J Therm Anal Calorim (2011) 104:969–973
DOI 10.1007/s10973-011-1321-3

Investigation of natural rubber composites with addition of montmorillonite fillers using thermal analysis

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CTAS2010 Conference Special Chapter

Abstract This paper is devoted to the investigation of the properties of the natural rubber composites prepared using the cation exchanged-montmorillonite fillers. The characteristics of the montmorillonite fillers were studied by Fourier transform infrared spectroscopy (FTIR) and thermogravimetry (TG). These characterized fillers were used to preparation of the natural rubber composites, which were submitted to measurements of dynamic-mechanical thermal analysis (DMTA) and vulcanizing characteristics (M_H, M_L, t_s, $t_{c(90)}$, R_v) as well as physico-mechanical properties (tensile strength, modulus at 300 elongation —M_{300}, tensibility).

Keywords Montmorillonite · TG · FTIR spectroscopy · NR/clay composites · DMTA · Vulcanizing characteristics · Physico-mechanical properties

Introduction

In recent years, polymer nanocomposites based on layered silicates have attracted great attention in different industrial spheres [1]. The reinforcement of polymers with nano-sized particles is a promising technique that is capable of yielding materials with enhanced performance but without involving expensive synthesis procedures [2]. The goal of the polymer/nano-filler composite sciences is not only to fill a matrix with nanometer sized particles but also to modify the matrix texture by interaction with nano-fillers during processing, in order to make new functional materials, especially with improved mechanical properties [3]. Interestingly, significant improvements in the mechanical and some other properties (barrier, flame retardance) could be achieved at relative low clay loading [4, 5].

Thermal, optical and spectral analyses are very important theniques for materials characterization. Therefore, many authors have used these techniques for a variety of material characterization [6–25]. Various characterization techniques have used to evaluate structure, morphology and properties of fillers and polymer nanocomposites. In addition to TG and spectral analyses, the present paper describes in detail DMTA that is very useful in studying composite structure and performance. DMTA can provide a complete description of the viscoelastic properties by dynamic experiments conducted over a range of time, temperature or frequency. This method is commonly used to determine the glass transition temperature of polymeric

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materials from the peak of loss angle tangent (tg), morphology of crystalline polymers and damping (heat dissipation) [26, 27].

Experimental

Materials

Various monoionic forms of montmorillonite (Ca-, Co- and Cu-MMT) used in this study were prepared by the conventional ion exchange reactions using aqueous solutions of appropriate metal chlorides. After the ion exchange, the resulting solids were washed repeatedly with deionized water until a negative $AgNO_3$ test was obtained [28–30]. The cation exchange capacities (CEC) are follows: Ca-MMT (79 meq/100 g), Co-MMT (83 meq/100 g), Cu-MMT (98 meq/100 g).

Characterization of montmorillonite fillers

The detailed characterization of the used montmorillonite fillers were obtained by measurements of thermal (TG) and spectral (FTIR) analysis.

Thermal decomposition of the montmorillonite fillers were performed on a NETZSCH TG 209 F1 instrument in the temperature range 25–1000 °C in nitrogen atmosphere at a heating rate of 10 °C/min.

The infrared spectra of investigated clay samles were recorded by a Fourier transform infrared (FTIR) spectrometer Tensor 27 in the region 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

Preparation of natural rubber (NR)/clay composites

Natural rubber SMR-20 was used as the elastomeric matrix. Carbon black N660 was used as the conventional filler. The effect of montmorillonite fillers (Ca-MMT, Co-MMT, Cu-MMT) on the vulcanizing characteristics, physico-mechanical properties, and dynamic-mechanical thermal behaviour was investigated at 2 phr filler loading. The composition of the NR/clay composites is given in Table 1.

The composite materials were prepared by two-stage mixing procedure in a laboratory mixer Plastograf-Brabender. The vulcanized slabs were obtained using a laboratory press Buzuluk at 150 °C. The vulcanization time corresponds to the optimum cure time (t_{90}) determined from the curing curves. The specimens with a shape of double-ended spatulas were mechanically cut out from the vulcanized slabs [31].

Table 1 The compositions of the NR/clay composites

Ingredient	Content/phr[a]
Natural rubber (SMR-20)	100
Clay (Ca-MMT, Co-MMT, Cu-MMT)	0 or 2
Carbon black (N660)	8 or 10
Zinc oxide	4.6
Sulphur N	1.8
CBS[b]	1.5

[a] Parts per hundred parts of rubber

[b] *N*-Cyclohexyl-2-benzothiazyl sulphenamide

Measurements

The prepared NR/clay composites were submitted to measurements of dynamic-mechanical thermal analysis (DMTA), vulcanizing characteristics and physico-mechanical properties.

Dynamic-mechanical properties of the NR/clay composites were measured using a dynamic-mechanical thermal analyzer TMA Q400 EM (TA Instruments). The temperature range was between −70 and 10 °C with a heating rate of 3 °C/min. The frequency was 0.5 Hz. The size (length × width × thickness) of the test samples was $16 \times 3 \times 0.3$ mm^3. During the test the storage modulus, loss modulus and tan δ were recorded as functions of the experimental temperature.

The vulcanizing properties (M_H, M_L, t_s, $t_{c(90)}$, R_v) were measured using a vulcameter Monsanto 100 at 150 °C during 60 min of registration with deviation of rotor 1° [32].

Physico-mechanical properties (tensile strength, modulus at 300 elongation—M_{300}, tensibility) were measured at room temperature on an Instron testing machine at deformation rate 50 mm/min [33]. The hardness of vulcanized rubber was determined at room temperature by a hardness tester IRHD. An average value from measurements at different position on the specimen with at least three parts was taken as a hardness value of the test sample [34].

Results and discussion

Thermogravimetry (TG)

The TG curves of the prepared monoionic forms of montmorillonite are shown in Fig. 1. For all samples of montmorillonites, two mass loss steps are observed at temperature ranges between 40–300 °C and 500–800 °C. The first step is attributed to the loss of adsorbed water from the clay surface and from the interlayer space while the second step is connected with the loss of water resulting from the decomposition of structural OH groups. The total mass losses for monoionic forms of montmorillonite are

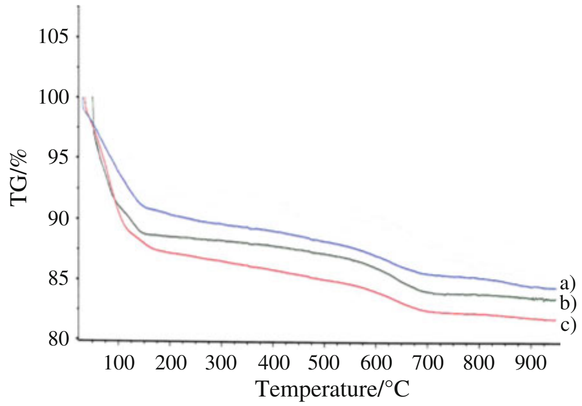

Fig. 1 TG curves of (*a*) Cu-MMT, (*b*) Ca-MMT, (*c*) Co-MMT

following: Ca-MMT (16.52%), Co-MMT (18.18%), Cu-MMT (14.47%). The experimental mass losses are in good agreement with the theoretical expectation.

FTIR spectroscopy

FTIR spectral data of the cation exchanged-montmorillonites are summarized in Table 2. Several peaks was observed in the studied region (400–4000 cm^{-1}) that were attributed to the stretching vibrations of OH groups (3624–3626 cm^{-1}) and water (3439–3443 cm^{-1}), stretching vibrations of Si–O groups (1031–1035 cm^{-1}), bending vibrations of OH groups (841–913 cm^{-1}): AlAlOH at 913 cm^{-1}, AlMgOH at 841–843 cm^{-1}, bending vibrations of Al–O–Si groups at 525 cm^{-1} and Si–O–Si at 468–471 cm^{-1} [28–30].

DMTA

Dynamic-mechanical properties were measured to examine the degree of filler–matrix or filler–filler interactions of NR/clay composites.

Table 2 Wavenumber/cm^{-1} of absorption bands in FTIR spectra of the clay samples

Type of vibration	Ca-MMT	Co-MMT	Cu-MMT
ν(AlOH)	3625	3626	3624
$\nu(H_2O)$	3439	3442	3443
$\delta(H_2O)$	1643	1632	1640
ν(SiO)	1035	1031	1033
δ(AlAlOH)	913	913	913
δ(AlMgOH)	841	843	841
δ(AlOMg)	627	627	626
δ(SiOAl)	525	525	525
δ(SiOSi)	470	468	471

The storage modulus (E'), loss modulus (E'') and loss factor (tan δ) of the standard composite (NR) and the NR/clay composites versus temperature are depicted in Figs. 2, 3 and 4, respectively.

As shown in Fig. 2, the composites exhibit a strong enhancement of the storage modulus in comparison to the

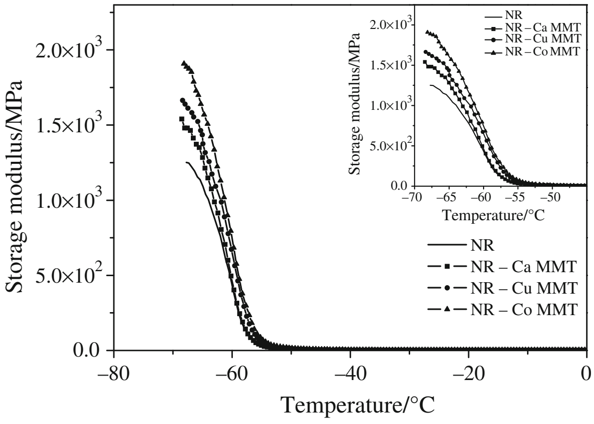

Fig. 2 The storage modulus of the NR/clay composites

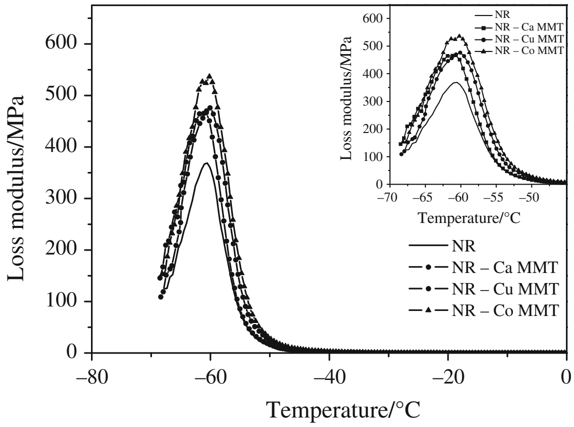

Fig. 3 The loss modulus of the NR/clay composites

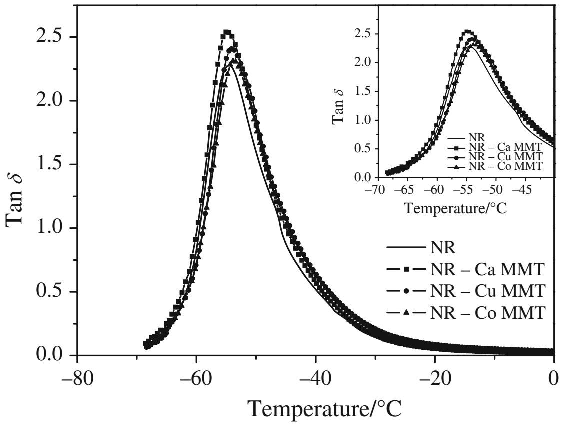

Fig. 4 The loss factor of the NR/clay composites

standard composite in order: NR–Co-MMT > NR–Cu-MMT > NR–Ca-MMT. The highest E' value showed the composite sample with the addition of Co-MMT filler. This evident E' reinforcement is ascribed to the nanoscaled dispersion of clay within the NR matrix.

The glass transition temperatures (T_g) of the standard composite and the NR/clay composites determined from the peaks of the loss factor (tan δ) [35] are follows: NR (−54 °C), NR–Ca-MMT (−55 °C), NR–Co-MMT (−53 °C), NR–Cu-MMT (−54 °C).

A slight increase in the glass transition temperature was observed in the NR/clay composite with Co-MMT filler. The T_g rising was probably caused by exfoliated MMT layers dispersed in NR matrix and strong interaction between rubber molecules and silicate layers [27, 35, 36].

The addition of montmorillonite fillers resulted in increases of the E'' for the all composite samples in comparison to the standard composite. The height (peak intensity) and position of E'' peaks of these composites also vary with the type of montmorillonite.

Vulcanizing characteristics

The vulcanizing characteristics (M_H, M_L, t_s, $t_{c(90)}$, R_v) of the prepared clay composites containing the various forms of the montmorillonite fillers are given in Table 3.

Vulcanizing curves were performed for all composites. All composites show a very low reversion. The behaviour of these curves is steeper in comparison with the standard composite. It shows that vulcanizing time ($t_{c(90)}$) was longer.

As can be seen, the all NR composites showed a slightly increased the scorch value (t_s) compared to the unfilled natural rubber. The values of the minimum torque (M_L) of the composite samples are almost invariant. Note that, in the case of the NR/clay composite with the addition of Ca-MMT filler was recorded a maximum value of the minimum torque of 7.7 N m. So, the maximum torque (M_H) had decreasing tendency toward the standard composite in order: NR–Ca-MMT = NR–Co-MMT > NR–Cu-MMT. The composite sample with Co-MMT filler exhibits the highest value of torque difference ($M_H - M_L$), which indicates the extent of crosslinking. As the value increases, the crosslink densities are expected to increase [2].

Table 3 Vulcanizing characteristics of the NR/clay composites

Composites	M_L/N m	M_H/N m	$t_{c(90)}$/min	t_s/min	R_v/min^{-1}
Standard	7.3	44.3	7.3	4.5	35.71
NR–Ca-MMT	7.7	42.5	7.7	4.8	34.48
NR–Co-MMT	7.3	42.5	7.7	4.5	31.25
NR–Cu-MMT	6.5	41.0	8.2	4.8	29.41

Table 4 Physical–mechanical properties of the NR/clay composites

Composites	Tensile strength/MPa	Tensibility/ %	Modulus 300/MPa	Hardness/ IRHD
Standard	27.90	730	11.47	41.66
NR–Ca-MMT	27.81	750	11.12	39.78
NR–Co-MMT	27.01	760	10.66	40.34
NR–Cu-MMT	27.24	768	10.64	39.83

Further addition of a various type of fillers resulted in a reduction of the values of rate coefficients of vulcanization (R_v), which characterize the activity of ingredients in rubber composites [37, 38]. It is clear from the comparison of the vulcanizing parameters that vulcanization is slower in comparison with the composite containing only carbon black.

Physico-mechanical properties

The values of physico-mechanical properties of the prepared NR/clay composites are summarized in Table 4.

It can be seen from Table 4 that the MMT fillers caused slightly decreased values of the tensile strength for the all composite samples toward the standard composite. The same trends are observed for the modulus at elongation at 300%. The elongation at break of the clay composites increased significantly in order: NR–Ca-MMT < NR–Co-MMT < NR–Cu-MMT. The values of hardness exhibited a slight decrease in compare with the unfilled natural rubber.

Conclusions

This work was focused on study of particular effects of various monoionic forms of montmorillonite on dynamic-mechanical thermal behaviour and vulcanizing characteristics as well as physical–mechanical properties of NR/clay composites. The results of FTIR and TG analyses of the prepared monoionic montmorillonite forms showed the values which are typical for clay and clay minerals. The prepared NR/clay composites exhibited the comparable values of studied vulcanizing characteristics and tensile properties with the composite containing only carbon black. This fact can lead to opportunity of the partial replacement of the conventional filler carbon black N660 by the montmorillonite fillers. The composites exhibited a strong enhancement of the storage modulus in comparison to the standard composite in order: NR–Co-MMT > NR–Cu-MMT > NR–Ca-MMT. The results of DMTA analysis of NR/clay composites were affected by the type of chosen matrix and by the type of interaction between matrix and used filler.

Acknowledgements The authors sincerely thank the Slovak Grants Agency AV 4/2014/2008 for their financial support.

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