

SBR COMPOSITES REINFORCED WITH *N*-ISOPROPYL-*N'*-PHENYL-*P*-PHENYLENEDIAMINE-MODIFIED CLAY

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Abstract SBR compounds including the *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine-modified clay (organoclay) were prepared. Effects of modified clay and antioxidant (IPPD) contents on mechanical and rheological properties of SBR composites were studied. FTIR results confirmed that the clay was chemically modified by IPPD and changed into an organoclay. X-ray diffraction (XRD) results confirmed the increase in interlayer distance of the clay due to the insertion of IPPD. Rheological and cure characteristics of SBR compounds were determined using RPA (Rubber Process Analyzer) and rheometer. Scorch time and cure time of SBR compounds decreased with introduction of the organoclay. Mechanical properties and heat aging resistance of the SBR composites were improved significantly by incorporation of the organoclay.

Keywords: SBR; Organoclay; Mechanical properties; Cure characteristics; Antioxidant.

INTRODUCTION

Polymers are usually used in conditions of high temperature, high stress, UV, ozone and high radiation, so stabilizers and antioxidants receive increasing appeals, as without them, physical and mechanical properties of polymeric articles may decrease due to oxidation reactions in production processes^[1–5]. Polymer oxidation may result in chain scission, cross linking and formation of oxygen-containing functional groups in polymer chains. Despite the low concentration (0.1 wt%–0.5 wt%) of stabilizers and antioxidants, these materials have a key role in many polymer compound formulations, as they reduce the degradation rate by reacting with the formed radicals. The most common of these materials are aromatic amines, phenols, organo-sulfur and organo-phosphor compounds^[6–8]. Their mechanisms depend on releasing an active hydrogen atom from phenolic or amine groups in order to deactivate peroxy sites and oxygen-containing groups along polymer chains like aldehydes and ketones. Efficiency of these antioxidants depends on their radicals stability and on capability of the hydrogen atom^[9–13]. Different parameters affect the performance of an antioxidant in rubber vulcanizates. First is the intrinsic activity of antioxidant or its products for stopping the oxidation radical chains which is somehow limited by its concentration. Second parameter is the compatibility or solubility of antioxidant in polymer matrix because the difference in surface tensions may result in agglomeration, non-solubility, migration to surface, so antioxidant cannot be uniformly dispersed in the matrix. Researchers believe that the third and also the most important parameter is volatility or unstable nature of antioxidant as the article performance is negatively affected by the increase in extractability or volatility of the antioxidant^[14–16]. Two ideas are represented to increase the stability of antioxidants. The first one is synthesizing them with higher molecular weights and so lower volatility and extractability. But it should be noted that polymerizable and high molecular weight antioxidants are low in efficiency because they cannot diffuse well in polymer matrix. The other one is making

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strong bonds between antioxidant and polymer so that its stability in the final product increases. High molecular weight antioxidants which bond with matrix chemically are the best protectors for unsaturated polymers^[17–22]. We should note that molecular weights of most antioxidants are low as a result they can migrate to polymer surface and be extracted from the compound^[16]. In this research the commercial antioxidant *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) was chemically bonded to a clay in order to increase its stability and then, mechanical and rheological properties of SBR compounds containing this antioxidant modified clay (organoclay) were investigated. Then, the degradation resistance of SBR compounds containing the organoclay was compared to that of the compounds having IPPD alone, in different intervals.

EXPERIMENTAL

Materials

In the present survey, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) was a product of Bayer Company in Germany, and Na-clay, specifications of which are listed in Table 1, was obtained from Kunimine Industries Company. Styrene butadiene rubber with the trade name of SBR 1502 was purchased from Bandar Imam Petrochemical Company (Iran). Oil with trade name of 840 was supplied by Behran Company in Iran. Carbon black (N330), zinc oxide (ZnO), stearic acid (St.Ac.) and sulfur from Iran Petrochemical Co. and other materials such as tetramethylthiuram disulfide (TMTD) and mercaptobenzothiazol (MBT) supplied by German Bayer Company were incorporated in compounds.

Table 1. Specification of Na-clay

Swelling	pH	Water content	Whiteness	Appearance	Cation exchange capacity
45 mL/2g	10	10%	60 or more	Fine powder	119 meq/100g

Preparation

In a three-neck flask, equipped with a mixer, water and Na-clay were mixed for 8 h at room temperature and mixing rate of 100 r/min. IPPD is an organic material and does not normally dissolve in water but, when reacted with HCl solution, it becomes completely soluble^[23]. Adding this solution to Na-clay which is swelled in water and mixed for 6 h, IPPD is exchanged with sodium ions between clay layers and sodium ions leave in the form of a salt (NaCl). Modified clay was extracted and filtered. After being washed with demineralized water for three times, it was dried in an oven at 50°C to be prepared for using in rubber compounds. Finally, rubber compounds based on SBR were prepared according to Table 2. A polymix 200L two-roll mill made in Germany was used to mix the compounds at 50°C.

Table 2. The composition of SBR compounds

Compound	1	2	3	4	5	6
SBR	100 phr	100 phr	100 phr	100 phr	100 phr	100 phr
St.Ac.	2	2	2	2	2	2
ZnO	5	5	5	5	5	5
HAF	30	30	30	30	30	30
Oil	7	7	7	7	7	7
TMTD	1.5	1.5	1.5	1.5	1.5	1.5
MBT	0.7	0.7	0.7	0.7	0.7	0.7
S	0.7	0.7	0.7	0.7	0.7	0.7
IPPD	–	1	–	–	–	–
Organoclay	–	–	1	2	3	4

Characterization

Compounds were cured at 150°C under 180 kg/cm² pressure, using a 25-ton hydraulic press obtained from Davenport Company in Britain. X-ray diffraction (XRD) analysis was performed at room temperature using an X-ray diffractometer (Philips model X'Pert) in the low angle range of 2θ . The X-ray beam was a Cu-K α radiation obtained from a 50 kV voltage generator and a 40 mA current. Specimens for X-ray diffraction were taken from compression-molded sheets of 2 mm in thickness. Cure characteristics of compounds were determined at 150°C

by a rheometer (Zwick 4308) made in Germany and their hardness was evaluated in Shore-A based on ASTM D2240 standard using an instrument obtained from Zwick company in Germany. The stress-strain properties of the composites were determined in accordance with the test procedures set forth in ASTM D412 using a Hiwa tensile machine with a crosshead speed of 500 mm/min. Samples were put into an oven at 100°C for 24, 48 and 72 h in order to do heat aging based on ASTM D573 standard. The rheological characterization of SBR compounds was carried out using a stress controlled Rheometer (RPA-2000). The experiments were performed at a temperature of 80°C and in the frequency range of 0.02–32 Hz.

RESULTS AND DISCUSSION

FTIR spectra of nanoclay, modified clay and IPPD are presented in Fig. 1. FTIR spectrum of unmodified clay is shown in Fig. 1(a), its characteristic peaks are at 468 and 1038 cm^{-1} [24, 25]. Free and hydrogen bonded OH stretching peaks also appeared at 3628 and 3444 cm^{-1} . FTIR spectrum of modified clay with characteristic peaks at 465 and 1045 cm^{-1} is indicated in Fig. 1(b). IPPD has the chemical structure of a secondary amine (Fig. 1c), so N–H sharp stretching peak coincides the O–H broad peak of the clay. This coincidence of the two peaks causes the O–H broad peak of nanoclay to become sharp. In addition, it is indicated in Fig. 1(b) that stretching absorbance of C=C appeared at 1519 and 1598 cm^{-1} while stretching absorbance of C–N was at 1322 cm^{-1} and bending absorbances of =C–H appeared at 697, 755 and 840 cm^{-1} . Thus, according to the resultant FTIR spectra, it can be concluded that Na-clay has reacted with IPPD and has changed into IPPD-modified clay. The IPPD content in the organoclay is 23 percent that was determined gravimetrically. Results of X-ray diffraction confirmed this reaction as shown in Fig. 2. X-ray diffraction pattern of Na-clay, modified clay and SBR compounds prepared with 1, 2, 3 and 4 phr organoclay are illustrated in Figs. 2(a), 2(b), 2(c), 2(d), 2(e) and 2(f) respectively. Specimens for X-ray diffraction were taken from compression-molded sheets of 2 mm in thickness. The diffraction peak corresponding to the (001) plane of unmodified clay appears at $2\theta = 7.95^\circ$. Based on Bragg's law ($d = \lambda/(2\sin\theta_{\max})$), the interlayer distance of the Na-clay is about 1.1 nm. The XRD pattern of modified nanoclay is shown in Fig. 2(b) which indicates the clay characteristic XRD peak has shifted to lower angles, $2\theta = 6.72^\circ$, hence the d -spacing of the silicate layers has increased to about 1.4 nm. The interlayer distance of the modified clay is larger than the original interlayer spacing of unmodified silicate layers which implies the clay can be intercalated by the IPPD. The XRD peak of SBR compound prepared using 1 phr clay formulation shows an increase in interlayer spacing ($2\theta = 5.2^\circ$, $d = 1.7$ nm) as a result of the intercalation of SBR as illustrated in Fig. 2(c). It should also be noted that the intensity of the diffraction peak in the SBR composite decreases and also the peak is broader than that of the modified nanoclay. The decrease in intensity

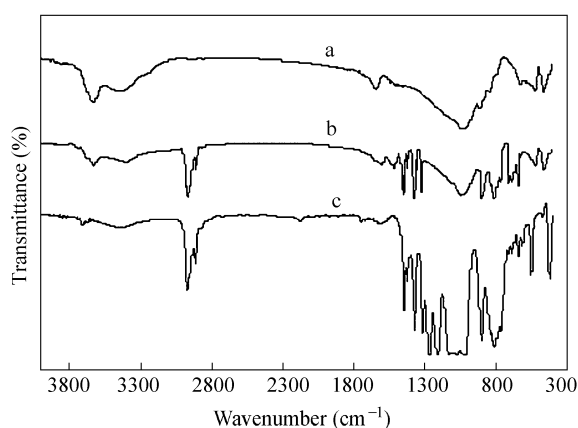


Fig. 1 FTIR of (a) Na-clay, (b) modified clay and (c) IPPD

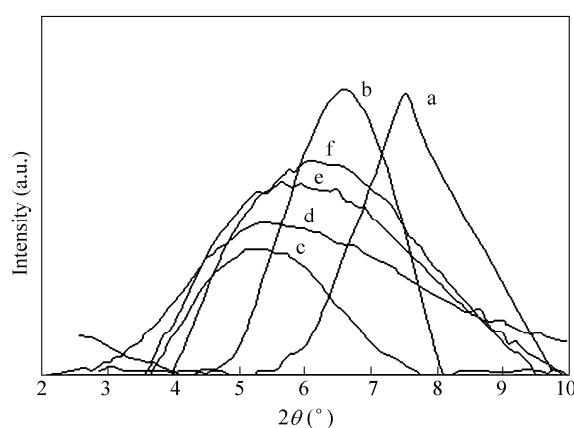


Fig. 2 X-ray diffraction patterns of (a) clay, (b) modified clay, and SBR compound prepared with (c) 1 phr, (d) 2 phr, (e) 3 phr and (f) 4 phr of modified clay

and the broadening of peaks indicate that the stacks of layered silicates become more intercalated or partially exfoliated^[21, 26]. In Fig. 2(d), we present the XRD pattern of SBR compounds prepared with 2 phr of organoclay. It can be seen that the intensity of the peak increased and appeared at higher angles compared to the composite prepared by 1 phr of the clay. Similar trends were observed for SBR compounds based on 3 and 4 phr of the silicate layers as shown in Figs. 2(e), and 2(f). This is due to the influence of the packing density, rendering more difficult the penetration of the polymer chains between the silicate layers^[21]. In a further characterization of these materials, cure characteristics for the SBR compounds have been obtained. Figures 3(a), 3(b) show the scorch and cure times of SBR compounds prepared with IPPD and 0, 1, 2, 3 and 4 phr of modified clay. It is observed that the scorch and cure times of the compounds decreased with introduction of IPPD and also by the organoclay loading.

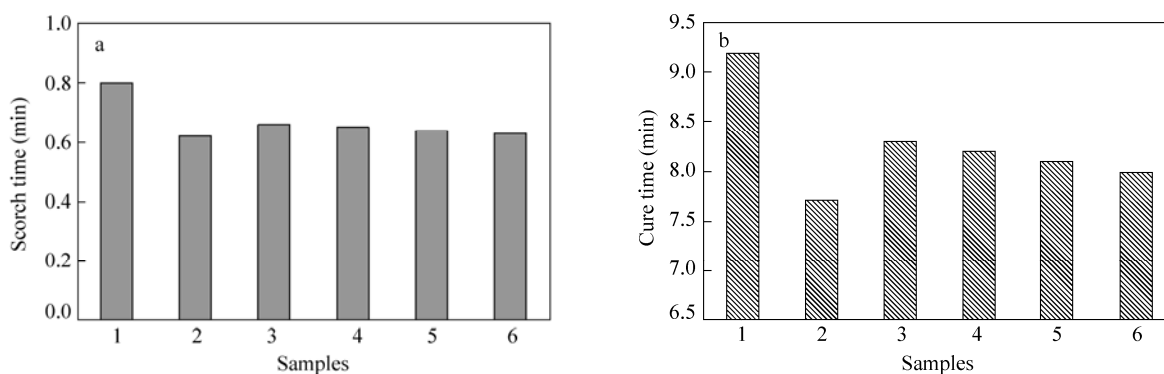


Fig. 3 The scorch (a) and cure times (b) of SBR compounds prepared with IPPD and 0, 1, 2, 3 and 4 phr of modified clay

The scorch time of the SBR compound prepared without IPPD and organoclay ($t_{s5} = 0.8$ min) is large than that of the samples with IPPD ($t_{s5} = 0.62$ min) and 4 phr of the organoclay ($t_{s5} = 0.64$ min) as shown in Fig. 3(a). It can also be seen from Fig. 3(b) that the cure time (t_{90}) of the sample without IPPD is about 9.2 min, while the cure time of the compound using IPPD is 7.7 min. The cure time of the SBR composite prepared by 4 phr of the modified clay is 8 min which indicates a decrease in the cure time of the compounds with increasing organoclay. Amine groups of IPPD can be the cause of decrease in scorch and cure times, as they increase cure rate due to increasing pH of the compound^[27].

Figures 4(a), 4(b) indicates tensile strength and elongation at break of SBR compounds according to Table 3. As illustrated in Fig. 4(a), tensile strength of compounds incorporating IPPD but without any clay decreased a little, however, mechanical properties of compounds incorporating modified clay improved by increasing the amount of modified clay. This improvement in mechanical properties can be attributed to diffusion of SBR chains in between clay layers which cause the formation of strong bonds between polymer matrix and clay. Aging test was done using an oven at 100°C for 24, 48, and 72 h to investigate degradation resistance of vulcanizates. Table 3 shows the results. According to this table, vulcanizates without clay and IPPD (compound 1) undergo a high tensile strength loss (37%) while vulcanizates incorporating modified clay (compound 3–6) undergo a lower tensile strength loss (22%–14%). This improved degradation resistance can be attributed to the presence of IPPD and strong bonds between SBR matrix and IPPD-modified clay. As distribution degree of nanoparticles and bonds strength of nanoclay with polymer matrix can be evaluated through rheological experiments, linear viscoelastic properties of compounds were determined before curing.

The results are illustrated in Figs. 5 and 6. According to Fig. 5 the elastic modulus of compound 2 which contains IPPD is less than compound 1, however, increasing the amount of modified clay increased the storage modulus. In low frequencies, moduli of vulcanizates containing organoclay reach an asymptote. This is the common behavior of solids and shows the formation of strong bonds in polymer matrix which is usually

observed in nanocomposites^[28]. Complex viscosities of SBR compounds are indicated in Fig. 6. All compounds showed pseudo plastic behavior in medium and high frequencies, but, compounds containing high amount of modified organoclay did not have a definite asymptote that, as reported for nanocomposites, can be a cause of yield stress^[28].

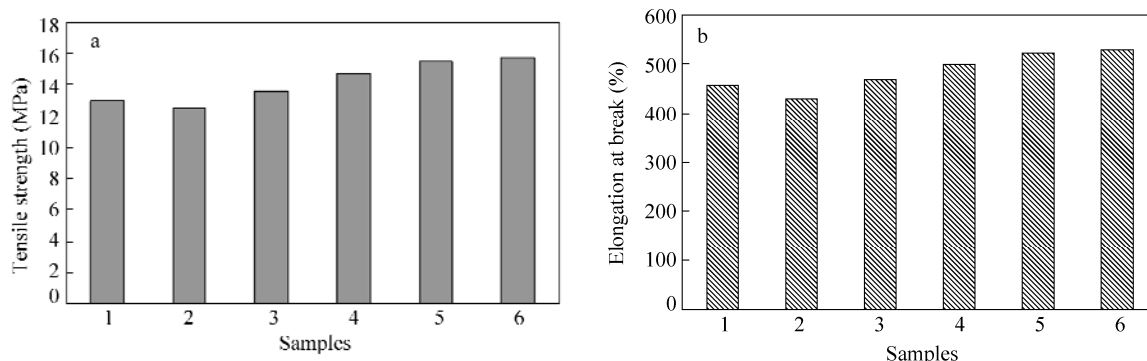


Fig. 4 The tensile strength (a) and elongation at break (b) of SBR compounds prepared with IPPD and 0, 1, 2, 3 and 4 phr of modified clay

Table 3. Mechanical properties and heat aging resistance of the SBR composites

Compound No.	Tensile strength (MPa)			Elongation at break (%)			Hardness (Shore A)			
	24 h	Aging at		Aging at			Aging at			
		48 h	72 h	24 h	48 h	72 h	72 h			
1	13	9.6 (-26%)	8.9 (-31%)	8.1 (-37%)	455	324	290	270	57	63
2	12.2	12 (-2%)	11.6 (-5%)	11 (-10%)	348	338	310	300	56	61
3	13.6	11.6 (-15%)	11 (-19%)	10.6 (-22%)	465	390	365	350	58	63
4	14.7	12.8 (-13%)	11.9 (-19%)	11.5 (-21%)	498	410	395	376	58	63
5	15.5	14 (-10%)	13.5 (-13%)	12.8 (-17%)	521	475	435	404	59	64
6	15.7	14.8 (-6%)	14.2 (-9%)	13.5 (-14%)	538	486	455	428	60	65

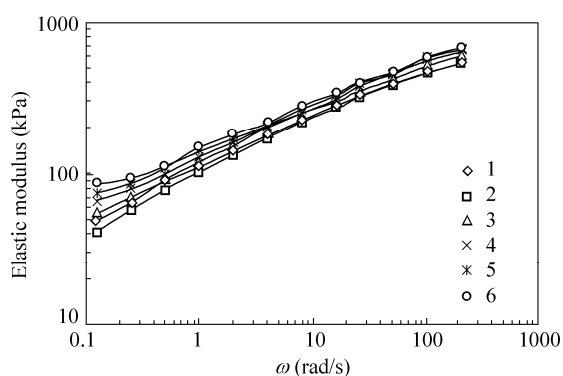


Fig. 5 Storage modulus versus angular frequency for SBR compounds
The compositions are given in Table 2.

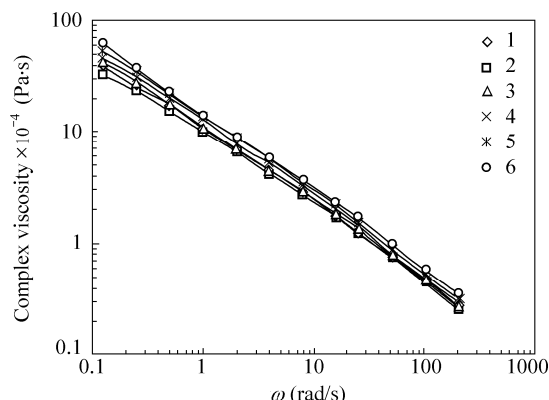


Fig. 6 Complex viscosity versus angular frequency for SBR compounds
The compositions are given in Table 2.

CONCLUSIONS

Compounds based on SBR and clay modified with *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD) were prepared. The increase in interlayer distance of Na-clay due to the reaction with IPPD was confirmed by XRD tests. As the amount of organoclay increased, scorch and cure times of SBR compounds decreased while their tensile strength increased. Loading more organoclay decreased the tensile strength loss due to aging as well. Elastic moduli and complex viscosities of prepared composites increased due to formation of strong bonds between organoclay and SBR matrix.

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