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Accepted for publication in Periodica Polytechnica-Mechanical Engineering
Published in 2015

DOI: [10.3311/PPme.8321](https://doi.org/10.3311/PPme.8321)

Novel Bifunctional Additive for Rubbers: Cyclic Butylene Terephthalate Oligomer

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RESEARCH ARTICLE

Received 11 June 2015; accepted after revision 04 September 2015

Abstract

In this paper the effect of a novel bifunctional additive [cyclic butylene terephthalate (CBT)] was investigated on the rheological, curing and mechanical properties of natural rubber (NR), styrene butadiene rubber (SBR), oil extended styrene butadiene rubber (oSBR), acrylonitrile butadiene rubber (NBR) and ethylene propylene diene rubber (EPDM). Results showed, that CBT acted as an effective lubricant, decreasing the viscosity of the raw mixtures significantly. Furthermore CBT recrystallized upon cooling and acted as semi-active filler, slightly increased the mechanical properties of the tested non strain-crystallizable synthetic rubbers. The polarity of the rubber matrix had a strong effect on the adhesion between rubber and CBT, the higher the polarity of the rubber, the better the adhesion between the two phases was.

Keywords

rubber, bifunctional additive, cyclic butylene terephthalate oligomer, CBT, plasticizer, processing aid, semi-active filler

1 Introduction

Rubber industry, rubber materials and products have undergone an enormous development since Charles Goodyear achieved the first sulphur curing process in 1839. Processing techniques, application fields, raw materials and additives are all involved in this progress. However, rubber products distinguish themselves from plastic ones in the formulation, mix preparation and processing technologies. For example, the number of compounding ingredients is markedly higher than those of thermoplastic or thermoset resins. Unfilled rubber vulcanizates (especially synthetic rubber based ones) possess poor mechanical and wear properties. As a consequence, they do not fulfil the practical requirements of technical applications. This problem can be solved by various fillers (usually carbon black and inorganic mineral fillers), but these fillers have a negative effect on the processability, namely by increasing the viscosity of the raw mixtures. In order to compensate this effect various types of plasticizers and processing aids are used. The latter, however, often negatively influence the mechanical properties of the rubber compounds. If processability of the raw mixtures and mechanical properties of the final vulcanizates could be improved by a single additive, then it would have a great impact on the properties and thus support the application possibilities of rubbers.

Cyclic butylene terephthalate oligomer (CBT) is a cyclic oligoester and a promising candidate for this purpose. Due to its very low melt viscosity (at about 30 mPas, 190°C) and its good compatibility with most thermoplastic polymers it is proved to be an excellent processing aid for thermoplastic resins [1, 2].

Potential application fields are broadened by the possibility of the in-situ polymerization of the material in the presence of a suitable catalyst via ring-opening polymerization [3, 4]. Therefore it is a suitable matrix material of various micro[5, 6] and nanocomposites [7, 8]. CBT is predestined as matrix materials for composites owing to its very low melt viscosity supporting the wet-out of the given reinforcement. However, the polymerized cyclic butylene terephthalate (pCBT) shows more rigid and brittle behaviour than its conventional counterpart, namely, PBT, produced by polycondensation. This is due to the fact that pCBT exhibits higher molecular weight

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Table 1 Rubber types, producers and properties

Abbreviation	Producer, Type	Properties
NR	Aslett Rubber, NR TSR 20	Mooney viscosity (ML, 1+4, 100°C): 60±5
SBR	Goodyear Chemical, Plioflex® 1502	Mooney viscosity (ML, 1+4, 100°C): 44 Bound styrene content: 23.5 m%
oSBR	Styron, Buna® SB 1723	Mooney viscosity (ML, 1+4, 100°C): 50 Bound styrene content: 23.5 m%
NBR	Versalis, Europrene 3345	Mooney viscosity (ML, 1+4, 100°C): 45 Bound acrylonitrile content: 33 m%
EPDM	Akrochem, Europrene 501A	Mooney viscosity (ML, 1+4, 100°C): 46 Bound ethylene content: 53 m% Bound ENB content: 4.1 m%

and crystallinity than PBT. Several techniques can be found in the literature for the compensation of this embrittlement, for example co-polymerization with ϵ -caprolactone [9], compounding with polycaprolactone, polycarbonate, polytetrahydrofuran, multiwalled carbon nanotubes [10], chain extending by a bifunctional epoxy resin during the polymerization [11], or reactive blending with isocyanates [12, 13].

Only a few papers dealt with CBT-rubber blends so far. In peroxide cured HNBR rubbers [14-16] the introduced CBT recrystallized during cooling in the corresponding rubber. The plate-like CBT crystals in the rubber matrix significantly improved the mechanical properties of HNBR. Attempt was also made to polymerize CBT to pCBT during the curing process of the HNBR. The pCBT conversion remained, however, very low (ca. 11% after 25 min at 190°C). A subsequent annealing at 250°C for 3 hours caused the conversion rate to increase to 70-90% [15]. Wear tests using different test configurations revealed that both CBT and pCBT prominently decreased the specific wear rate and the coefficient of friction of the related HNBR [14-16].

Based on previous results it can be stated, that the investigation of rubber-CBT blends is a promising research field. To get deeper understanding, the effects of CBT on the curing mechanisms and processability of the raw mixtures, as well as the potential reinforcing behaviour of the recrystallized CBT oligomer should be investigated. This work is devoted to study the effect of CBT on the rheological, mechanical and morphological properties of various rubber systems. Considering the results presented in the literature we start our work with an 'unpolymerizable' CBT variant (i.e. CBT without catalyst).

2 Materials and processing

Properties of the rubbers used for compounding are given in Table 1.

The oligomer was CBT 100®, produced by Cyclics Europe GmbH (Schwarzheide, Germany). The other ingredients used were: zinc-oxide (ZnO 500, provided by Zinc Oxide LLC, Dickson, Tennessee, USA), stearic acid (Radiacid 0444, product of Oleon, Ertvelde, Belgium). N-cyclohexyl-2-benzothiazole

sulfenamide (CBS) and sulphur were purchased from Ningbo Actmix Polymer (Ningbo, China) under the trade names of Curekind CBS and Curekind Sulphur, respectively.

Formulation of the tested rubbers is listed in Table 2.

Table 2 Recipes of the compounds. Note: phr – parts per hundred parts rubber

	oSBR	NR, SBR, NBR, EPDM
	phr	
Rubber	137.5	100
ZnO	5	5
Stearic acid	1	1
CBS	1	1
Sulfur	2	2
CBT	0, 20	0, 20

Rubber compounds were made using a laboratory two-roll mill (Labtech LRM-SC-110, Labtech Engineering Co.Ltd. Samutprakarn, Thailand), with a roll temperature of 100°C and 80°C (front and rear) for the EPDM and 70, 50°C for the other compounds. Friction was set to 1.15 for EPDM while 1.3 for all the others.

The compositional difference among oSBR and other rubbers is due to the fact that the formers contained 37.5 phr extender oil (accordingly, the neat rubber content of 137.5 phr oSBR is 100 phr SBR).

Curing into sheets with 2 mm thickness occurred at 170°C under 2 MPa pressure in a Collin Teach-Line Platen Press 200E laboratory press (Dr. Collin GmbH, Ebersberg, Germany). Curing times ($t_{0,9}$ - time corresponding to 90% curing) were read from the curing curves. The vulcanized sheets were cooled in air without pressure, with a cooling rate of ca. 50°C/min.

3 Testing methods

3.1 Curing tests

Curing curves were recorded with a MonTech Monsanto R100S rheometer (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) in isothermal (T=170°C) time sweep mode (1.667 Hz, 3° angle) for 20 min.

3.2 Viscosity tests

Absolute values of the complex viscosities of the raw mixtures (i.e. without sulphuric curatives) were measured using a TA AR 2000 parallel plate rheometer (TA Instruments, New Castle, Delaware, USA), at 170°C with a sinusoidal oscillation. The strain amplitude and oscillation frequency were set for 25 and 40 rad/s, respectively. The gap was 1.5 mm between the parallel plates. The duration of the tests was 3 min, and the actual values were recorded in every 3 s. Values from the 2nd and 3rd min were averaged and standard deviation was also calculated.

3.3 Tensile and tear tests

Tensile tests were performed on a Zwick Z250 universal testing machine equipped with a 20 kN load cell (Zwick GmbH, Ulm, Germany). Type 1 specimens of DIN 53504 standard with a clamping length of 60 mm were loaded at 500 mm/min cross-head speed. Tear tests were made on the same testing machine and test speed by the ASTM D624 standard (Type C specimen), with a clamping length of 56 mm. Both tests were run at room temperature.

3.4 Hardness tests

Hardness tests were carried out on the prepared sheets with ten parallel measurements on each material by DIN 53505 standard. A Zwick H04.3150 hardness tester (Zwick GmbH, Ulm, Germany) was used with Shore A head using 12.5 N load.

3.5 DMTA tests

Dynamic mechanical properties of the rubber blends were investigated using a TA Q800 DMTA machine (TA Instruments, New Castle, Delaware, USA) in tensile mode on rectangle specimens with dimension of ca. 2x2.5x10 (thickness x width x clamped length) mm. Tests were run between -100 and 100°C with 3°C/min heating rate at 10 Hz frequency with 0.01 N preload, and superimposed 0.01% sinusoidal strain.

3.6 Scanning electron microscopy (SEM)

In order to observe the morphology of the related rubbers SEM images were taken from the fracture surfaces of the tensile specimens. Cryogenic fracture surfaces were also made by cooling the rubbers in liquid nitrogen, and the resulting cryo-fractured surfaces were also investigated. SEM images were taken using a Jeol JSM-6380LA (Jeol LTD., Tokyo, Japan). The observed surfaces were sputter-coated with gold.

4 Results and discussion

4.1 Curing properties

Maximum and minimum torque values decreased in the presence of CBT for all rubber mixes (Table 3). This can be explained by the low viscosity molten state of the oligomer at temperature during the test (170°C), so it lowered the modulus values of the rubber blends. A slight increment could be

observed in the $t_{0.1}$, $t_{0.5}$ and $t_{0.9}$ values of the CBT containing blends in NR, NBR and EPDM blends. Interestingly, CBT had an opposite effect on SBR and oSBR compounds which effect needs further investigation. The retardation effect can be traced to the chemical structure of CBT being in analogy with traditional rubber retarders, like phthalic-anhydride [17].

Table 3 Curing properties of the tested rubbers

Sample	M_L	M_H	$t_{0.1}$	$t_{0.5}$	$t_{0.9}$
	[dNm]	[dNm]	[min]	[min]	[min]
NR	2.6	23.7	2.2	2.6	3.2
NR+20CBT	1.3	12.2	2.4	3.1	3.7
SBR	3.2	22.5	6.7	9.0	12.4
SBR+20CBT	1.6	8.0	5.5	7.0	10.5
oSBR	4.1	15.5	7.0	9.1	10.9
oSBR+20CBT	3.0	10.4	6.7	8.8	10.2
NBR	2.6	27.5	4.7	5.4	10.4
NBR+20CBT	1.6	21.0	5.2	6.0	12.7
EPDM	4.3	36.1	9.2	12.5	21.5
EPDM+20CBT	1.6	10.4	9.6	13.5	27.5

4.2 Viscosities

Results of the viscosity tests are depicted in Fig. 1. One can see that the absolute values of the complex viscosities significantly decreased in every tested system. So, it can be stated, that CBT has a beneficial effect on the processability of these rubbers. Note that our aim was to demonstrate the viscosity reducer effect of the CBT for SBR and oil extended SBR. However, these two cannot be compared due to their different producers, i.e. different base polymer properties.

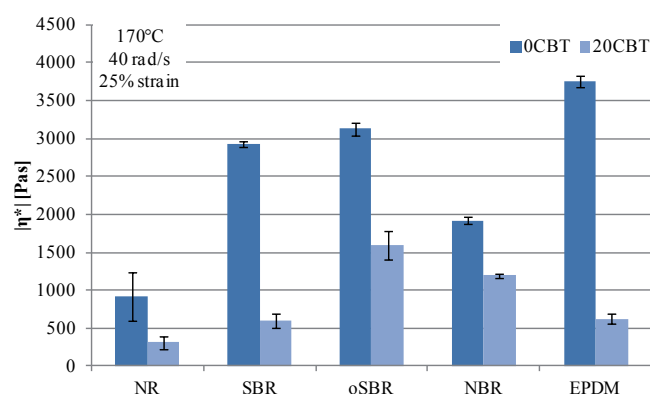
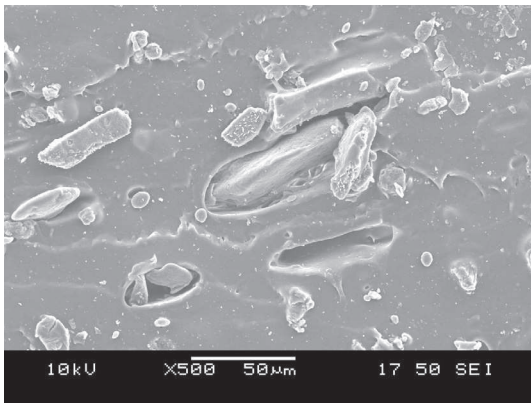


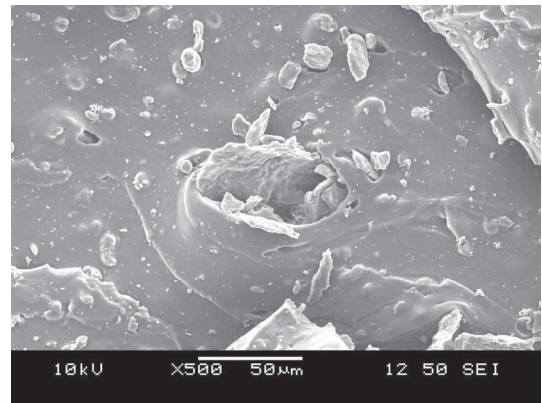
Fig. 1 Viscosities of the raw mixtures

4.3 Morphology

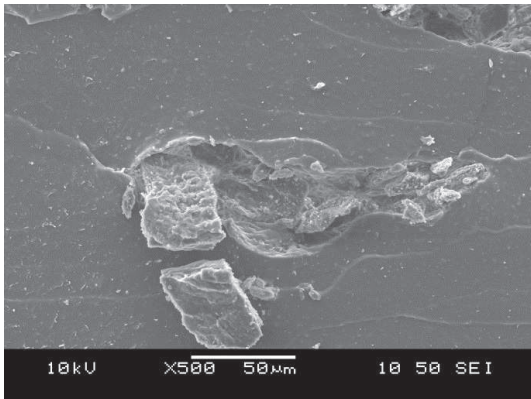
Inspecting the fracture surfaces it can be clearly seen that CBT recrystallized in each rubber formulation and formed a separate second phase (Fig. 2 and 3). The appearance of the CBT phase (shape of the related crystals) was, however, different in rubber mixes studied.



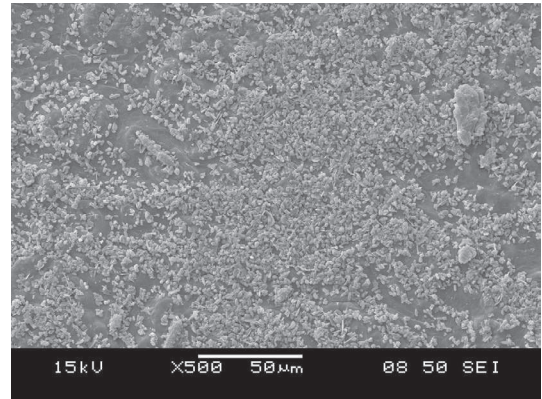
a)



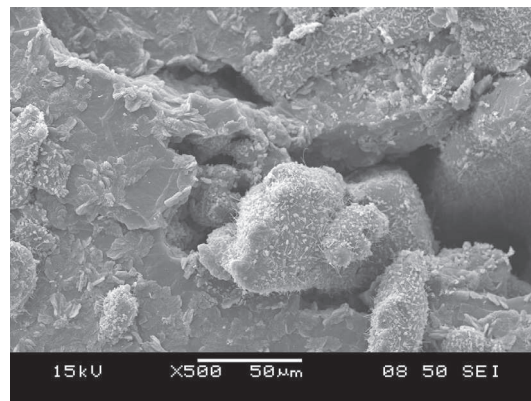
b)



c)



d)



e)

Fig. 2 Tensile fracture surfaces of the 20 phr CBT containing NR (a), SBR (b), oSBR(c) NBR (d) and EPDM (e)

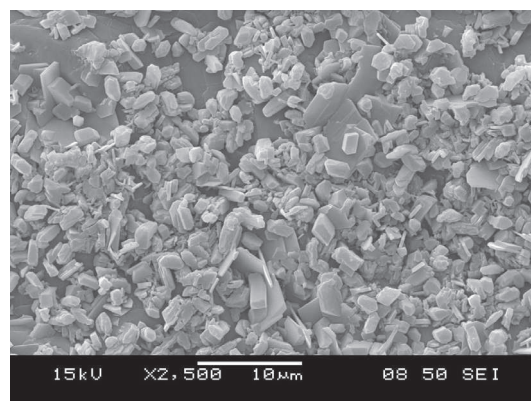


Fig. 3 Fracture surface of the 20 phr CBT containing NBR tensile specimen at higher magnification

Table 4 Tensile properties, tear strength and hardness values of the tested rubbers (M50, M100 and M200 represents the stress values measured at elongations of 50, 100 and 200%, respectively)

Sample	Tensile strength	Elongation at break	M50	M100	M200
	[MPa]	[%]	[MPa]	[MPa]	[MPa]
NR	17.81 ± 2.39	899 ± 11	0.50 ± 0.02	0.73 ± 0.04	1.18 ± 0.06
NR+20CBT	13.05 ± 0.80	882 ± 47	0.63 ± 0.08	0.82 ± 0.10	1.17 ± 0.09
SBR	1.47 ± 0.14	261 ± 30	0.61 ± 0.04	0.82 ± 0.05	1.19 ± 0.05
SBR+20CBT	1.91 ± 0.18	390 ± 40	0.82 ± 0.03	0.98 ± 0.03	1.21 ± 0.06
oSBR	1.12 ± 0.09	341 ± 7	0.35 ± 0.04	0.47 ± 0.04	0.70 ± 0.05
oSBR+20CBT	1.73 ± 0.11	428 ± 26	0.50 ± 0.02	0.66 ± 0.03	0.88 ± 0.03
NBR	2.30 ± 0.09	349 ± 19	0.77 ± 0.06	1.09 ± 0.02	1.49 ± 0.06
NBR+20CBT	3.93 ± 0.50	593 ± 43	0.76 ± 0.05	0.94 ± 0.07	1.24 ± 0.08
EPDM	1.37 ± 0.09	190 ± 24	0.78 ± 0.01	1.03 ± 0.02	
EPDM+20CBT	1.61 ± 0.12	320 ± 29	0.82 ± 0.01	0.95 ± 0.01	1.15 ± 0.02

Excluding the NBR compounds, the CBT formed relatively large agglomerated particles (blocks) with dimensions of 50-100 µm, or larger. Under tensile load, the adhesion between these blocks and the rubber matrix broke up and the blocks cracked and separated from the matrix.

NBR based compounds showed obviously better compatibility with CBT. The CBT phase consisted of prismatic and plate like crystals (as well as in Reference [14]) with a mean dimension of few microns (Fig. 2 and 3). The adhesion between the crystals and the matrix was also superior to other compounds. It can be clearly seen at both fracture surfaces (tensile and cryofracture – cf. Fig. 2 and 3), that the crystals remained in contact with the rubber matrix even under high load. This can be explained by the fact, that from the investigated rubber systems NBR has the most polar molecular structure (due to the acrylonitrile groups), and thus a relatively strong interaction between NBR and CBT can be surmised.

4.4 Mechanical properties

Tensile mechanical properties are summarized in Table 4, tear strength and hardness values are listed in Table 5.

Results confirm that except the NR compounds, all tested rubbers showed improved mechanical properties upon addition of 20 phr CBT. Note that the tensile strength, elongation at break and tear strength values, all increased for each rubber mix. Possible reason for the unexpected poor performance of CBT in NR may be linked with the strain induced crystallization ability of the NR. This leads to a strength improvement via some kind of self-reinforcement. Observing the M50 and M100 values, incorporation of CBT has a positive effect on NR system, too. One can thus hypothesize that the separation of CBT and NR phases started at higher strain levels. Debonding between the rubber matrix and CBT (that can be clearly seen on the SEM images taken from the tensile fracture

Table 5 Tear strength and hardness values of the tested rubbers

Sample	Tear strength	Hardness
	[kN/m]	[Sh A°]
NR	23.95 ± 1.85	42.6 ± 0.3
NR+20CBT	16.89 ± 0.50	49.6 ± 0.5
SBR	5.74 ± 0.38	44.3 ± 0.5
SBR+20CBT	8.90 ± 0.17	50.6 ± 0.5
oSBR	4.89 ± 0.47	29.6 ± 1.1
oSBR+20CBT	6.91 ± 0.55	35.9 ± 0.6
NBR	9.14 ± 1.54	53.6 ± 0.5
NBR+20CBT	14.00 ± 1.45	54.1 ± 0.5
EPDM	7.27 ± 0.86	45.1 ± 0.7
EPDM+20CBT	7.85 ± 0.71	50.3 ± 1.0

surfaces – cf. Fig. 2), CBT particles produce voids in the rubber matrix thereby lowering the load bearing cross section of the specimen. One can see, that only a marginal increase could be observed in the hardness of NBR compounds by the addition of CBT compared to the other compounds, which can be explained by the finer dispersion of the CBT in the NBR based compounds (due to the better compatibility). This finer dispersion (and the better adhesion between CBT particles and the rubbery matrix) led to a more pronounced reinforcing effect of CBT in NBR compounds compared to the other rubbers.

Results of DMTA tests are summarized in Fig. 4 and Table 6. Using the plateau moduli of the rubbers an apparent crosslink density can be calculated. According to the rubber elasticity theory, the inverse of the plateau modulus (E_{pl}) at temperatures above the glass transition temperature (T_g) correlates with the mean molecular mass between the crosslinks (M_c):

$$M_c = \frac{3\rho RT}{E_{pl}} \quad (1)$$

where M_c mean molecular mass between crosslinks [g/mol], ρ is the density [kg/m³], R is the universal gas constant [8.314 J/Kmol], T is the absolute temperature [K], ($T=293$ K) E_{pl} is the plateau modulus [Pa].

The apparent crosslink density:

$$v_c = \frac{\rho}{M_c} = \frac{E_{pl}}{3RT} \quad (2)$$

where v_c is the apparent crosslink density [mol/m³].

It has to be emphasized that v_c is an apparent value, reflecting not only the chemical crosslinking of each rubbers, but also the various interactions between the rubber matrix and CBT. One can see that v_c increases with added CBT for each tested rubber at room temperature ($T=293$ K).

Maximum values of the loss factor decreased in all the tested rubbers, and an increment in the T_g was also caused by CBT dosage. This increment was the most notable in NBR rubber, so the molecular segment mobility was hindered the most in NBR by CBT. It can be explained by the likely occurring transreactions between CBT and the acrylate moieties of NBR rubber (same tendency was observed in [14]).

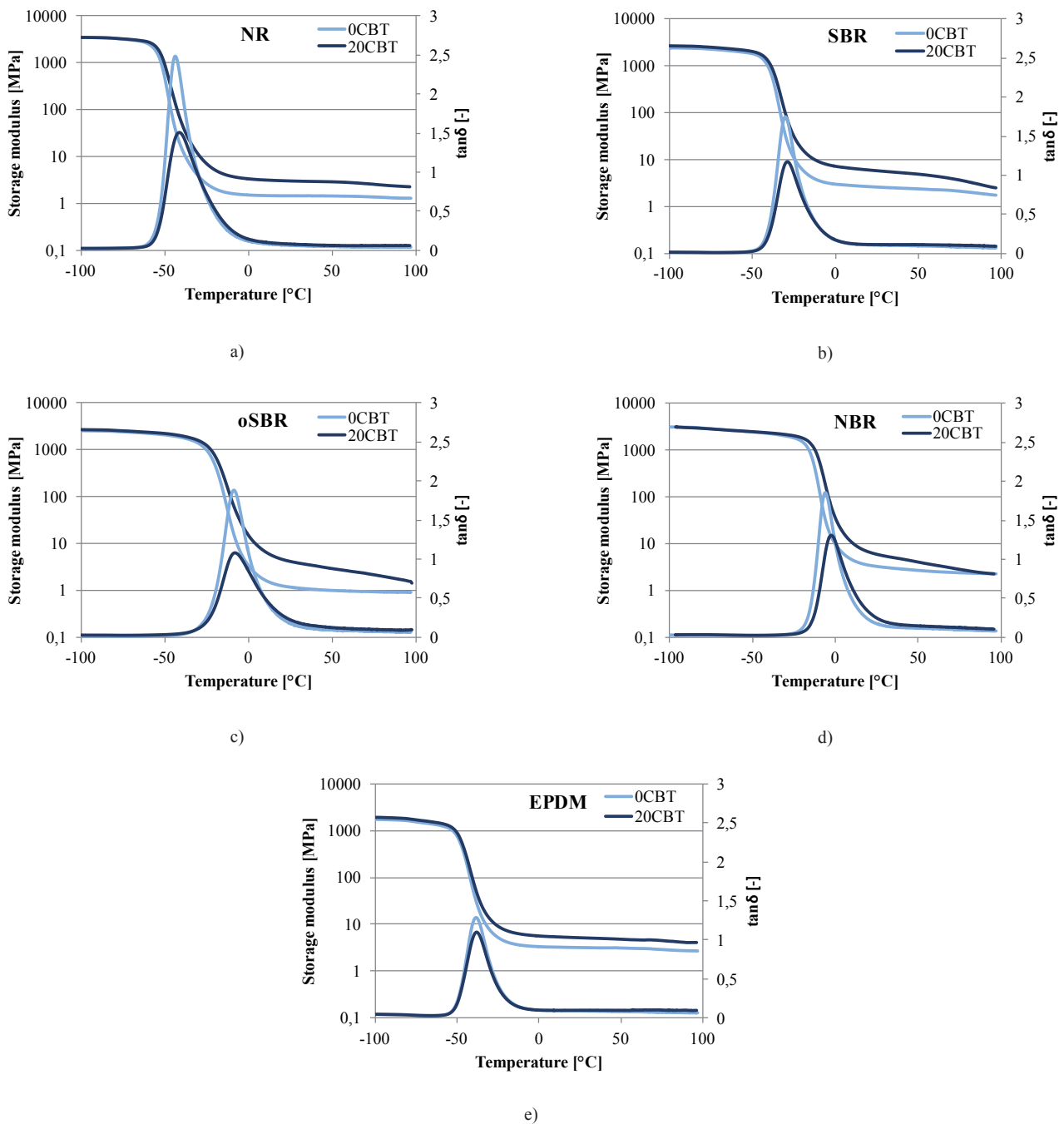


Fig. 4 E' vs. temperature and $\tan\delta$ vs. temperature traces of the NR (a), SBR (b), oSBR (c), NBR (d) and EPDM (e) compounds

Table 6 Moduli, maximal $\tan\delta$ and glass transition temperatures of the tested rubbers derived from DMTA measurements

Sample	E_{pl}	v_c	$\tan\delta_{max}$	T_g
	[MPa]	[mol/m ³]	[-]	[°C]
NR	1.48	202.2	2.48	-43.74
NR+20CBT	3.11	425.1	1.51	-41.27
SBR	2.73	373.7	1.74	-30.18
SBR+20CBT	6.05	828.2	1.18	-28.75
oSBR	1.23	168.2	1.88	-8.81
oSBR+20CBT	4.52	618.6	1.08	-8.22
NBR	3.47	475.2	1.86	-6.11
NBR+20CBT	6.74	922.5	1.30	-2.75
EPDM	3.14	429.2	1.29	-38.39
EPDM+20CBT	5.43	717.9	1.10	-37.39

5 Conclusions

Based on the results the following conclusions can be drawn:

- CBT acted as an effective viscosity reducer in all tested rubber compounds. Accordingly, CBT improves the processability of rubber mixes, which can be considered as a general rule.
- Curing time was slightly delayed in NR, NBR and EPDM based rubbers. In SBR and oSBR compounds an opposite effect was observed, curing times slightly decreased.
- CBT had an observable reinforcing effect for all rubbers not capable for strain-induced crystallization. This was reflected in increasing tensile and tear strength, and surprisingly also in enhanced elongation at break values.
- Adhesion between CBT particles and the rubber matrix is becoming stronger with increasing polarity of the rubber. This was associated with strong improvement in the mechanical properties.

Acknowledgements

This work was supported by OTKA Hungarian Scientific Research Fund by grants (K100294) in Hungary. This work is connected to the scientific program of the "Development of quality-oriented and harmonized R+D+I strategy and functional model at BME" project. This project is supported by the New Széchenyi Plan (Project ID:TÁMOP-4.2.1/B-09/1/KMR-2010-0002).

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