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Effect of montmorillonite modification on mechanical properties of vulcanized natural rubber composites

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Abstract Natural rubber-clay composites were prepared by direct polymer melt intercalation. Ca-montmorillonite Jelšový Potok (JP; Slovakia) and Na-montmorillonite Kunipia-F (KU; Japan) were ion exchanged with octadecyltrimethylammonium (ODTMA) bromide and were used as aluminosilicate fillers. Silica Ultrasil VN3 was used in amount of 15 phr as conventional filler. The effect of clay or organoclay loading from 1 up to 10 phr on the mechanical properties was evaluated from the tensile tests (stress at break, strain at break and modulus M100). Organic modification resulted in an increase of toluene uptake degree for both fillers. While an addition of unmodified KU had no effect on tensile strength and deformation at break, a reinforcing effect was observed for the mixture containing 10 phr of unmodified JP. Both ODTMA modified fillers (KU and JP) exhibited substantial increase in tensile strength and deformation at break; JP proved to be more effective compared to KU also if modified with ODTMA. The highest stress at break and strain at break values for natural rubber composites were obtained with 15 phr of SiO_2 and 10 phr of montmorillonite; however, the effect of exchangeable cation was minor.

Introduction

Nanocomposites with macromolecular matrices offer a design of materials with many interesting properties. Among these, layered silicates belong to the most often used fillers potentially forming nanostructures in the matrix [1]. While clay nanocomposites have been investigated in combination with many thermoplastics and thermosetting polymers, much less attention has been paid to the elastomers as matrices [2–5]. Besides increased modulus and strength, other factors such as tear properties, fracture toughness and abrasion resistance are claimed to be improved as a result of clay addition to rubber [6–8]. Polymer-clay nanocomposites can be prepared by several methods [9], such as in situ polymerization or intercalation via solution, while in the case of rubber nanocomposites also intercalation of rubber via latex compounding can be used [10]. However, direct melt intercalation method is considered to be the most effective route for all clay-polymer nanomaterials [9, 10].

In the case of clay, conventional micron-size fillers should be also considered; in that case the micron-size clay can be used as a partial substitution for other reinforcing fillers such as carbon black [11] or silica [2]. A formation of nanocomposites requires a penetration of macromolecules between the filler layers resulting in a broadening of the interlayer distance or at least partial decay of layered structure leading to a formation of individual particles of nanosize dimensions. Taking this into account, intercalated or exfoliated nanocomposites can be formed; in the latter case rather often intermediate structures are formed, consisting of a combination of intercalated and exfoliated fillers [2].

Properties of rubber/organoclay nanocomposites were investigated for a number of rubber matrices, e.g. natural rubber (NR) [12, 13], EPDM [14, 15], SBR [16], nitrile rubber [16], silicon rubber [16] or polybutadiene rubber [17]. An increase in tensile strength was usually observed as expected; in most cases the increase was substantial. However, surprisingly also elongation values rose, e.g. for

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EPDM with organoclay [14]; rather general interpretation of these results was offered. Important improvement was reported regarding an increase in tear strength originated from an increased resistance to crack growth [14, 18].

Similar to thermoplastic matrices, a decrease in gas permeability [14, 18] and increased solvent resistance [19] was reported also for rubber nanoclay composites.

Besides changing the properties of vulcanized rubber compositions resulting from the presence of nanoparticles, the nanofillers affect also chemistry of vulcanization process [11]. A substantial reduction of optimum vulcanization time was observed in the presence of organoclay [12]. The effect is explained by the presence of amino groups which act as accelerator of the curing process. It is worth to mention that the intercalation of octadecylamine into organoclay galleries leads to further acceleration of reaction of sulphur with NR, compared to a mixture where only amine was added without the clay.

The incorporation of organoclay into rubber leads also to a slight increase in glass transition temperature, obviously resulting from a restricted motion of the rubber chains on the intergallery space. Similar reasoning may be used to explain certain increase in temperature of thermal decomposition, although this effect may not be a consequence of higher thermal stability of the material decomposing at higher temperature but just due to a prevention of diffusion of volatile remnants immobilized between galleries [12, 13].

In this paper, NR-based composites were prepared using two different montmorillonite-based fillers; the effect of filler surface modification was investigated and mechanical properties were compared with the rubber filled with unmodified particulate filler.

Materials and methods

Preparation of rubber-clay composites

Natural rubber SMR was used as the elastomeric matrix; the composition of the model rubber compound is given in Table 1. Silica Ultrasil VN3 was used as the conventional filler.

Two clay-based fillers were used, namely commercial montmorillonite (MMT) Kunipia-F (Na–KU; Kunimine Industries Co. Ltd, Japan) and montmorillonite from Jelšový Potok (Ca–JP; Envigeo, Slovakia). The detailed characterization as well as the procedure of modification of both fillers with octadecyltrimethylammonium bromide (ODTMA) is described in [20].

Table 1 Composition used for the rubber mixtures

Material	phr
Natural rubber	100
MMT	0–10
Silica	0 or 15
Zinc oxide	5
Stearic acid	2
Sulfenax CBS/MG	3.5
Sulphur	3.5

The blends were prepared by mixing the NR with the filler and all the vulcanization ingredients except the sulphur (composition in Table 1) in a 50 mL mixing chamber of Brabender Plasticorder PLE 331 at 70 °C for 14 min at the mixing speed 30 rpm. Composites with 1, 3, 5 and 10 phr (parts by weight per hundred parts of rubber) of organoclay filler were compounded. A comparative set of composites with the corresponding Na–KU and Ca–JP were also prepared. Slabs were obtained by a compression moulding of the mixed composite using a laboratory press Fontijne 200 (Fontijne, The Netherlands) at 150 °C for 35 min (optimum vulcanization time determined as t_{90} by rheometry) under 22.5 kN/cm^2. The dumbbell specimens with a working area of $35 \times 3.6 \times 1$ mm^3 were mechanically cut out from the vulcanized slabs.

Mechanical properties

Mechanical properties were measured at room temperature using an Instron 4301 universal testing machine at deformation rate (crosshead speed) 50 mm/min. Tensile strength, elongation at break and modulus at 100% elongation (M100) were determined.

XRD measurements

X-ray diffraction profiles (XRD) for composites containing 3 phr of the filler were recorded on a diffractometer Bruker D8 Discover (Cu-Kα radiation, 40 kV/300 mA).

Measurement of toluene uptake

Swelling tests were performed using the remnants from the slabs after cutting the testing specimens for mechanical testing. Each sample was weighed, immersed in an excess of toluene and kept at 30 °C. Toluene uptake was measured by simply weighing the specimens after predetermined time periods. The surface of the sample was softly dried by a tissue and weighed. The complete operation took about 30 s, so possible minor evaporation of the solvent was neglected. The scatter of the parallel measurements was well below 1% of the measured value of toluene uptake.

The equilibrium was achieved after 240 h of swelling. Therefore the data were used only as comparative values; no calculations regarding cross-link density were done.

Results and discussion

Mechanical properties

In the first stage, the mechanical properties were compared for two basic MMT fillers, namely Kunipia-F and Jelšový Potok, both either unmodified or modified with ODTMA bromide. The mechanical properties for NR in dependence on the filler content in the range 0–10 phr are shown in Fig. 1a–c. Besides two component systems consisting of rubber and varying content of the MMT filler, three component systems were investigated as well, where also constant amount 15 phr of common highly reinforcing filler silica Ultrasil VN3 was added. These data are shown in Fig. 2a–c.

It is seen that both tensile strength and deformation at break differ for the individual fillers. While an addition of unmodified Na–KU has no effect at all on the both parameters, a reinforcing effect was observed for the mixture containing 10 phr of JP. Both ODTMA modified fillers (KU and JP) exhibit quite substantial increase in tensile strength; JP proved to be more effective compared to KU also if modified by ODTMA.

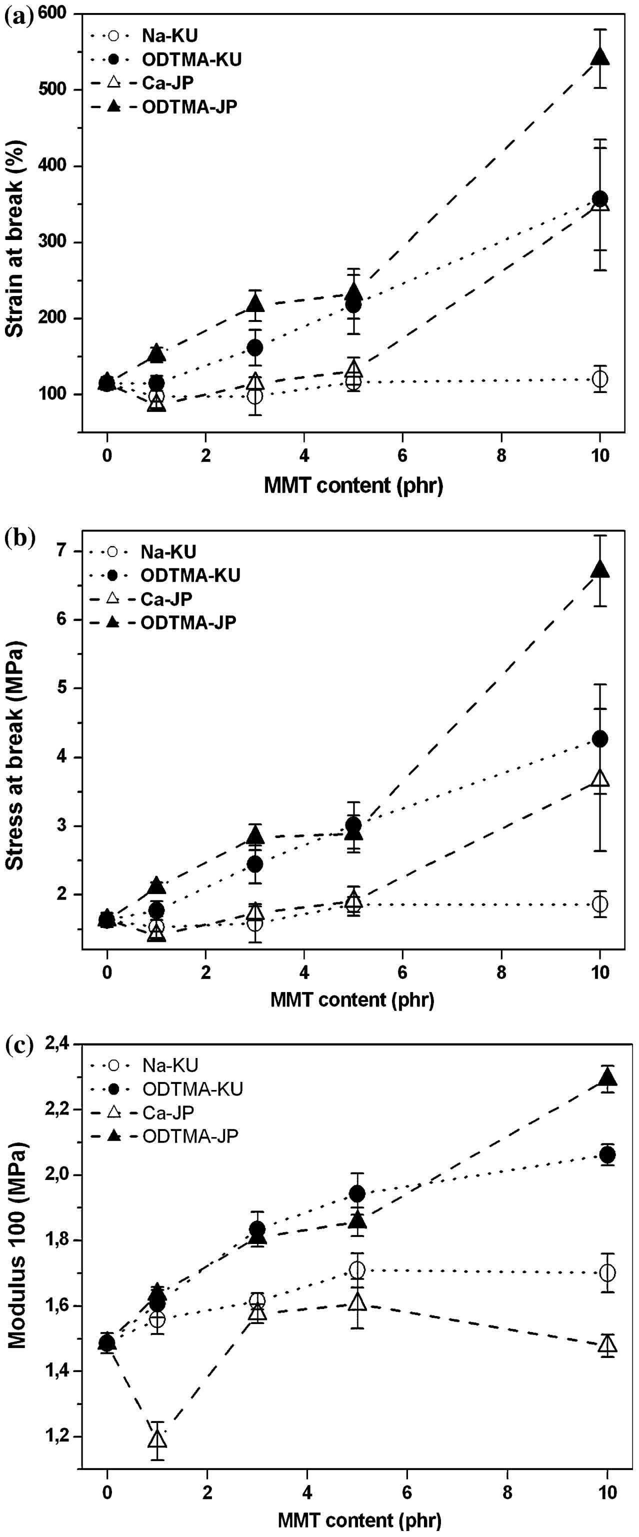

Fig. 1 Mechanical properties of the composites of NR rubber in dependence on content of Ca–JP, ODTMA–JP, Na–KU and ODTMA–KU: strain at break (**a**), stress at break (**b**) and M100 (**c**)

Interesting feature was observed regarding deformation at break. The shape of the concentration dependences is almost identical with those of tensile strength, as seen also in Fig. 3, where the dependence of tensile strength versus deformation at break is rising monotonously with the slope almost identical for all fillers. This indicates that a kind of reinforcement occurs during progressing deformation. This effect can be attributed either to orientational strengthening of the rubber due to orientation of the macromolecules in the direction of the deformation or to improved interactions between filler and matrix. While the former effect is expected to contribute to the observed behaviour since orientational strengthening has been observed and is well described for NR (unlike for a number of other synthetic rubbers), the nature of the latter effect is difficult to identify according to the data obtained. However, the important, perhaps the key contribution of the increasing strengthening due to filler contribution has to be accepted especially because the effect itself differs according to the nature of the MMT filler and its modification. While for modified fillers the effect is observed also at low filler concentration (1 phr), for unmodified filler the increase occurs only at 10 phr for JP and not at all for unmodified Na–KU. On one hand, this may mean that improved dispersion is formed during deformation; most probably due to small extent of additional exfoliation of the fillers (ODTMA modified fillers present substantially higher effect, Na–KU does not contribute at all). On the other hand, we may admit that

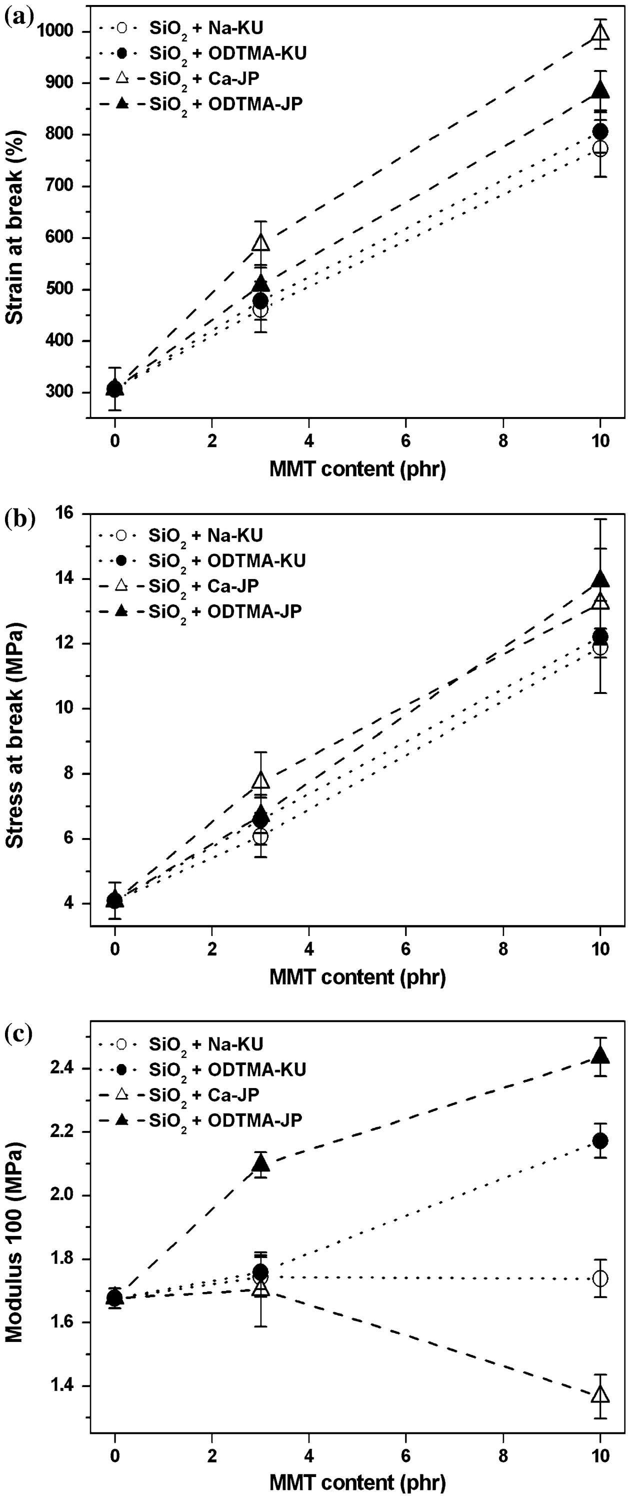

Fig. 2 Mechanical properties of the composites of NR rubber with 15 phr of silica in dependence on content of Ca–JP, ODTMA–JP, Na–KU and ODTMA–KU: strain at break (**a**), stress at break (**b**) and M100 (**c**)

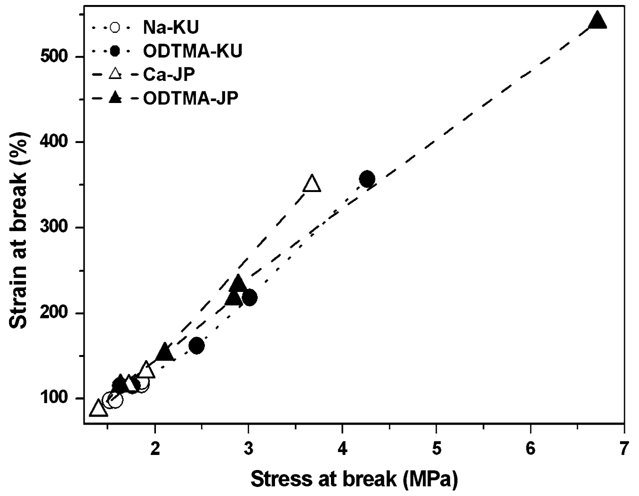

Fig. 3 The dependence of tensile strength versus deformation at break

during deformation, the orientation is applied not only to macromolecules but also to the small platelet-like particles of the exfoliated filler. This explains the substantial effect for both modified fillers (certain portion of exfoliated particles can be expected to be formed, although it was not detected by any used method, obviously because of small portion of exfoliation achieved). However, the increase in elongation at break with rising (nano)filler content is not general feature for this kind of composites. Opposite behaviour was described, e.g. by Cataldo [5], who observed a decrease in elongation with rising montmorillonite content in combination with carbon black mixed in elastomeric matrix.

The blends containing a combination of various amounts of MMT-based fillers together with constant amount of 15 phr of silica exhibit the same behaviour. An addition of silica itself without any MMT filler results in an increase in both tensile strength and deformation at break. However, it is seen that an addition of either 5 phr of ODTMA modified MMT filler or 10 phr of unmodified JP to NR without silica (Fig. 1a, b) is almost equivalent to the addition of 15 phr of silica (Fig. 2a, b) without the MMT filler. An addition of the MMT filler to the blend containing 15 phr silica leads to a significant increase in both tensile strength and deformation at break; it is worth to mention that in this case almost no difference was observed between the modified and unmodified fillers.

Finally, the reinforcing effect was estimated according to the values of a so-called modulus 100 (M100), which is a parameter commonly used in rubber technology and means stress necessary to achieve deformation 100%. The data are shown in Figs. 1c and 2c. When either the two modified fillers or the two unmodified fillers are compared, the dependences are similar; however, the modification leads to a significant difference in M100 values. According to this parameter, JP filler seems to be inferior even when compared to Na–KU. The trend is obvious especially for the blends containing silica besides the MMT filers. While addition of both modified fillers leads to further increase of M100, addition of unmodified Na–KU has no effect and the

Table 2 Equilibrium toluene uptake after 240 h (percentage of the original sample weight) for vulcanized NR filled with various fillers and ratio between uptake by composites with modified/unmodified fillers

Filler (phr)	Ca–JP	Na–KU	ODTMA–JP	ODTMA–KU	ODTMA–JP/Ca-JP	ODTMA–KU/Na–KU
0	330	330	330	330	–	–
5	349	295	364	347	1.04	1.18
10	388	328	410	394	1.06	1.20

presence of unmodified JP even results in a decrease of the M100 parameter. This means that unmodified JP exhibits something like softening effect in the early stage of deformation, which is not easy to interpret.

Toluene uptake

Additional data regarding the morphology of the materials can be obtained from the data of equilibrium swelling in good solvent, shown in Table 2. In this case toluene was used. It is seen that in all cases except for Na–KU, the presence of the filler leads to higher degree of swelling; this tendency is even higher for modified fillers compared to the unmodified analogues. Further on, the increase in the filler content leads to an increase in the degree of equilibrium swelling values. The explanation of this effect can be seen in the ability of the filler to be swelled by toluene even when mixed in the rubber matrix. These two fillers differ substantially from this point of view; while unmodified Na–KU has no effect at all (the degree swelling for the composite containing 5 and 10 wt.% of the filler is the same as for unfilled rubber), Ca–JP exhibits higher toluene uptake as revealed from comparison with unfilled rubber and with composites filled with Na–KU. Modification results in an increase in swelling degree for both fillers. It is certainly worth to mention that the increase in toluene uptake is the same regardless of concentration of the filler. The KU is more activated by modification from this point of view, although also after modification it does not achieve the swelling degree of composites filled with JP.

X-ray diffraction

The possible formation of intercalated and/or exfoliated structures was investigated by XRD. The XRD patterns are shown in Figs. 4 and 5 and include also the calculated interlayer distances. It is seen that for modified fillers the increase in interlayer distance was observed for mixtures without silica addition. This demonstrates the positive effect of intercalation due to the filler surface organomodification. The effect of organomodification on interlayer distance is completely eliminated by silica presence for KU and to certain extent also for JP. These observations, although somewhat surprising, correspond to the mechanical properties, where the addition of 5 phr of KU has no effect on modulus M100 and only marginal effect on the tensile strength and elongation at break, compared to composites containing Na–KU. This is unlike for composites filled with JP, where mechanical properties are affected significantly (although not tremendously) by modification with the alkylammonium salt.

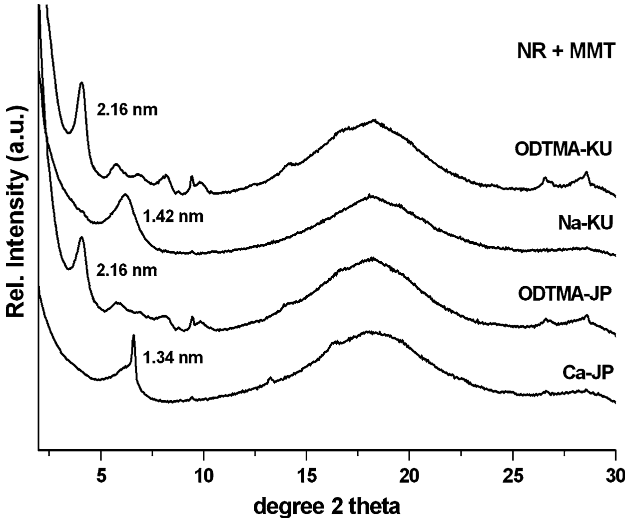

Fig. 4 XRD patterns of composites of NR rubber with 3 phr Ca–JP, ODTMA–JP, Na–KU and ODTMA–KU

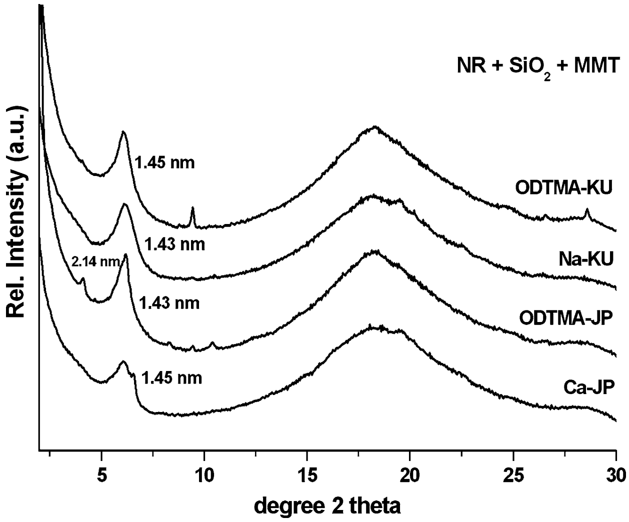

Fig. 5 XRD patterns of composites of NR rubber with 15 phr of silica and 3 phr Ca–JP, ODTMA–JP, Na–KU and ODTMA–KU

Conclusions

The addition of montmorillonite-based fillers to NR has a positive effect on mechanical properties of the vulcanizates. Modification of the fillers with ODTMA+ cation results in higher positive effects.

The presence of MMT fillers in NR matrix results in an increased capability of the composite to absorb apolar solvents. Also in this case the organic modification of the filler leads to increased sorption. The results of mechanical behaviour correspond to the XRD data indicating the importance of intercalated structures formation.

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References

1. Alexandre M, Dubois P (2000) Mater Sci Eng R28:1
2. Mohammad A, Simon GP (2006) In: Mai Y-W, Yu ZZ (eds) Polymer nanocomposites, chap 12. CRC Press, Boca Raton, p 297
3. Sadhu S, Bhowmick AK (2005) J Mater Sci 40:1633
4. Kader MA, Kim K, Lee Y-S, Nah C (2006) J Mater Sci 41: 7341
5. Cataldo F (2007) Macromol Symp 247:67
6. Zhang L, Wang Y, Wang Y, Sui Y, Yu D (2000) J Appl Polym Sci 78:1873
7. Arroyo M, Lopez-Machado MA, Herrero B (2003) Polymer 44:2447
8. Nah C, Ryu HJ, Han SH, Rhee JM, Lee M-H (2001) Polym Int 50:1265
9. Ray SS, Okamoto M (2003) Prog Polym Sci 28:1539
10. Karger-Kocsis J, Wu CM (2004) Polym Eng Sci 44:1083
11. Cataldo F (2005) Macromol Symp 228:91
12. López-Manchado MA, Herrero B, Arroyo M (2003) Polym Int 52:1070
13. Varghese S, Karger-Kocsis J (2003) Polymer 44:4921
14. Zheng H, Zhang Y, Peng Z, Zhang Y (2004) Polym Test 23: 217
15. Gatos KG, Thomann R, Karger-Kocsis J (2004) Polym Int 53:1191
16. Sadhu S, Bhowmick AK (2004) J Appl Polym Sci 92:698
17. Wang S, Long C, Wang X, Li Q, Qi Z (1998) J Appl Polym Sci 69:1557
18. Wang Y, Zhang L, Tang C, Yu D (2000) J Appl Polym Sci 78:1879
19. Wu YP, Jia Q-X, Yu D-S, Zhang L-Q (2003) J Appl Polym Sci 89:3855
20. Hrachová J, Chodák I, Komadel P (2007) Chem Papers (submitted)