 21\%$.

Although this reduction is significant, the $|\Delta T_S|$ values measured in WTR-based samples are still within the range of giant barocaloric changes, suggesting the use of WTR powder as a refrigerant in barocaloric cooling devices is technically viable.

Furthermore, we investigated the ΔT_S of WTR-based samples within the 223–333 K temperature range ($\Delta p = 173, 260$, and 390 MPa) in decompression. Figs. 2(a) and 2(b) show ΔT_S as a function of initial temperature, corresponding to the WTR 88 wt% and 100 wt% samples, respectively. Qualitatively speaking, both samples present the same trend: at lower temperatures, $|\Delta T_S|$ tends to decrease; above a temperature threshold, the curve changes its slope and $|\Delta T_S|$ varies at a lower rate. Moreover, analyzing $-\Delta T_S \times T$ curves, it is possible to notice this threshold shifts to higher temperatures as applied pressure increases. This behavior is consistent with the glass transition occurring in elastomers, already reported for VNR.^[31] Below the glass transition temperature (T_g), the movements of polymer chains are largely limited, reducing the number of accessible states of the system, decreasing the barocaloric effect as a consequence. Considering WTR is mainly composed of elastomeric material, this mechanism can also explain the results in Fig. 2. Finally, $|\Delta T_S|$ values for the 88 wt% sample are consistently higher in comparison with the 100 wt% sample, reaching the maximum $|\Delta T_S|$ of ~ 21 K (for pressure change of 390 MPa at 323 K).

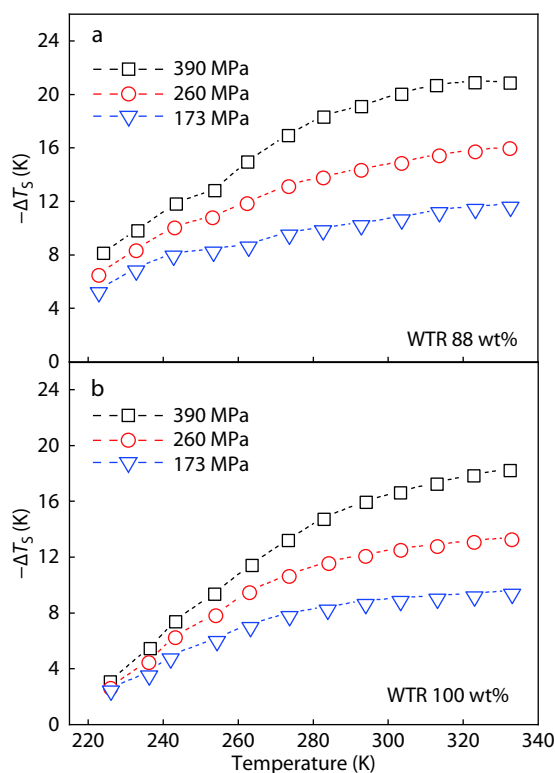


Fig. 2 Direct measurements of ΔT_S in decompression as function of initial temperature, for samples with 88 wt% (a) and 100 wt% (b) of WTR. The experiments were performed within the 223–333 K temperature range for pressure changes of 173(3), 260(8) and 390(12) MPa.

The isothermal entropy changes (ΔS_T) from the barocaloric experiments can be indirectly determined using the follow-

ing thermodynamic relation:^[42]

$$\Delta S_T(T, \Delta p) = -\frac{c_p(T)}{T} \Delta T_S(T, \Delta p) \quad (2)$$

where $c_p(T)$ is the specific heat at constant pressure. In our study, we obtained $c_p(T)$ from differential scanning calorimetry (DSC) measurements. ΔS_T obtained by this method for the 88 wt% and 100 wt% samples is shown in Fig. 3, where ΔS_T is plotted as a function of temperature, within the 223–333 K range and for $\Delta p = 173, 260$, and 390 MPa. Considering this calculation was based on the directly measured ΔT_S (Fig. 2a) and $c_p(T)$ presents a linear behavior within the considered temperature range, we can verify the qualitative behavior is the same in both data sets. For 390 MPa, the maximum values of $\sim 95 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ (WTR 88 wt%) and $\sim 75 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ (WTR 100 wt%) are comparable to the giant values obtained for VNR^[31] and PDMS.^[32]

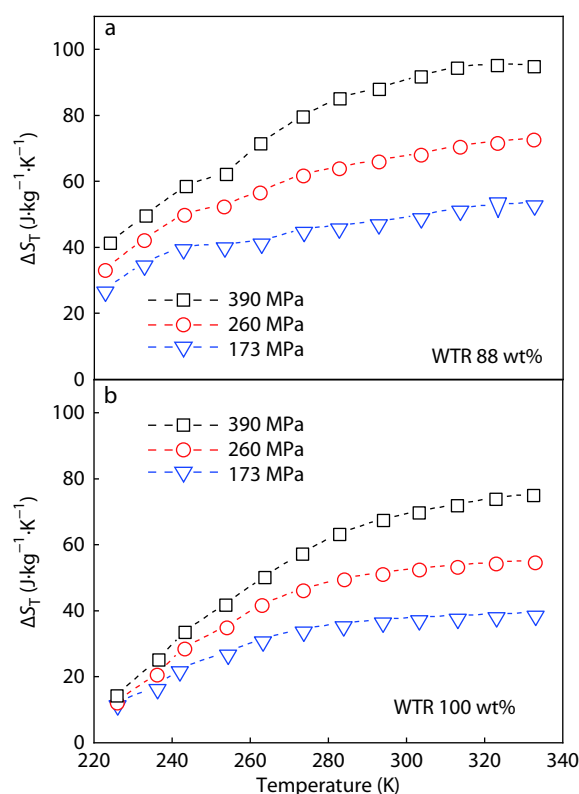


Fig. 3 Isothermal entropy change as a function of temperature calculated using Eq. (2) and ΔT_S data. The curves correspond to the WTR 88 wt% (a) and 100 wt% (b) samples, within the 223–333 K temperature range for pressure changes of 173(3), 260(8), and 390(12) MPa.

Performance Parameters

Following the normalization of i -caloric effects recently proposed,^[43] we calculated the normalized ΔT_S ($|\Delta T_S/\Delta p|$) and plotted against temperature (Fig. 4a) for VNR, WTR 88 wt% and 100 wt% samples, to provide a proper evaluation of their barocaloric performance. It is worth mentioning that the best materials are located at the top right corner of the plot: the materials exhibiting high normalized values with high-temperature change. One can see the dataset corresponding to VNR presents $|\Delta T_S/\Delta p|$ values consistently higher than those of

WTR-based samples. Nevertheless, the values reached by the WTR 100 wt% ($55.6 \text{ K}\cdot\text{GPa}^{-1}$ at 333 K) are still remarkable, comparable or superior to other barocaloric materials in literature, as displayed in the graph.^[32,44–47]

It is also crucial to analyze and compare the normalized refrigerant capacity (NRC) for barocaloric effect, which is defined as:^[31,33]

$$\text{NRC}(\Delta T_{\text{h-c}}, \Delta p) = \left| \frac{1}{\Delta p} \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_{\text{T}}(T, \Delta p) dT \right| \quad (3)$$

where $\Delta T_{\text{h-c}}$ is the difference between the hot reservoir (T_{hot}) and the cold reservoir (T_{cold}). Fig. 4(b) shows the NRC curves calculated for $\Delta p = 173 \text{ MPa}$, using the ΔS_{T} determined from Eq. (2). We have fixed the hot reservoir at 315 K for all samples.

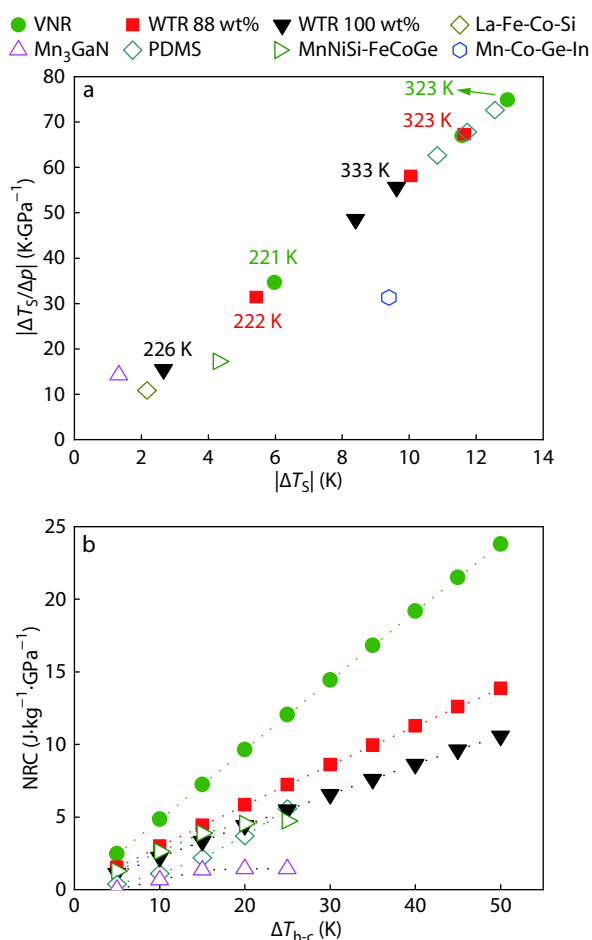


Fig. 4 Performance parameters for VNR, WTR 88 wt% and 100 wt% samples. (a) $|\Delta T_{\text{S}}/\Delta p|$ versus $|\Delta T_{\text{S}}|$. The solid symbols correspond to the measured data for $|\Delta p| = 173 \text{ MPa}$; the maximum and minimum temperatures of these data sets are indicated. The open symbols represent the following values from literature: PDMS ($|\Delta p| = 173 \text{ MPa}$),^[32] Mn_3GaIn ($|\Delta p| = 93 \text{ MPa}$),^[44] La-Fe-Si-Co ($|\Delta p| = 200 \text{ MPa}$),^[45] Mn-Co-Ge-In ($|\Delta p| = 300 \text{ MPa}$),^[46] and MnNiSi-FeCoGe ($|\Delta p| = 250 \text{ MPa}$).^[47] (b) Normalized refrigerant capacity curves as a function of $\Delta T_{\text{h-c}}$ for $|\Delta p| = 173 \text{ MPa}$ (solid symbols). The hot reservoir was fixed at 315 K for the three measured samples. Values from literature (open symbols): PDMS ($T_{\text{hot}} = 315 \text{ K}$ and $|\Delta p| = 173 \text{ MPa}$), Mn_3GaIn ($T_{\text{hot}} = 295 \text{ K}$ and $|\Delta p| = 139 \text{ MPa}$), and MnNiSi-FeCoGe ($T_{\text{hot}} = 335 \text{ K}$ and $|\Delta p| = 270 \text{ MPa}$). The dotted lines are guides for the eyes.

The initial values in the three curves are very close, but this difference increases for higher $\Delta T_{\text{h-c}}$. The maximum NRC value for WTR samples is lower than VNR at $\Delta T_{\text{h-c}} = 50 \text{ K}$, but once again higher than other materials with giant barocaloric effect.^[32,44,47]

The whole analysis developed in this study reveals an encouraging scenario involving the use of waste rubbers in solid-state cooling applications. The values observed for ΔT_{S} , ΔS_{T} , and the performance parameters ($|\Delta T_{\text{S}}/\Delta p|$ and NRC) demonstrate WTR-based samples exhibit the required characteristics to act as refrigerants in barocaloric devices, surpassing most of the best barocaloric materials in literature.

An additional advantage regarding WTR performance is its faster thermal exchange in comparison with VNR. A proper way to evaluate the thermal exchange is to analyze the temperature-time data of our direct ΔT_{S} measurements and calculate, using Eq. (1), the time constant (τ) of the curve after the pressure is released.^[41] Fig. 5 shows the time-constant (τ) versus WTR content for $\Delta p = 173 \text{ MPa}$ at $T = 273 \text{ K}$. We observe a significant decrease of the time constant (τ) as the WTR content is increased in the samples. The time-constant drops from 25.6 s, for VNR, to 14.4 s, for WTR. Even in the WTR 88 wt% sample, the value is 16.5 s. Taking other temperatures, for the same pressure change (Table S2, in ESI), the average τ decrease in the WTR 100 wt% sample, in comparison with pure VNR, is 11.1 s (~48% lower). These results show that the heat flows faster from WTR in the barocaloric process, an effect that can be explained by the relatively high concentration of carbon black^[48,49] and other fillers in WTR powder. Bearing in mind the slow thermal exchange is still a challenge for elastomeric materials regarding cooling applications, using WTR as refrigerant would concomitantly address this issue, besides its eco-friendly appeal. Finally, the particle size of WTR powder employed in our study was not controlled, and the VNR+WTR blends did not receive any post-synthesis processing. Nevertheless, several studies show the precise control of particle size and blending conditions can highly improve the characteristics of the synthesized blends.^[4,17] Thus, we expect even better caloric performances of VNR+WTR blends in further studies involving a systematic optimization of synthesis and processing.

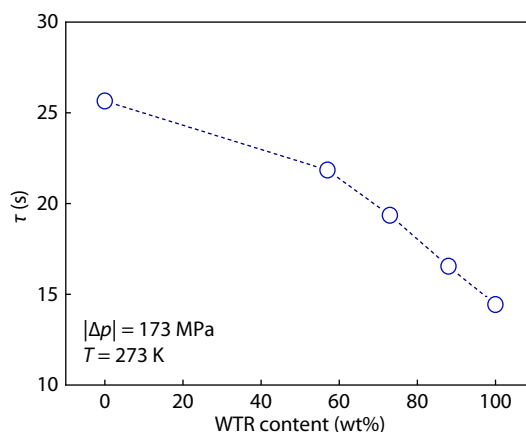


Fig. 5 Time constant τ as a function of the WTR content for $|\Delta p| = 173 \text{ MPa}$ and $T = 273 \text{ K}$. The values of τ were obtained from the direct ΔT_{S} measurements.

CONCLUSIONS

A systematic investigation of the barocaloric characteristics of VNR and WTR polymer blends revealed that WTR-based samples present a slight reduction in the barocaloric effect in comparison with pure VNR. Nevertheless, the measured values are still within the giant barocaloric range: the maximum $|\Delta T_S|$ is 23.2 K (57 wt% WTR, at 333 K for $\Delta p = 390$ MPa) and the maximum ΔS_T is 95 J·kg⁻¹·K⁻¹ (88 wt% WTR, at 333 K for $\Delta p = 390$ MPa). Also, the performance parameters are impressive, comparable to or better than several barocaloric materials reported in the last years. Besides, WTR samples exhibit a faster thermal exchange than VNR, which may represent a substantial advantage for barocaloric cooling devices. All these findings evidence the promising potential of WTR for solid-state cooling applications, fostering a new alternative for the recycling of waste tire rubber, besides contributing significantly to the field of sustainable energy technology.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2385-y>.

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