

POLYETHYLENE WAX/EPDM BLENDS AS SHAPE-STABILIZED PHASE CHANGE MATERIALS FOR THERMAL ENERGY STORAGE

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ABSTRACT

Various amounts of a paraffinic wax were dispersed by melt mixing in an ethylene/propylene diene monomers (EPDM) rubber matrix. The resulting compounds were then vulcanized to obtain shape-stabilized rubbery phase change materials for thermal energy storage. The addition of the paraffinic wax induced a retardation in the vulcanization kinetics of the EPDM matrix. Calorimetric measurements evidenced how the homogenous distribution of the wax domains within the rubber, confirmed by electron microscopy observations, allowed for retaining the melting enthalpy of the neat paraffinic wax even at elevated concentration. The thermal energy storage and release capabilities of the investigated compounds were maintained even after various thermal cycles. The incorporation of polyethylene wax had a positive effect (increasing proportionally to its content) on the mechanical properties of the EPDM matrix, as documented from both the dynamical and the quasi-static tensile tests. [doi:10.5254/rct.82.83719]

INTRODUCTION

Thermal energy storage (TES) is a technology that allows thermal energy to be stocked by heating or cooling a storage medium, in order to use the stored energy for heating/cooling applications or power generation. These systems are particularly interesting for building constructions, in which about one-half of the energy consumed is in the form of thermal energy, and the energy demand may vary in time. Therefore, TES systems can help to balance the energy demand and supply. They can also reduce peak demands, energy consumption, CO₂ emissions, and costs while increasing the overall efficiency of energy systems.¹ Furthermore, the conversion and storage of variable renewable energy in the form of thermal energy can also help to increase the share of renewables in the energy mix. For instance, TES is becoming particularly important in combination with concentrating solar power plants, where solar heat can be stored for electricity production when sunlight is not available.

Latent heat TES is particularly attractive because it provides a high-energy storage density at a constant temperature, corresponding to the transition temperature of the phase change material (PCM). The change of phase could be either a solid/liquid or a solid/solid process. Melting processes involve energy densities on the order of 100 kWh/m³ (e.g., ice).^{2–7} Among organic PCM, paraffin waxes are the most widely investigated because of their high thermal storage density, wide phase transition temperature range, and relatively limited costs.⁸ However, the relatively low thermal conductivity and leakage during the melting process limits its applications in several fields, such as building materials. In addition, the paraffin could also present problems of compatibility with hosting materials.⁹

Therefore, to prevent its flow and/or leakage, the paraffin must be encapsulated in other polymer matrices. To form a so-called shape-stabilized phase change material (SSPCM), several matrices have been considered, such as polyolefins, elastomers, and polymer blends.^{1,10–19} In particular, various research groups have prepared different SSPCMs with various hosting matrices such as high-density polyethylene,²⁰ polypropylene,^{10,21} acrylic resins,²² poly(methylmethacry-

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TABLE I
LIST OF THE PREPARED SAMPLES (UNITS IN PHR)

Sample code	C-000	C-025	C-050	C-075	C-100	C-125
EPDM rubber	100	100	100	100	100	100
Wax	0	25	50	75	100	125
Zinc oxide	4	4	4	4	4	4
Stearic acid	1	1	1	1	1	1
Suphur	1.9	1.9	1.9	1.9	1.9	1.9
MBT	0.6	0.6	0.6	0.6	0.6	0.6
TMTM	1.9	1.9	1.9	1.9	1.9	1.9

late),^{23,24} polyurethane block copolymer,^{25,26} and styrene–butadiene–styrene triblock copolymer.^{19,27} Generally speaking, various confinement abilities of these SSPCMs have been reported with the phase change temperatures in a range of 313–333 K and a latent heat between 100 J/g and 200 J/g. In addition, thermal conductivity enhancement²⁸ and flame retardancy^{29,30} of SSPCMs have been investigated.

On the basis of these considerations, the objective of the present article is to prepare novel SSPCM based on an ethylene/propylene diene monomers (EPDM) rubber^{31,32} containing different amounts of a paraffin wax having a relatively high melting temperature (i.e., around 110 °C). Therefore, a systematic investigation of the correlation between the microstructural behavior and the thermomechanical properties of the resulting materials was carried out.

EXPERIMENTAL

MATERIALS

EPDM rubber (Royaledge 5041), with a 75/25 ethylene/propylene weight ratio, 2.8 wt% DCPD, Mooney viscosity ML (1+4)/125 °C = 26, was obtained from Lion Copolymer Geismar (Geismar, LA, USA). Paraffinic wax (Polywax 1000) with melting point 113 °C was obtained from Baker Hughes (Houston, TX, USA). The vulcanizing agents zinc oxide, stearic acid, sulphur, 2-mercaptobenzothiazole (MBT), and tetramethylthiuram monosulfide (TMTM) were obtained from Rhein Chemie (Cologne, Germany).

PREPARATION OF THE SAMPLES

EPDM/wax blends with different paraffin wax contents (see Table I) were prepared by melt compounding in an internal mixer (Thermo Haake Rheomix 600) with counterrotating rotors. The temperature was kept at 100 °C (i.e., about 10 °C below the melting point of polyethylene [PE] wax), and the rotor speed was 60 rpm. First, EPDM was fed into the mixer and mixed for 3 min, then the vulcanizing agents were added and mixed for another 3 min. The PE wax was gradually fed into the mixer after 6 min; then, after 13 min, the mixer was stopped. After vulcanization in a hydraulic press at 160 °C at a pressure of 8 bar, square sheets (140 × 140 mm²) of each blend, with thickness values between 1 and 2 mm, were obtained.

EXPERIMENTAL TECHNIQUES

Vulcanization kinetics were determined by using an oscillating disc rheometer (Monsanto R-100) at 184 °C, according to ASTM D2084 standard.

TABLE II
RESULTS OF RHEOMETRIC MEASUREMENTS ON EPDM/PARAFFIN WAX SAMPLES, ACCORDING TO ASTM D2084^a

Sample code	C-000	C-025	C-050	C-075	C-100	C-125
M_L (lb·in)	2.59	1.14	0.62	0.41	0.41	0.41
M_H (lb·in)	25.78	15.84	10.1	6.87	4.97	3.47
t_2 (min:s)	3:37	5:17	6:38	7:40	9:19	12:40
t_{90} (min:s)	9:19	11:37	13:11	14:30	16:08	17:26
Vulcanization time at 160 °C (min)	50	60	70	75	80	85

^a M_L , lowest torque value; M_H , highest torque value; t_2 , scorch time; t_{90} , vulcanization time.

Differential scanning calorimetry (DSC) analysis was carried out with a DSC1 instrument (Mettler Toledo, Columbus, OH, USA) under nitrogen flow. The heating/cooling rate was set at 10 °C/min for all the measurements, starting from -100 °C up to 200 °C. Disc-shaped specimens (5 mm in diameter, about 10 mg) were cut from vulcanized sheets and placed in the bottom of aluminum crucibles of 40 μ L in capacity. Melting temperature (T_m), melting enthalpy (ΔH_m), and encapsulation efficiency (E_f) of the blends, determined as the ratio between the effective melting enthalpy of the paraffin wax in the samples and the ΔH_m values of the paraffin PE wax, were measured.

Field emission scanning electron microscopy (FESEM) observations of the cryofractured surfaces of the specimens were performed through a Zeiss Supra 40 microscope, operating at an acceleration voltage of 3.0 kV.

Dynamic mechanical thermal analysis (DMTA) under tensile configuration was carried out with a DMA Q800 device by TA Instruments (New Castle, DE, USA) on rectangular specimens $30 \times 5 \times 2$ mm³. Tests were performed in the temperature range from -100 °C to $+150$ °C at a frequency of 1 Hz.

Uniaxial tensile tests on ISO 527 1BA type specimens were performed with an Instron 4502 testing machine equipped with a 1 kN load cell. A long travel extensometer (Instron model 2603-080, High Wycombe, UK) with a gauge length of 25 mm was applied to the specimens to measure the strain during tensile tests. Tests were performed at a testing speed of 200 mm/min, and at least five specimens were tested for each sample.

Hardness was measured at room temperature with a Shore Micro-O-Ring hardness tester supplied by Instron, according to ASTM D2240 standard for type M, on samples 1.5 mm thick.

RESULTS AND DISCUSSION

RHEOLOGY AND MICROSTRUCTURE

After mixing, all of the EPDM/paraffin wax blends appear to be homogeneous at a visual inspection. Therefore, rheometric curves were acquired for each compound, and the most significant parameters are listed in Table II. Both the lowest torque (M_L) and the highest torque (M_H) decrease as the wax concentration increases, because at 184 °C, the paraffin wax is molten and it lowers the overall compound viscosity. For the same reason, the vulcanization kinetics are slower as the amount of paraffin wax increases. It has also to be considered that at higher wax amounts, the concentration of curatives and polymer reactive sites (DCPD) is reduced. In these conditions, the vulcanization reaction kinetics is slower.

The thermomechanical properties of the prepared blends and the possibility of exploiting the peculiar thermal properties of the paraffin are related to the microstructural features of the samples.

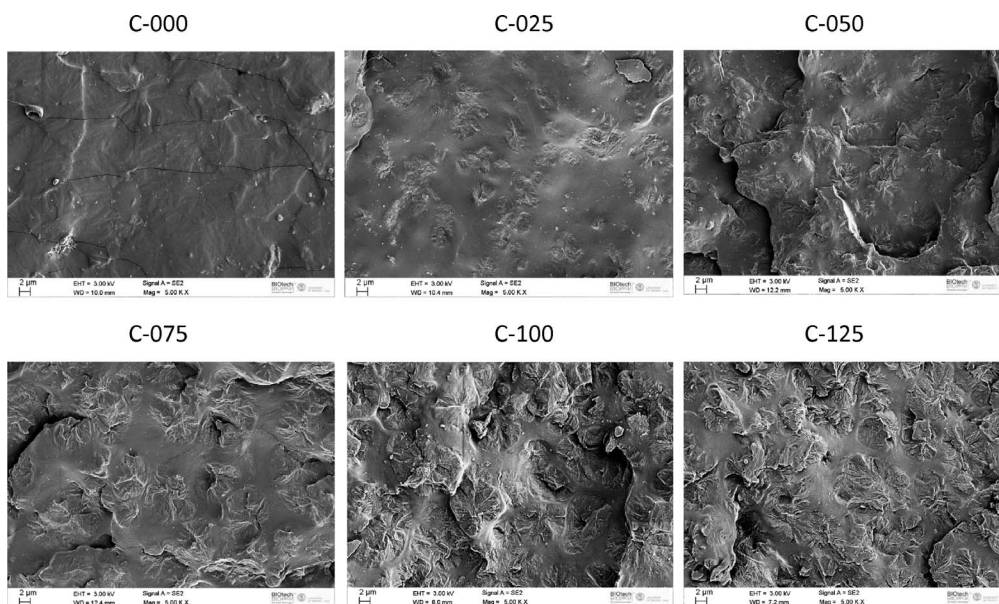


FIG. 1. — FESEM micrographs of EPDM/paraffin wax samples.

In Figure 1, FESEM micrographs of the cryofractured surfaces of the samples with various paraffin amounts are reported. Although the C-000 sample presents a smooth surface, in the C-025 blend, a homogeneous distribution of paraffin wax domains within the EPDM matrix, having a mean diameter of 2.5 μm , can be detected. Moreover, a good interfacial adhesion between the two polymeric phases can be observed in all the prepared specimens. The increase of the paraffin content in the samples leads to an increase in the dimension of the wax domains, with a mean diameter of 3 and 4 μm for C-050 and C-075, respectively. For the C-100 and C-125 standards, the dimension of the PE domains remains fairly constant at 4 μm , and an interconnection between the paraffin phase domains begins to be clearly evident. Moreover, when increasing the wax amount, the fracture profile is more irregular and jagged because of the plastic deformation of the paraffin domains within the EPDM matrix. It can be therefore concluded that the microstructure of the prepared samples is characterized by the presence of domains dispersed within the EPDM phase. Even if the dimension of the wax domains increased with the wax concentration, the paraffin remained entrapped within the EPDM phase. An SSPCM was thus obtained at all compositions, and no bleeding of the wax was observed above the melting temperature.

THERMAL BEHAVIOR

The possibility of applying PCMs in engineering applications is related to their capabilities to store/release thermal energy in a certain temperature interval. Therefore, the investigation of the thermal properties of the prepared specimens plays a key role in the present investigation. In Figure 2a, DSC thermograms of the first heating stage of the EPDM/paraffin blends is reported, whereas the most important results are summarized in Table III. It is evident that the melting temperature is not substantially affected by the confinement of the paraffin wax within the EPDM matrix, because the melting temperature of the paraffin in the blends is very near to that of the wax (i.e., 112 $^{\circ}\text{C}$). Interestingly, the E_f values are around 90–95% for all of the tested compositions. This means that the incorporation of the paraffin wax within the EPDM matrix does not affect the thermal properties

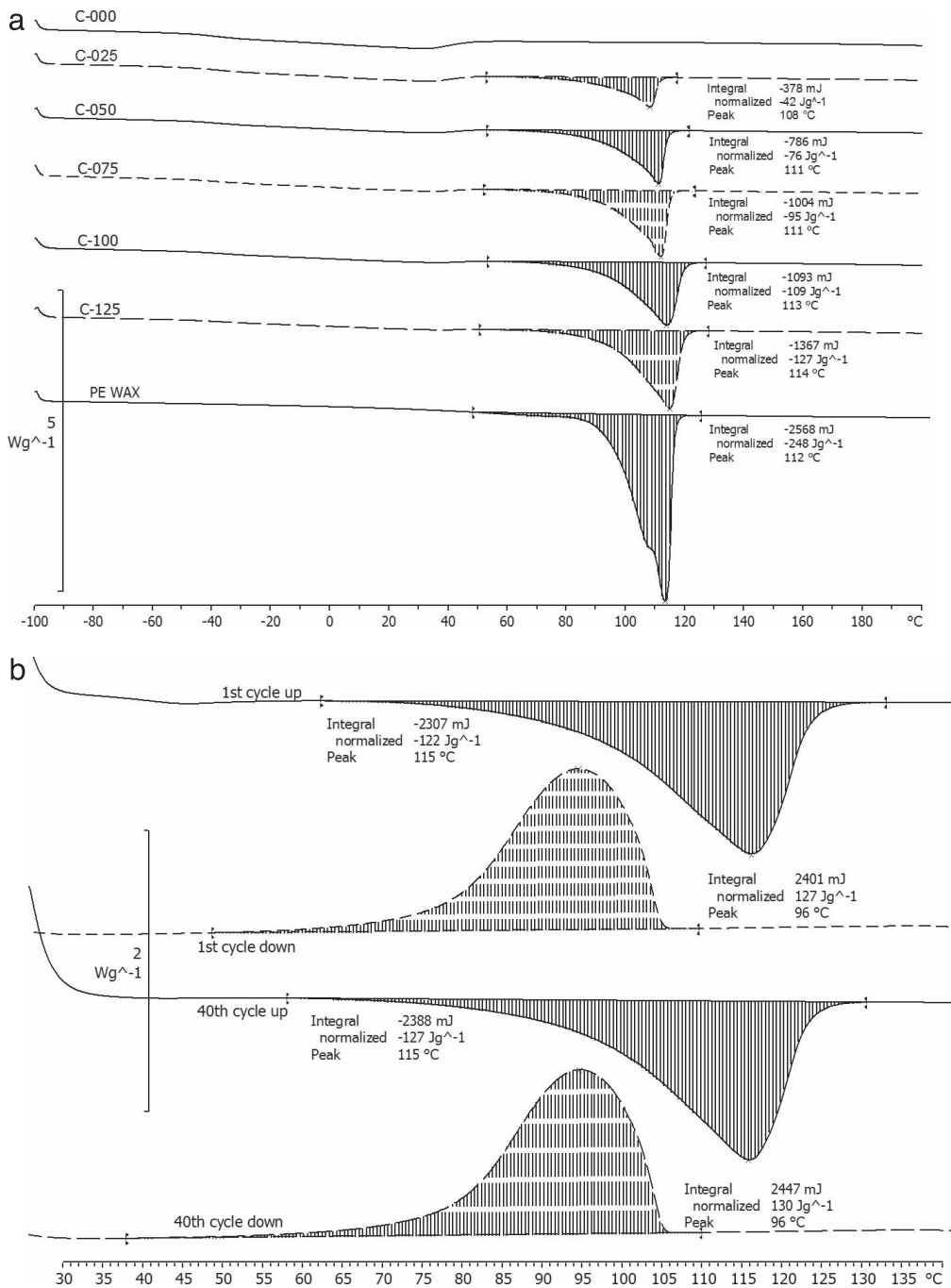


FIG. 2. — DSC thermograms of EPDM/paraffin wax samples. (a) First heating scan. (b) Comparison between DSC thermograms of the C-125 sample at the first and the 40th cycle.

TABLE III
RESULTS OF DSC TESTS ON EPDM/PARAFFIN WAX SAMPLES (FIRST HEATING CYCLE)^a

Sample code	C-000	C-025	C-050	C-075	C-100	C-125	wax
T _m (°C)	n.a.	109 ± 1	111 ± 1	112 ± 1	113 ± 1	113 ± 1	112 ± 1
ΔH _m (J/g)	n.a.	41 ± 1	74 ± 3	95 ± 1	112 ± 3	122 ± 7	113 ± 1
E _f (%)	n.a.	90	95	94	95	92	N.A.
ΔH _{TOT} (J/g)	260 ± 10	300 ± 10	340 ± 10	350 ± 10	360 ± 10	390 ± 10	N.A.

^a T_m, melting temperature; ΔH_m, melting enthalpy; E_f, encapsulation efficiency; ΔH_{TOT}, total enthalpy in the interval 20–130 °C.

of the paraffin, and the heat developed during the thermal transition of the various samples is practically proportional to the paraffin content in the blends. Furthermore, it is also interesting to evaluate the retention of the thermal effect after several thermal cycles. In Figure 2b, the DSC thermograms of the C-125 sample after the first and after the 40th heating/cooling cycles are compared. It is interesting to observe how the thermal properties of the tested sample are not affected by the number of the testing cycles, because the melting and crystallization properties of the C-125 sample after the first heating/cooling stage are very near to that detected after 40 consecutive cycles. The melting enthalpy values reported for these system are comparable to those obtained by other authors on SSPCMs at similar paraffin concentrations.²⁸

MECHANICAL BEHAVIOR

The incorporation of the paraffin wax in the EPDM matrix affects the mechanical behavior of the prepared blends. Therefore, the investigation of the tensile behavior of these samples is of crucial importance. In Figure 3a–c, the results of the DMTA analysis are represented in terms of the storage modulus (E') and of the loss tangent ($\tan\delta$) values as a function of the temperature. It is evident that the paraffin wax leads to a remarkable stiffening effect on the EPDM matrix below the melting temperature of the wax (around 110 °C), with a progressive increase of the E' values with the paraffin amount. For instance, the E' value at –100 °C of the C-000 sample is 1750 MPa, whereas C-125 at the same temperature shows an E' value of 2960 MPa (+69%). This behavior could be explained considering that the elastic properties at the ambient temperature of the used wax are higher than that of the EPDM rubber. Above the melting temperature, an opposite trend can be detected, because the molten paraffin acts as liquid plasticizer within the EPDM matrix (see Figure 3b), and E' values of the prepared blends systematically decrease with the wax amount. From loss tangent trends, it is evident that the position of the T_g (i.e., $\tan\delta$ peak) of the EPDM is not affected by the incorporation of the paraffin. As could be expected, the intensity of this transition decreases with the progressive increase of the paraffin content in the samples, because of the stabilizing effect played by the paraffin within the EPDM matrix (see Figure 3c). Correspondingly, the transition evidenced around 100 °C is simply due to the melting of the paraffin, and in fact, the intensity of this signal is proportional to the amount of paraffin wax in the system.

The mechanical behavior of the prepared blends at ambient temperature was also investigated by uniaxial tensile tests under ramp conditions. Representative stress–strain curves are reported in Figure 4, whereas the most important mechanical parameters are summarized in Table IV. Also, these tests confirm what was previously reported for the DMTA analysis, that is, the stabilizing effect of the wax paraffin on the EPDM matrix at room temperature. In fact, a progressive increase of the tensile modulus at strain levels of 5%, 50%, and 100% with the paraffin amount can be observed. In the same way, considering that the hardness of the considered wax at the solid state is

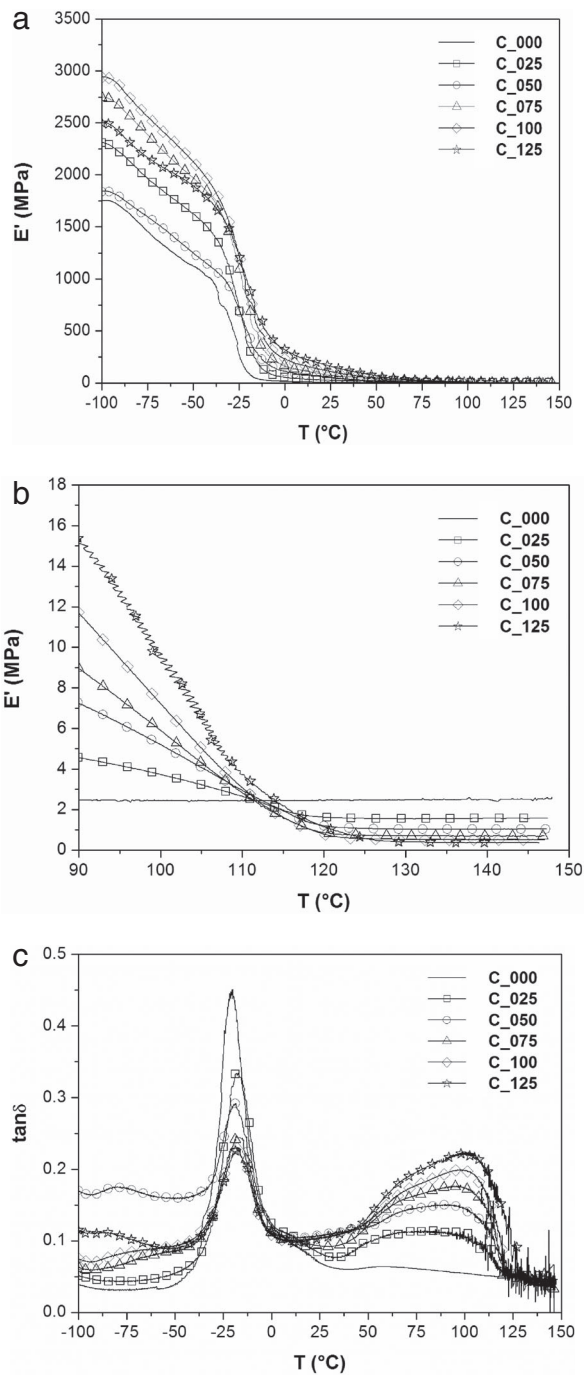


FIG. 3. — Results of DMTA analysis on EPDM/paraffin wax samples. (a) Storage modulus (E'). (b) Detail of storage modulus (E') curves in the interval 90–150 °C. (c) Loss tangent ($\tan\delta$).

TABLE IV
RESULTS OF QUASI-STATIC TENSILE TESTS AND HARDNESS EVALUATION ON EPDM/PARAFFIN WAX SAMPLES

Sample code	$E_{5\%}$ (MPa)	$E_{50\%}$ (MPa)	$E_{100\%}$ (MPa)	σ_y (MPa)	ϵ_b (%)	hardness (shore)
C-000	6.72 ± 1.84	2.29 ± 0.10	1.36 ± 0.03	—	>500	61
C-025	17.52 ± 1.55	3.70 ± 0.04	2.01 ± 0.03	1.69 ± 0.02	>500	71
C-050	32.03 ± 3.81	4.81 ± 0.12	2.56 ± 0.07	2.40 ± 0.05	>500	77
C-075	40.85 ± 1.65	5.77 ± 0.05	2.95 ± 0.02	2.88 ± 0.02	>500	81
C-100	54.08 ± 2.24	6.62 ± 0.10	3.34 ± 0.05	3.35 ± 0.06	>500	83
C-125	61.76 ± 1.74	7.16 ± 0.10	3.58 ± 0.03	3.71 ± 0.04	>500	88

much higher than that of the EPDM rubber, the shore hardness strongly improves with the wax concentration, increasing from 61 for the C-000 sample to 88 for the C-125 sample. Also, the flow stress (σ_y) significantly increases upon paraffin addition. Even if paraffin waxes are generally very brittle at the solid state, it is interesting to note how the paraffin introduction does not significantly impair the failure properties of the samples, and the strain at break values remain above 500%, even with a wax content of 125 phr. This result can be explained considering that the distribution of the wax within the EPDM matrix is rather homogeneous even at elevated paraffin concentrations.

CONCLUSIONS

A paraffin wax was melt compounded with an EPDM rubber matrix at different concentrations, and the blend was vulcanized. The resulting materials were then thermomechanically characterized. It was observed that the vulcanization kinetics of the EPDM matrix were retarded

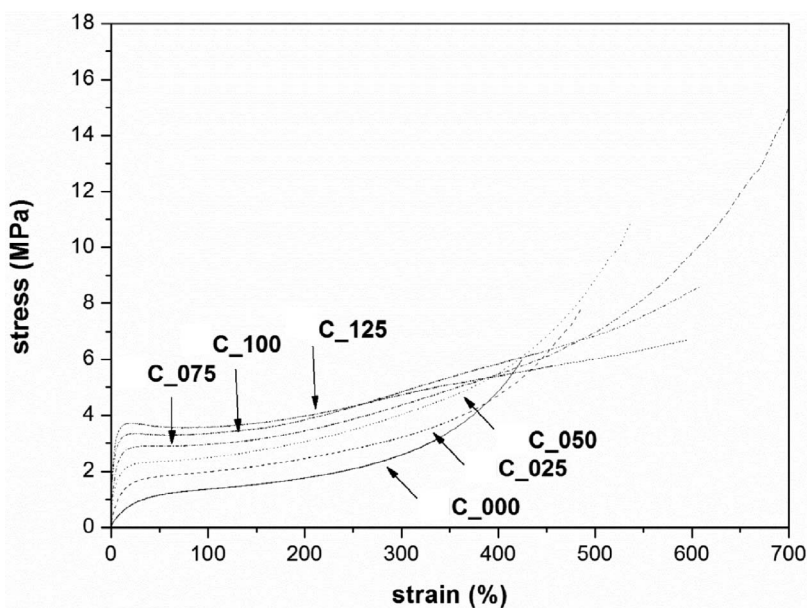


FIG. 4. — Representative stress–strain curves of EPDM/paraffin wax samples as determined from tensile tests.

upon paraffin addition, probably because at higher wax amounts, the concentration of curatives and polymer reactive sites was reduced.

The homogenous distribution of the wax phase within the rubber even at elevated concentrations detected in FESEM images confirmed the formation of shape-stabilized material, in which the melting enthalpy was practically proportional to the PE wax amount, even after several thermal cycles. Paraffin wax had a stiffening effect on the EPDM matrix, with a progressive increase of the dynamic modulus (E') of the elastic and flow properties of the samples proportionally to the paraffin amount, without impairing the failure resistance of the samples.

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