

# Effect of Surface-Modified Zinc Oxide as Cure Activator on the Properties of a Rubber Compound Based on NR/SBR

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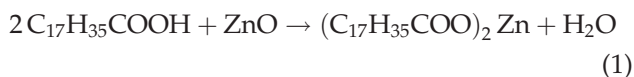
**ABSTRACT:** Zinc oxide (ZnO) and nano-zinc oxide (nZnO) were surface modified by polyethylene glycol (PEG) and poly propylene glycol (PPG). Modification of particles were controlled by transmission electron microscopy, Brunauer, Emmett, Teller specific surface area measurement, infrared (IR) spectroscopy, and differential scanning calorimetry. IR spectra were shown that the interactions between surface modifiers and particles are hydrogen bonding. Modified particles were applied as an activator in vulcanization of natural rubber/styrene butadiene rubber (NR/SBR) blend. Dispersion of modified particles in rubber matrix was investigated by scanning electron microscopy and shown good results. Blend properties were improved by using modified particles. These

improvements were due to the better hydrophobicity of modified particles, which were more compatible with non-polar rubber matrix and caused better participation in curing process. Modification by PEG and PPG were shown better compound properties for ZnO and nZnO, respectively. Application of ZnO-modified particles were presented better compound properties in comparison with nZnO-modified particles. It has confirmed more effective mixing of ZnO-modified particles in rubber matrix by using ordinary mixers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 249–256, 2011

**Key words:** dispersion; modification; rubber; surfaces; vulcanization

## INTRODUCTION

ZnO is a common activator used in rubber industry for improving the vulcanization rate and efficiency. ZnO reacts with stearic acid to form the rubber compatible zinc stearate and liberates water according to reaction (1).



Zinc stearate together with accelerator cause more efficient sulfur vulcanization.<sup>1–3</sup> Although ZnO enhances the vulcanization efficiency and vulcanization properties and reduces the vulcanization time, there is a major problem consequent of applying it in rubber compounds as a low efficiency incorporation in rubber matrix. This comes out through three

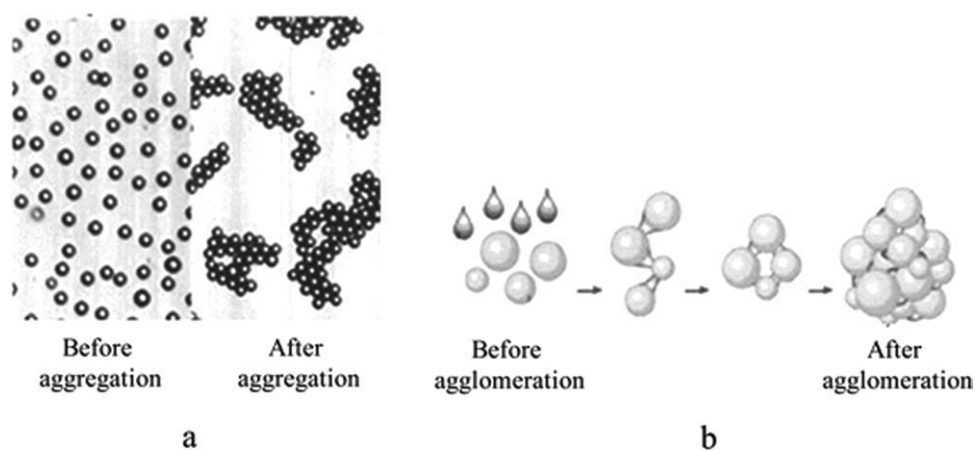
factors. The first one is the hydrophilic surface of the ZnO. It is an inorganic compound that has an ionic bond between zinc and oxygen in its structure. This causes ZnO low affinity, toward organic rubber matrix. The second factor is the high surface energy of ZnO, which causes the formation of aggregate clusters as it is shown in Figure 1(a). The third factor is making hard agglomerates due to the adsorption of water molecules on the surface of zinc oxide and forming surface hydroxyl groups. In this case, further molecules are adsorbed physically through hydrogen bonding and making hard agglomerates as it is presented in Figure 1(b).<sup>4</sup>

Nowadays, application of nZnO in rubber industry attracts researchers' attention.<sup>5–8</sup> These nanoparticles have outstanding characteristics, mainly originating from finite size and high ratio of surface to volume. The problems involved in using these nanoparticles are higher surface energy and smaller size that cause the above-mentioned problems more serious.<sup>9,10</sup> These problems may impede nanoparticles usage.

Application of surface-modified particles can be a solution for the above-mentioned problems. It is a way to improve the incorporation of particles in rubber matrix by using organic materials to achieve more hydrophobic surface that is more compatible

Additional Supporting Information may be found in the online version of this article.

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**Figure 1** (a) Formation of ZnO aggregates (b) Formation of ZnO agglomerates.

with the nonpolar matrix. This surface characteristic causes better participation of ZnO and nZnO in curing process. Generally, there are two ways for modifying a surface. Electrostatic stabilization, in which an electrical layer due to ion adsorption, forms on the surface of particle. On the other way which named as steric stabilization, adsorption of macromolecules on the surface of particles use.

Posthumus et al. modified various oxidic nanoparticles using 3-methacryloxypropyl-trimethoxysilane and investigated the grafting.<sup>11</sup> Hong et al. modified nZnO by oleic acid and better compatibility gained between inorganic nanoparticle and organic matrix.<sup>12</sup> Tang et al. used polymethacrylic acid for nZnO modification and dispersion in aqueous system improved.<sup>13</sup> In another work, Hong et al. used poly methyl methacrylate for grafting nZnO and applied it in nanocomposite preparation with styrene and better thermal behavior obtained.<sup>14</sup> Ma et al. modified nZnO surface by KH570 silane coupling agent and dispersion improved.<sup>15</sup>

In the present investigation, the surfaces of ZnO and nZnO were modified by polyethylene glycol (PEG) and poly propylene glycol (PPG). These two modifiers are cheap, compatible with rubber matrix and are available as petrochemical products in comparison with other modifiers. The grafted particles were used as an activator in vulcanization of a natural rubber/styrene butadiene rubber (NR/SBR) blend (normal tire tread recipe).

## EXPERIMENTAL

### Materials

ZnO 91.2% was obtained from Pars Oxide Parto Iran with the average particle size 500 nm and specific surface area  $4.30 \pm 0.04 \text{ m}^2/\text{g}$ . Zinc acetate dehydrate 99%, sodium hydroxide 99%, triethanol amin 98%, PEG ( $M_w = 400$ ) and PPG ( $M_w = 2000$ ) all were supplied by Merck Company. SMR 20 (NR) with mooney viscosity

ML(1 + 4)@100°C of 52.5. SBR 1500 containing 23% styrene with mooney viscosity ML(1 + 4)@100°C of 52 was obtained from Bandar Imam Petrochemical Company, Iran. Carbon black N-375 was provided from Iran Carbon Company with  $N_2$  surface area 95–105  $\text{m}^2/\text{g}$ . Rubber process aromatic oil no. 290 was obtained from Behran Oil Company, Iran. Sulfur 99.7% was supplied by Tesdak Company, Iran. CBS Vulkasit CZ/C 98.5% was obtained from Lanxess. Dusantox 6PPD was provided from Duslo with minimum 97% active substance content. Flectol TMQ-PST was obtained from Flexsys. Antilux 654 was supplied by Rheinchemie. Stearic acid 95% was provided by Palmo-leo Sdn. Bhd.

### Methods

Particle size distribution (PSD) was measured by Laser Light Scattering Optilab Wyatt, SEMATECH. The particles were mixed with ethanol and in order to minimize the effect of aggregation and agglomeration, the mixture were placed in the ultrasonic bath before the test. Transmission Electron Microscopy (TEM) images were obtained by TEM, Philips EM 208 for the similar concentration of particles that were dispersed in the ethanol media and were placed in the ultrasonic bath before the test to minimize the effect of aggregation and agglomeration. Brunauer, Emmett, Teller (BET) surface area measurements have done on three samples of each case by ChemBET 3000 Quantachrome TRP and the mean values were reported. Infrared (IR) analysis were carried out on KBr pellets of samples. The conditions of pellets preparation were same for each set of samples and the spectra were taken on a FTIR Spectrum GX, Perkin-Elmer. Differential scanning calorimetry (DSC) analyses have done by TA 1500, Scinco. Samples were heated in oxygen atmosphere to 600°C from room temperature at the speed of 20°C/min. Scanning electron microscopy (SEM) images of the compounds were obtained by Cam Scan MV2300, Obducat. The cure characteristics of different compounds were measured

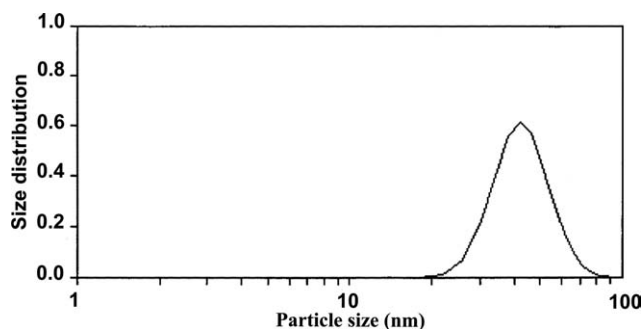


Figure 2 Particle size distribution of prepared nZnO.

at 160°C with MDR 900, HIWA Company. The compounds were cured in a laboratory press PTP 600, PGH Company at 160°C and 220 KN. Abrasions were measured for three samples of each case, by Bareiss 2243 according to ASTM D5963 and the mean values were reported. Fatigue tests have done for three samples of each case to 300 KC by HIWA 600, HIWA Company according to ISO 6943. Tensile tests were done on the three samples of each case, and the mean values were reported. They were carried out on dumb-bell shaped specimens by M-350-5019, Testometric Company, according to ASTM D412.

### Statistical analysis

Statistical analyses of data were performed at 95% confidence level with one-way analysis of variance (ANOVA) method and the multiple comparisons were made by *post hoc* Tukey, using SPSS software (Supporting Information Tables I–VI).

### Preparation of nZnO

Hundred milliliter aqueous solution of 1M zinc acetate was mixed with 200-mL aqueous solution of 2M sodium hydroxide. After 24 h stirring, 7.5 mL of triethanolamine was slowly added to the reaction mixture. It was then stirred for 10 more minutes. Finally,

the mixture was placed under microwave irradiation (20% power) for 20 min. The white solid product was vacuum filtered, washed with distilled water, and dried in air at room temperature. It was then calcinated at 900°C for 1 h. The size of prepared nanoparticles was investigated by PSD and TEM and was in the range of 30–70 nm [Figs. 2 and 3(a)]. The BET test was shown the particles specific surface area as  $39.70 \pm 0.31 \text{ m}^2/\text{g}$ .

### Surface modification of particles by PEG and PPG

Twenty-five grams of ZnO in water (100 mL) was stirred for 30 min under ultrasonic agitation. 1.25 g PEG was dissolved in 100-mL water and was added to the zinc oxide suspension. The mixture was stirred at room temperature for 24 h. The particles were then collected in centrifuge and were washed with distilled water followed by centrifugation to remove the unreacted polymer. The powder was dried at 120°C for 6 h.<sup>16</sup> The same procedure has done for the other surface modifications.

### Mixing recipe

Masterbatches were prepared in an internal mixer (Wellshayang, 2 L) to get homogenous mixtures and to minimize the influence of mixing condition. The components were added to the mixer respectively in 20 min as follows in addition times:

- 0 min: NR (mastication)
- 1.5 min: SBR (blending of NR and SBR)
- 6 min: carbon black, zinc oxide, and other chemicals
- 10 min: oil
- 20 min: discharge

The vulcanization system was added in a separate operation on a two-roll mill (Wellshayang, 6" \* 18")

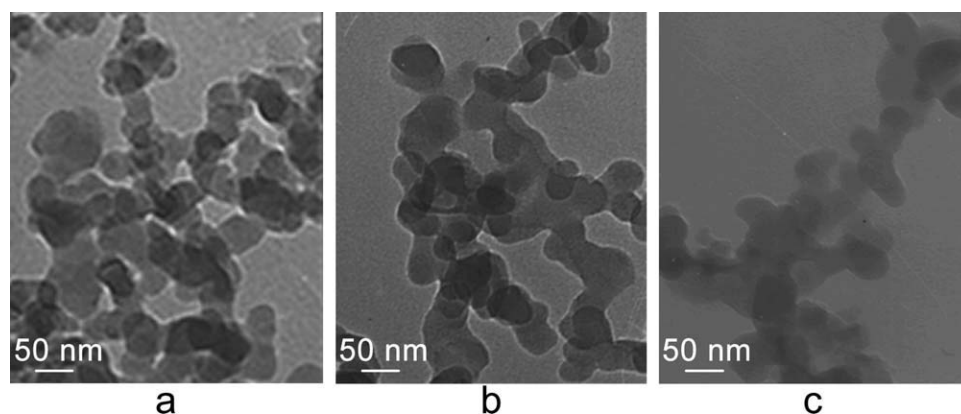


Figure 3 TEM images in ethanol matrix (a) nZnO, (b) nZnO + PEG, (c) nZnO + PPG.

TABLE I  
Compounds Formulation

	phr					
	Z	Z + PEG	Z + PPG	NZ	NZ + PEG	NZ + PPG
SMR <sup>a</sup> (NR)	75	75	75	75	75	75
SBR	25	25	25	25	25	25
CB <sup>b</sup>	50	50	50	50	50	50
Aro.oil	10	10	10	10	10	10
S	1.5	1.5	1.5	1.5	1.5	1.5
CBS <sup>c</sup>	0.75	0.75	0.75	0.75	0.75	0.75
6PPD <sup>d</sup>	1.5	1.5	1.5	1.5	1.5	1.5
TMQ <sup>e</sup>	1	1	1	1	1	1
Anti lux <sup>f</sup>	2	2	2	2	2	2
St. ac. <sup>g</sup>	2	2	2	2	2	2
ZnO	2	–	–	–	–	–
ZnO + PEG	–	2	–	–	–	–
ZnO + PPG	–	–	2	–	–	–
nZnO	–	–	–	2	–	–
nZnO + PEG	–	–	–	–	2	–
nZnO + PPG	–	–	–	–	–	2

<sup>a</sup> Standard malaysian rubber.

<sup>b</sup> Carbon black.

<sup>c</sup> N-Cyclohexyl-2-benzothiazole sulfonamide.

<sup>d</sup> N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

<sup>e</sup> 2,2,4-trimethyl-1,2 di-hydroquinoline.

<sup>f</sup> Blend of selected paraffins and microwaxes.

<sup>g</sup> Stearic acid.

at 70°C and mixing was continued for 15 min. The compounds formulation is shown in Table I.

## RESULTS AND DISCUSSION

### TEM images in ethanol matrix

TEM images were prepared to investigate the effect of modification on nZnO particles. nZnO, PEG- and PPG-modified nZnO particles are shown in Figure 3. The images were not shown appreciable change in particle size after modification. The interaction between ethanol as matrix and modifiers was formed the partially matrix separated modified nZnO. This was caused the formation of smaller colonies of nZnO clusters in ethanol matrix.

### BET specific surface area measurement

The particles specific surface areas are presented in Table II. The measured values were statistically compared and the *P*-values for ZnO- and ZnO-modified particles were less than 0.05 and were confirmed the

modification. There were no significant differences between the modification by PEG and PPG. The results were repeated for nZnO- and nZnO-modified particles. These changes probably have caused by the effect of modifier molecules that have reduced the size of the colonies of ZnO and nZnO clusters.

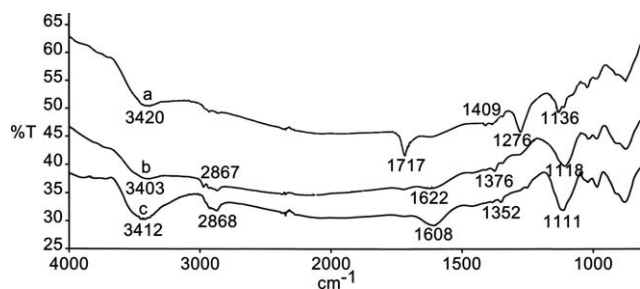
### IR spectra

IR spectroscopy gave qualitative information about the way in which the adsorbed molecules were grafted to the surface of ZnO and nZnO particles. Figures 4 and 5 show the comparison of IR spectra of ZnO and nZnO without modifier [Figs. 4(a), 5(a)], with PEG as modifier (4b, 5b) and with PPG modifier [Figs. 4(c), 5(c)], respectively. The peak around 1110 cm<sup>-1</sup> was concerned with the stretch vibration of C—O. The series of peaks in the region from 2800 to 3000 cm<sup>-1</sup> were correlated with C—H stretches. The increasing in peak intensity in these two regions was approved the interaction between particles and polymers. The series of peaks in the region extending from 1300 to 1450 cm<sup>-1</sup> are likely due to the

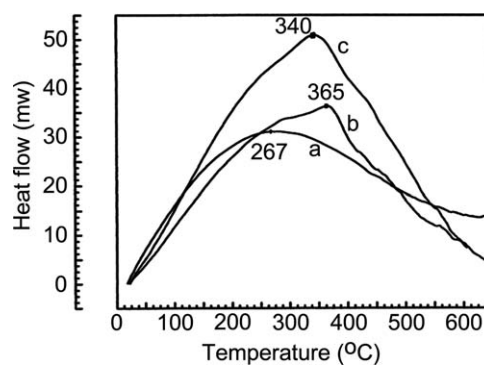
TABLE II  
BET Specific Surface Area Measurement for Modified and Unmodified Particles

Label	ZnO	ZnO + PEG	ZnO + PPG	nZnO	nZnO + PEG	nZnO + PPG
BET specific surface area (m <sup>2</sup> /g) [SE] <sup>a</sup>	4.30 [0.02]	5.05 [0.03]	5.03 [0.03]	39.70 [0.18]	46.52 [0.28]	47.38 [0.30]

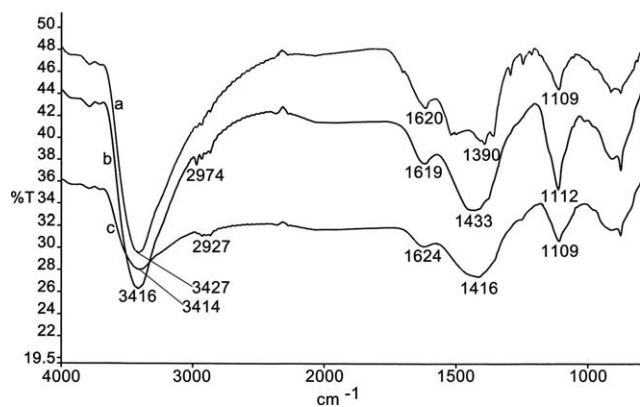
<sup>a</sup> Standard error of mean SE = S/n<sup>0.5</sup> where, S is the standard deviation and n is the number of measurements.



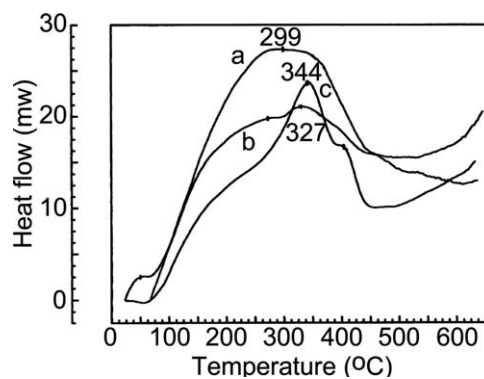
**Figure 4** IR spectra (a) ZnO, (b) ZnO + PEG, (c) ZnO + PPG.



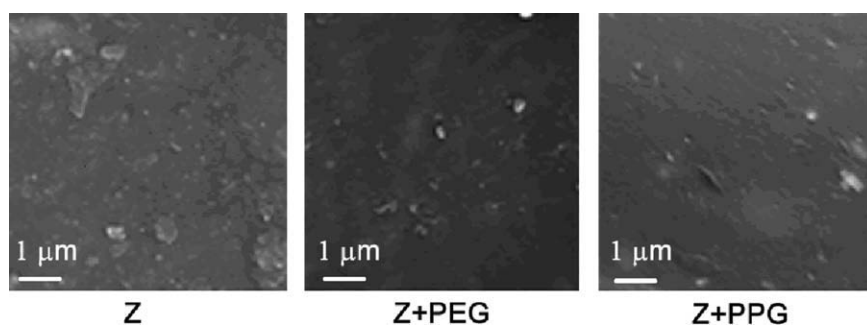
**Figure 6** DSC curves (a) ZnO, (b) ZnO + PEG, (c) ZnO + PPG.



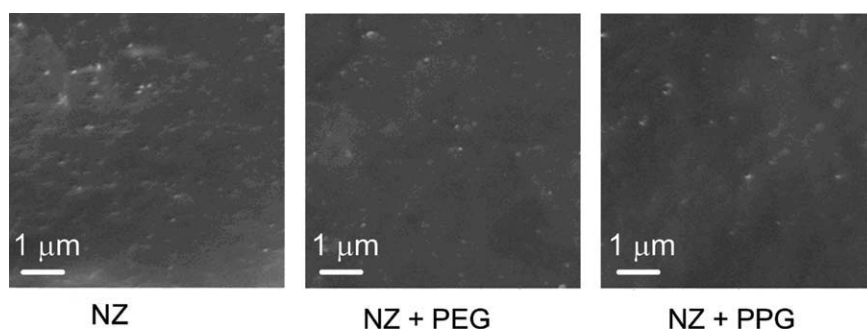
**Figure 5** IR spectra (a) nZnO, (b) nZnO + PEG, (c) nZnO + PPG.



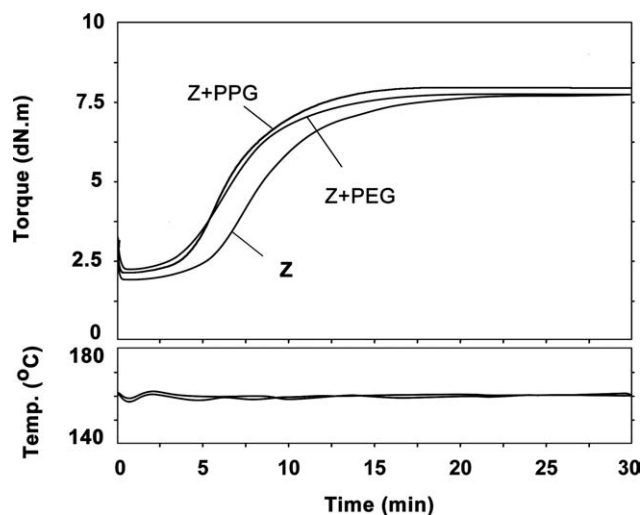
**Figure 7** DSC curves (a) nZnO, (b) nZnO + PEG, (c) nZnO + PPG.



**Figure 8** SEM images of Z, Z + PEG and Z + PPG.



**Figure 9** SEM images of NZ, NZ + PEG and NZ + PPG.

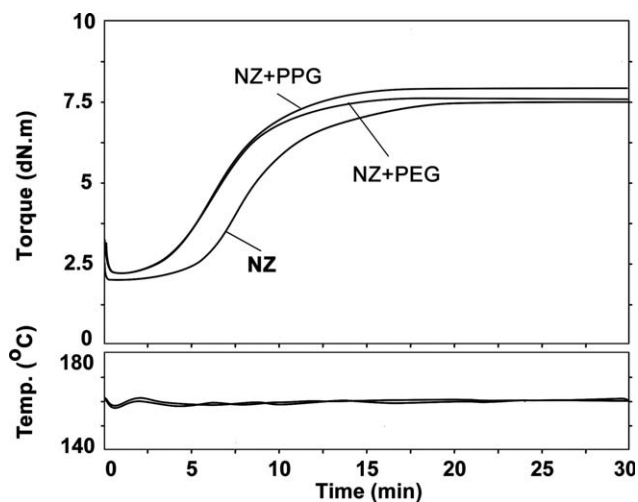


**Figure 10** Rheometric curves of the compounds containing ZnO and ZnO modified particles.

bending modes of O—H. The broad peak between 3200 and 3600  $\text{cm}^{-1}$  was suggested the presence of hydroxyl group. This strong band, was shifted toward low wave numbers<sup>16</sup> after modification. These evidences were verified the grafting of PEG and PPG on particles surfaces and indicated that hydrogen bond formed at the ZnO/polymer and nZnO/polymer interfaces.

### DSC results

DSC analysis has given qualitative information about the interaction between modifiers and particles.<sup>15</sup> Figures 6 and 7 show the DSC curves of unmodified and modified ZnO, unmodified and modified nZnO, respectively. Heat flows in these curves were considered from 200 to 400 °C due to the elimination of volatile matters in the mentioned temperature range. Maximum heat flow at 267°C that could be attributed to volatile matters of ZnO is shown in Figure 6(a). After ZnO modification [Figs. 6(b,c)], maximum heat flows were shifted to higher temperatures. These changes were verified the interaction between the polymers and particles. For ZnO, the PEG-modified particles were shown higher temperature shift (365°C)



**Figure 11** Rheometric curves of the compounds containing nZnO and nZnO modified particles.

in comparison with PPG-modified particles (340°C). It might be due to a better modification.

The DSC curve in Figure 7(a) is shown an exothermic peak near 299°C that could be attributed to volatile matters in nZnO. After nZnO modification [Figs. 7(b,c)], maximum heat flows were shifted to higher temperatures. For PPG modification of nZnO, the temperature was shifted higher (344°C) than PEG (327°C). It might be due to a better modification.

The peak temperature changes were verified the interaction between the polymers and particles and loss of water on the surface of grafted ZnO and nZnO. These evidences were confirmed the modification.

### SEM images

Figures 8 and 9 are compared the SEM images of the prepared rubber compounds. Modified particles were shown much better dispersion in rubber matrix. It was demonstrated that after surface modification, the hydrophilicity of particles was reduced.

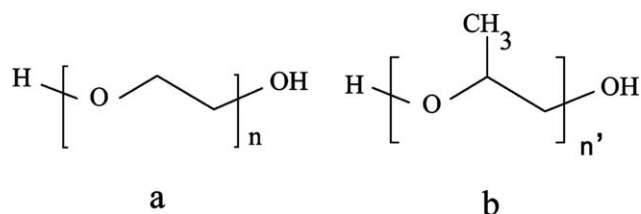
### Compounds properties

Rheometric curves for different compounds are shown in Figures 10 and 11.  $T_{C90}$  is a time to reach 90% of maximum torque was increased by using

**TABLE III**  
Compounds Properties

	Z	Z + PEG	Z + PPG	NZ	NZ + PEG	NZ + PPG
Abrasion ( $\text{mm}^3$ ) [SE] <sup>a</sup>	170 [2]	118 [2]	128 [2]	130 [2]	137 [3]	125 [2]
Fatigue (KC)	252	>300	>300	>300	>300	>300
Tensile strength (MPa) [SE]	9.11 [0.35]	18.31 [0.56]	18.24 [0.58]	12.22 [0.41]	13.86 [0.45]	16.08 [0.50]
Modulus 100% (MPa) [SE]	0.77 [0.01]	1.54 [0.03]	1.39 [0.03]	1.05 [0.01]	1.18 [0.01]	1.28 [0.01]
Modulus 300% (MPa) [SE]	2.82 [0.02]	7.40 [0.15]	6.35 [0.09]	4.93 [0.09]	5.35 [0.06]	6.45 [0.4]
Elongation (%) [SE]	600 [4]	536 [11]	595 [2]	568 [5]	555 [10]	536 [5]

<sup>a</sup> Standard error of mean  $SE = S/n^{0.5}$  Where,  $S$  is the standard deviation and  $n$  is the number of measurements.



**Figure 12** Structural formula (a) PEG and (b) PPG.

nZnO instead of ZnO. This might be due to the aggregation and agglomeration of the nanoparticles, which was caused the delay in the formation and disappearance of the crosslink precursors.  $T_{C90}$  was decreased by modification and was shown that the reactivity of activator has increased due to the better hydrophobicity of particles and faster formation of zinc ion to incorporate in vulcanization process. Cure rate index (CRI) was increased by using modified particles and was shown the faster curing system. PEG modification was signified faster curing system for both ZnO and nZnO modified particles containing, compounds. It might be due to its smaller size that was caused faster zinc ion release for complex formation with the accelerator.

The compounds properties are presented in Table III. The measured values were statistically compared, and the mean differences were considered significant if the  $P$ -values were less than 0.05. Abrasion of the compound was decreased by modifying ZnO particles. PEG-modified ZnO was shown better results. Application of nZnO was decreased the abrasion in comparison with ZnO but it was not significantly changed by applying nZnO-modified particles in comparison with nZnO. Fatigue was increased by nZnO and modified particles, and there was no track on the dumbbells till 300 KC. Tensile strength of the compounds was increased by applying modified ZnO particles. There were no significant changes between using PEG- and PPG-modified ZnO particles. PPG-modified nZnO particles have improved the tensile strength in comparison with nZnO. Increase of modules 100% and 300% after modification of ZnO was seen and using PEG-modified ZnO better results were shown. Application of nZnO-modified particles was increased modulus 100% but modulus 300% increased by using PPG-modified

nZnO. Elongation was reduced by using PEG-modified ZnO and PPG-modified nZnO.

From the discussion, it could concluded that by applying nZnO instead of ZnO in the compounds, physico-mechanical properties were improved. The smaller size of nZnO was increased the ratio of surface to volume of the particles in the rubber matrix, which was caused the more effective curing process. The hydrophilicity, aggregation, agglomeration, and bad dispersion of nZnO in the matrix were caused that this improvement was not correlated with the reduction of particle size from ZnO to nZnO.

After modification, the better properties were obtained due to the better hydrophobicity of the particles. The modified particles were more compatible with the nonpolar rubber matrix and were made cure process more effective. Modification by PEG and PPG were shown better results for ZnO and nZnO, respectively. ZnO-modified particles were improved the properties much more than nZnO-modified particles. It was seen that in spite of surface increase after modification as BET tests were shown before, the ordinary mixers were unable to mix nZnO effectively in rubber matrix.<sup>17,18</sup>

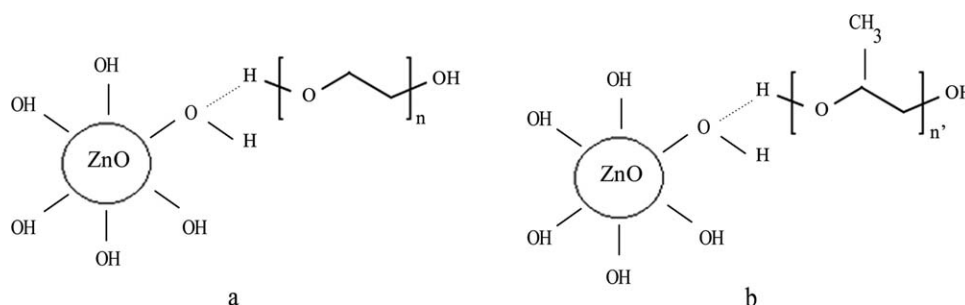
### Surface modification mechanism

The simple structural formulas of PEG and PPG are shown in Figure 12. The schematic process for surface modification of ZnO and nZnO by PEG and PPG are illustrated in Figure 13. In this figure, the hydrogen bonds were formed between one of the surface hydroxyl groups of ZnO and nZnO, and the modifiers. The long chains of polymers and their hydrophobic characteristics were increased the compatibility of the activator particles in organic rubber matrix.

### CONCLUSIONS

From the results, the following conclusion was obtained:

1. TEM images of nZnO in ethanol matrix were shown that the size of the particles was not changed after modification, and the interaction



**Figure 13** Schematic process for hydrogen bond formation on ZnO surface (a) PEG and (b) PPG.

between ethanol and modifiers was formed the matrix separated modified nZnO, with smaller colonies of nZnO clusters.

2. The values of BET specific surface areas were increased after modification. These values were increased approximately similar for ZnO and nZnO particles. These increases might be caused by the effect of modifier molecules that reduced the size of the colonies of ZnO and nZnO clusters.
3. IR spectra were presented that the surface hydroxyl groups of ZnO and nZnO, were interacted with PEG and PPG to form hydrogen bonding.
4. DSC results were indicated that the surface of ZnO and nZnO particles contained polymer molecules, and better modification was correlated to the amount of maximum heat flow peak shift to higher temperatures.
5. Using PEG- and PPG surface-modified ZnO and nZnO in the compounds formulation have presented faster cure system due to the better hydrophobicity, better compatibility with rubber matrix and faster formation of zinc ions. PEG has shown faster cure system as it is a smaller molecule and looser interact in comparison with PPG and the zinc ions could be released faster for incorporating in the vulcanization process.
6. According to Table III, ZnO-modified particles were shown better effects on the compounds properties due to the better incorporation in mixing procedure by using ordinary mixers in comparison with nZnO-modified particles. Dispersion of nZnO and its modified particles has need more effective mixing procedure.

ZnO-and nZnO-modified particles could successfully applied as a cure activator due to the better

hydrophobicity and better compatibility with rubber matrix. The better physico-mechanical properties which was seen by using modified ZnO and ordinary mixer was helped to reduce the ZnO content in the compounds formulary with properties preservation.

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