Effect of Titanate Coupling Agent on the Mechanical Properties of Clay-Filled Polybutadiene Rubber

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Received 17 July 2003; accepted 16 December 2003
DOI 10.1002/app.20549
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Clays belong to an economic class of fillers, which are used extensively in rubbers and plastics. Being nonreinforcing in nature, there are limitations upon its use. If the properties of filler are modified, it will get a higher value as a filler. To achieve this modification of surface properties is one of the avenues. In the present work, the effect of treatment of the coupling agent on clay has been studied, with polybutadiene as a matrix. Composites were made with a varying proportion of untreated and treated clay. A two-roll mill was used for dispersing the filler in the rubber, and a compression-molding technique was used to cure the compounded in sheet forms. Tensile properties were measured on a computerized UTM using the ASTM procedure. Comparison of properties of composites filled with treated and untreated clay established that treatment of clay imparts better reinforcing properties. The properties under consideration were tensile strength, modulus at 100 and 400%, Young's modulus, hardness, etc. Tensile strength was improved by 52%, while modulus at 400% was improved by 150%. Similarly Young's modulus also was improved by 27%. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1299–1304, 2004

Key words: polybutadiene; clay; composites; mechanical properties

INTRODUCTION

Clay is a low-cost inorganic filler used extensively in rubbers and plastics. Although it is economic it does not contribute to reinforce the composites, and there are severe limitations on its use. In our efforts to find an economical yet reinforcing filler, a study was undertaken on flyash earlier. Flyash was treated with various percentages of coupling agents, and was incorporated in polybutadiene rubber.[1–4] Because coupling agents work as molecular bridges at the interface between two dissimilar substrates, it was reasoned that the treatment of coupling agents would convert an ordinary filler into a value-added one. The results were quite encouraging, and hence, the study has been continued for clay. In the present work clay was treated with a titanate coupling agent (1.0% solution).[2–8] The treated filler (in various percentages) was incorporated in polybutadiene rubber using a two-roll mill. Finally, the composites were molded in sheet form using a compression-molding technique at 150°C. Properties under consideration were tensile strength, Young's modulus, modulus at various elongations, hardness, etc. Comparisons of magnitudes of property reveal that the treatment had a favorable effect on properties of composites. In the case of NR, there was no improvement even after treatment of clay by silane Si-69.[7,8] However, our results indicate that treatment of Si-69 imparts improvement for clays in polybutadiene.

EXPERIMENTAL

Materials

The Titanate coupling agent [(LICA 01): Neopentyl (diallyl) oxy, trineodecanonyl titanate] was imported from Ken-React Petrochemicals, Inc., USA. Chain a clay was procured from a local supplier. PBR, a *cis*-1, 4-polybutadiene rubber, was manufactured by Indian Petrochemical Corporation limited (IPCL), Baroda India. Other chemicals [such as a stearic acid, zinc oxide, *N*- (1,3-dimethyl butyl)-*N*-phenyl-*p*-phenylene diamine (antioxidant), tetramethyl thiuram disulphide (TMTD), zinc diethyl dithiocarbamate (ZDC), and sulphur] were manufactured by Bayer India Ltd.

Physical parameters of Polybutadiene, a titanate coupling agent, and constituents of clay are reported in Tables I, II, and III, respectively.

Particle size analysis

Surface area is a major parameter in connection with filler–matrix interaction for reinforcing purposes. The

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TABLE I
Properties of Polybutadiene Rubber

Trade name	Cisamer 1220
Manufacturer	Indian Petrochemicals Corporation Ltd.
Appearance	Light Amber/Bale.
Polymerization system	Solution
Microstructure	98% *cis*
Specific Gravity	0.91
Mooney viscosity	43 ML_{1+4} 100°C
Ash Content	0.1%

TABLE III
Constituents of China Clay

Compounds	Percentage
SiO_2	46.29
Al_2O_3	38.38
Fe_2O_3	0.30
TiO_2	0.02
CaO	0.161
MgO	0.59
Na_2O	0.15
K_2O	0.15
Ignition loss at, 100°C	13.59

finer the particle size, the higher the surface area and the higher the reinforcement. The details regarding particle size distribution of the clay used in the study are given in Figure 1. The figure clearly indicates that about 60% particles had a diameter of 2 μm or less. Although 90% of the filler had a particle diameter of 6 μm, the analysis was done on a Shimadzu SALD-2001 instrument by Shimadzu (Asia Pacific) Pvt. Ltd., Singapore.

Treatment on clay by titanate coupling agent

As per the recommendations of the manufacturer of the coupling agent, 1.0% solution of the coupling agent was prepared in isopropyl alcohol.[1,6] It was applied to 100 g of clay.

The solution was stirred for 30 min with filler to ensure uniform distribution.

The treated filler (clay) was then dried at 100°C in an oven for about 5 h to allow complete evaporation of the alcohol.

Preparation of composites

The compounding of the rubber was carried out on laboratory-scale two-roll mill. The rubber was first masticated for 5 min. Additives were added sequentially, as given in the Table IV. After the addition of all of the additives, the compounding was continued for 30 min for homogeneous mixing. This compounded matter was then vulcanized using a sulfur system by a press-curing method (compression molding machine) at 150°C for 30 min in a chrome-plated mold having cavity dimensions of 15 × 15 × 0.3 cm. The curing characteristics were determined using a multichannel DTA. The curing time was determined by subjecting compounds to DTA at 150°C, for various intervals and observing the thermograms.[4–10]

TABLE II
Physical Characterization of Titanate Coupling Agents (LICA 01)

Chemical Name	Neopentyl (diallyl) oxy, trineodecanonyl titanate
Typical purity	99%
Physical form	Liquid
Color	Brownish orange
Specific gravity	1.02
Flash point	160
Boiling point	320
Viscosity	850 c P
pH	5.1
Solubility	Isopropyl alcohol, xylene, Toluene, DOP, Mineral oil, MEK

Scanning electron microscopy (SEM)

SEM was carried out by a Leica Cambridge (Stereoscan 440) scanning electron microscope (Cambridge, UK). Polymer specimens were coated with gold (50 μm thick) in an automatic sputter coater (Polaron Equipment Ltd., Scanning electron micro-

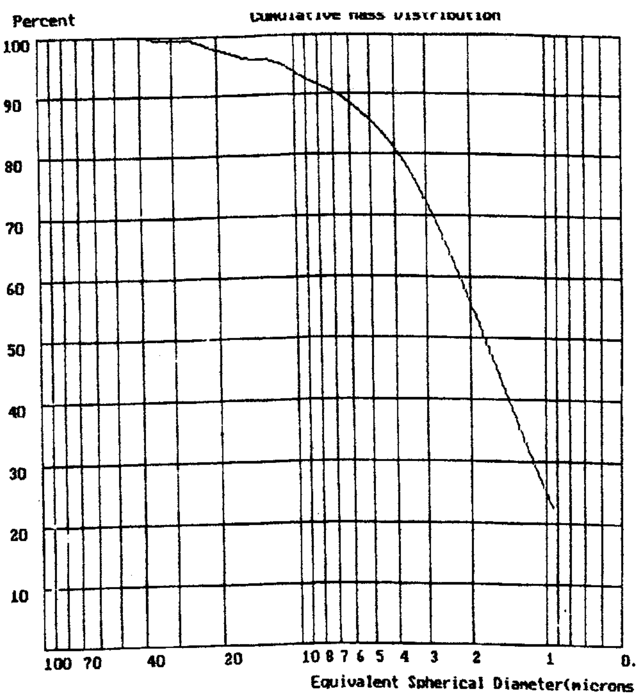


Figure 1 Graph of particle size distribution of clay.

TABLE IV
Compounding Recipe

Component	Proportion
PBR	100
Stearic acid	2.0
Zinc oxide	3.0
Antioxidant (*N*-(1,3-dimethyl butyl)-*N*-phenyl-*p*-phenylene diamine)	1.0
Accelerator (1) (Tetramethyl thiuram disulphide (TMTD)	0.5
Accelerator (II) [Zinc diethyl dithiocarbamate (ZDC)]	0.5
Sulphur	1.5
Filler (treated/untreated)	Variable
Curing time	30 min
Curing temp.	150°C

scope coating unit E 5000,UK). Acceleration potential was 20 kV. Photographs of representative areas of the sample were taken at 1000× magnifications.

Measurement of mechanical properties

Mechanical properties such as tensile strength and modulus at 100 and 400%, were determined by subjecting dumbbell-shaped specimens (in confirmation with ASTM D-412) to a universal testing machine (R&D Equipment, Mumbai, India). The sheets from which specimens were cut had been conditioned for 24 h prior to subjecting them to a universal testing machine (100-kg load cell), at a crosshead speed of 50 cm/min. Hardness was measured on a Durometer (Blue-Steel, India) on shore-A scale.

RESULTS AND DISCUSSION

Treated clay composites showed improvement in mechanical properties, and the mechanism of adhesion due to the coupling agent is proposed for clay as a filler.

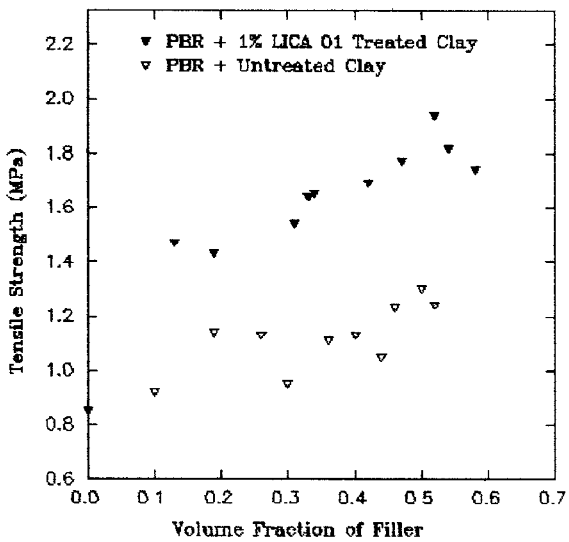


Figure 2 Tensile strength as a function of the volume fraction of treated and untreated clay–PBR composites.

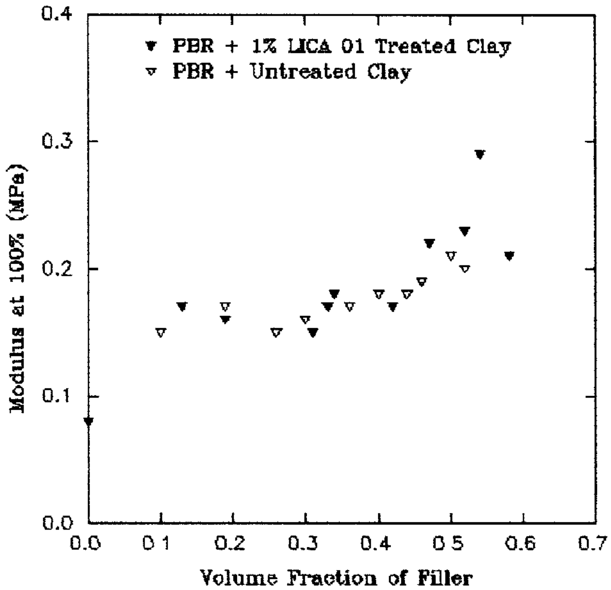


Figure 3 Modulus at 100% as a function of volume fraction of treated and untreaded clay–PBR composites.

Tensile strength

The dependence of the tensile strength on the volume fraction of clay is represented in Figure 2. It is seen that on increasing the volume fraction of (both treated and untreated) clay, the tensile strength increases up to a certain value and then it declines. The peak values of the tensile strength of the composites correspond to 1.82 and 1.30 MPa for treated and untreated clay composites, respectively. It is noteworthy that the tensile

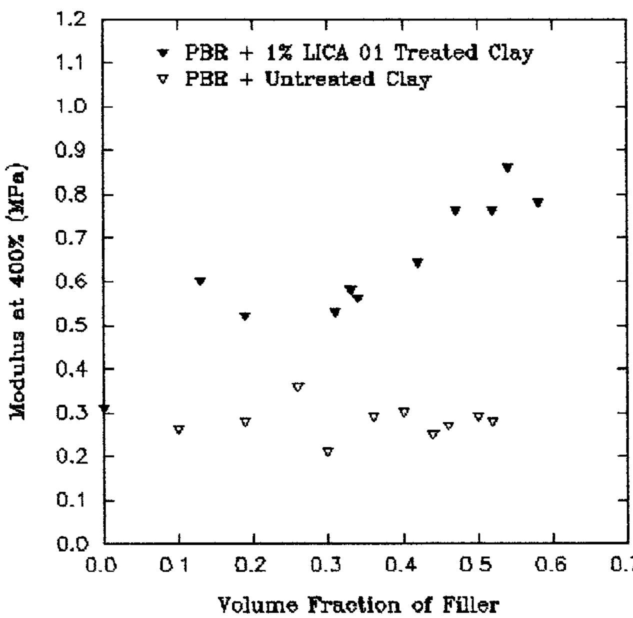


Figure 4 Modulus at 400% as a function of volume fraction of treated and untreaded clay–PBR composites.

strength of composites filled with treated clay (0.50 volume fraction) is 52% higher than that of untreated clay composites.

Modulus at 100% and 400% elongations

The dependence of modulus at 100 and 400% elongation with volume fraction of treated and untreated clay–PBR composites is depicted in Figure 3 and Figure.4 for 100 and 400% modulus, respectively. In both cases moduli increased initially, attained the maximum value for a particular value of concentration of fillers, and decreased. The peak values of moduli of both the composites lie at 0.51 volume fraction of clay (treated and untreated). The modulus of treated clay is about 2.97 times higher than that of untreated clay. The rate of increment in the property with increasing volume fraction of the filler was similar initially in both cases; however, after the volume fraction of 0.30, the rate of increment for composites filled with treated clay become substantially high.

Young's modulus

Young's modulus as a function of volume fraction of filler for treated and untreated clay-filled PBR composites is represented in Figure 5.

The peak value for treated clay composites is obtained to be 0.98 MPa at 0.54 volume fraction and that for untreated is 0.82 MPa at 0.48 volume fraction, that

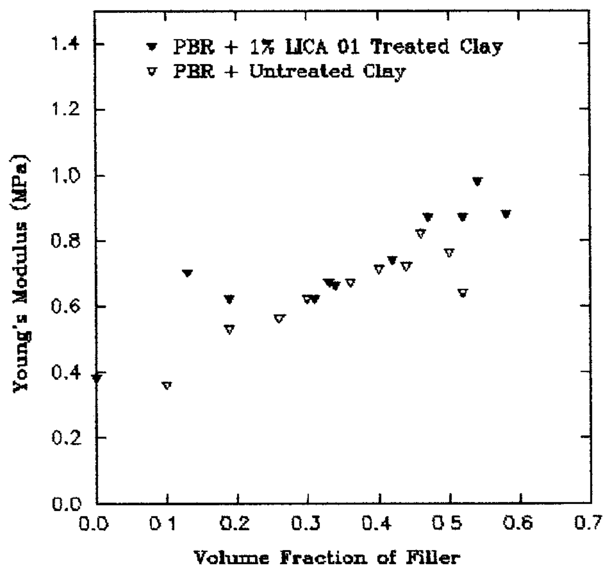
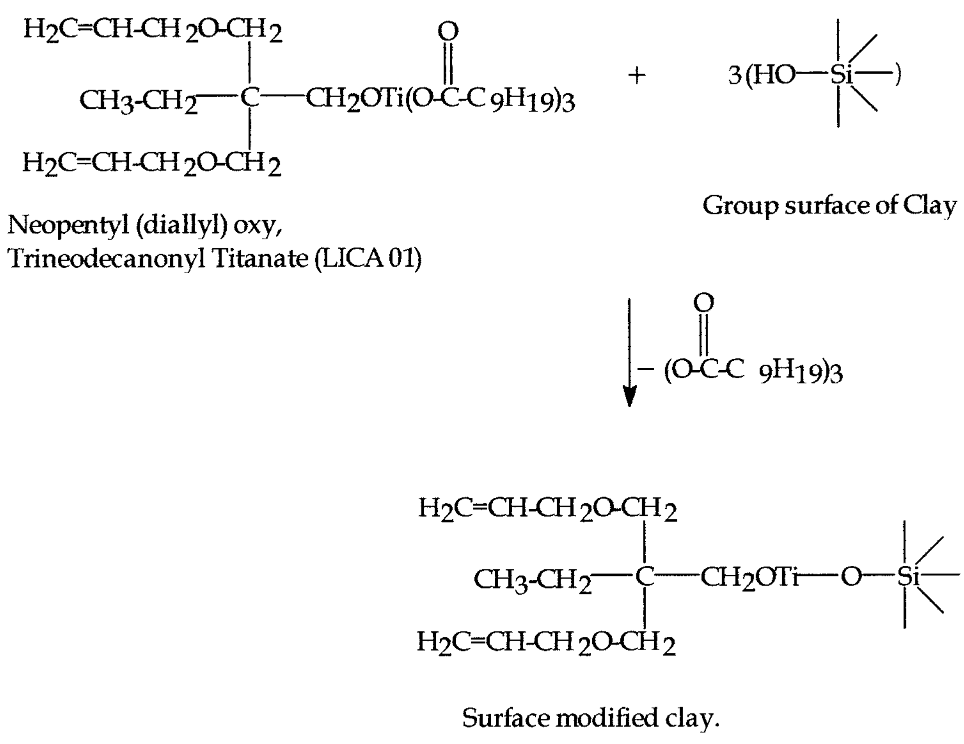


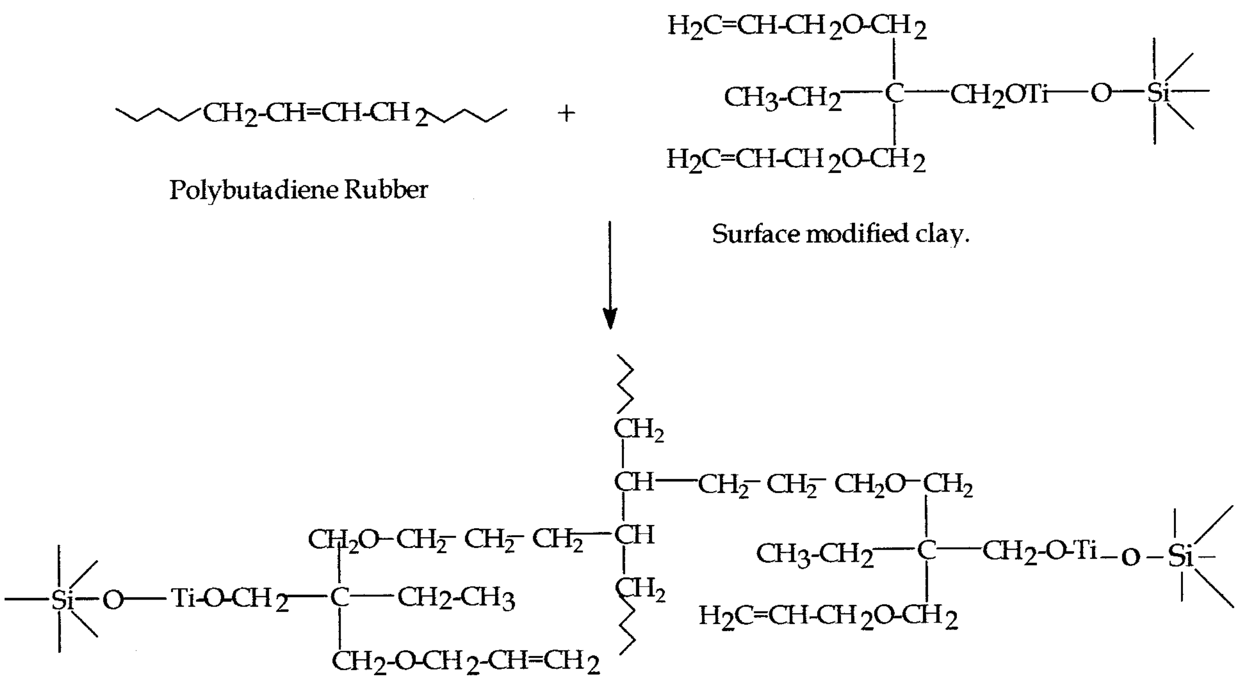
Figure 5 Young's modulus as a function of volume fraction of treated and untreaded clay–PBR composites.

is, the Young's modulus of treated clay is a bout 1.20 times higher than that of untreated clay composites.

Mechanism of PBR–filler interaction

The proposed mechanism, of PBR–filler (clay) interaction due to the incorporation of LICA 01 has the following two steps: Step I—reaction between titanate coupling agent and a clay (surface); Step II—reaction between surface-modified clay and unsaturation in PBR.





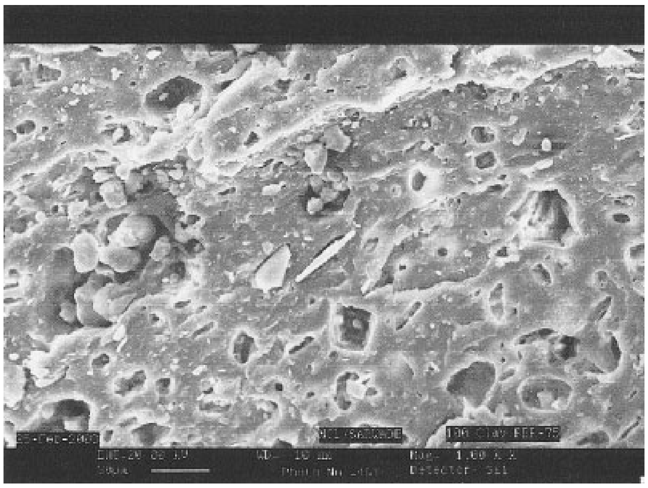


Figure 6 SEM of untreated clay–PBR composites with volume fraction (0.52).

Thus, a single molecule of LICA 01 can couple free radically with one olefinic unit of the elastomer molecule and also two —OH groups of filler, resulting in an increased elastomer–filler interaction.

SEM of composites

SEM of clay-filled vulcanizates are shown in Figures 6 and 7 for composites containing untreated and treated clay, respectively. Careful observation of Figure 6, that is, untreated composites, reveals that the fractured surface has vacuoles indicates that the matrix–filler adhesion was inadequate. The reason lies in the heterogeneity of the surfaces of clay and the matrix, that is, polybutadiene. On the other hand, Figure 7 indicates significantly less vacuoles on the fractured surface of composites containing treated clay. The size of the vacuoles is much smaller in the photograph (although the magnification is same for both scanning, i.e., 1000× original magnification) established the the agglomeration of the filler in the fractured surface containing treated clay was much less. Thus, the treated composites exhibited a uniform distribution, which helped enhancement in polymer–filler adhesion.

Hardness

Figure 8 shows the dependence of hardness on concentration of treated and untreated filler in PBR. It is

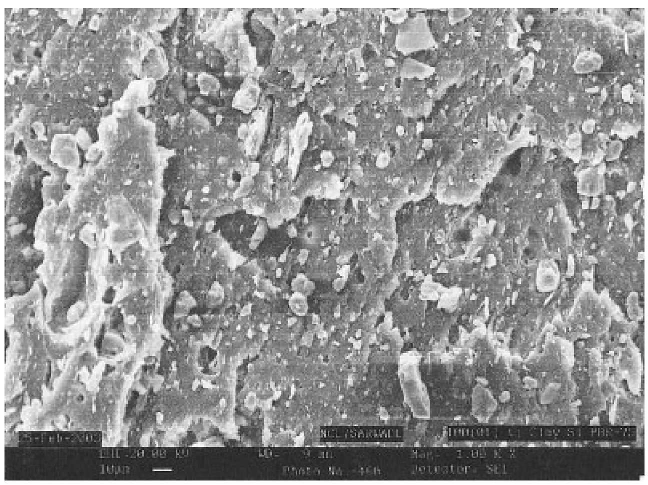


Figure 7 SEM of LICA 01 treated clay–PBR composites with volume fraction (0.58).

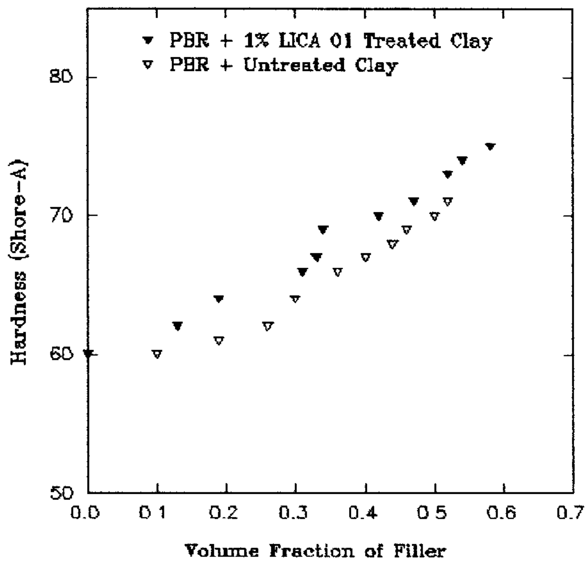


Figure 8 Hardness as a function of volume fraction of treated and untreaded clay–PBR composites.

seen that hardness of both the treated and untreated clay–PBR composite increased linearly upon increasing the concentrations of fillers, with a constant rate of increment for composites containing treated and untreated filler (separately), as evidenced by constant and identical slopes of the lines (Fig. 8).

CONCLUSIONS

The treatment of clay with a coupling agent (Neopentyl (diallyl) oxy, trineodecanonyl titanate) has effected magnitudes of modulus at 400% elongation, tensile strength, and Young's modulus. The filler treatment proved to be beneficial by enhancing polymer–filler adhesion, as evidenced by SEM study. Considering the cost of the filler and the improvement in properties, the treatment is advisable.

One of the authors (N.A.N.Alkadasi) would like to thank Prof. Taufick Sufian, Vice Graduate Studies & Scientific Research, Prof. Mohammed A. Alkadasi, Division of Geology, Sana'a University, and Mr. Mohammed A. Alqawai, for their help in this project. I also thank Mr. Salvatore J. Mote Kenm React Petrochemicals, Inc., USA, for providing chemicals free of cost for my research work.

References

1. Alkadasi, N. A. N.; Hundiwale, D. G.; Kapadi, U. R. J Appl Polym Sci 2004, 91, 1322.
2. Alkadasi, N. A. N.; Sarwade, B. D.; Hundiwale, D. G.; Kapadi, U. R. J Sci Indust Res 2004, 63, 287.
3. Alkadasi, N. A. N.; Sarwade, B. D.; Hundiwale, D.G.; Kapadi, U. R. J Polym Plast Technol Eng, to appear.
4. Alkadasi, N. A. N.; Sarwade, B. D.; Hundiwale, D. G.; Kapadi, U. R. J Appl Polym Sci 2004, 93, 1293.
5. Monte, S. J. "KEN–REACT" Reference Manual—Titanate, Zirconate and Aluminate Coupling Agents; American Chemical Society: Washington, DC, 1995.
6. Pal, P. K.; De, S. D. Rubber Chem Technol 1983, 56, 736. P. Chakravrty, P. S. N.; De, S. K. J Appl Polym Sci 1983, 28, 659.
7. Mandal, S. K.; Kumar Basu, D. Rubber Chem Technol 1994, 67, 672.
8. Bajaj, P.; Jha, R. Polym Eng Sci 1989, 29, 557.
9. Disawal, S. K.; Hundiwale, D. G.; Kapadi, U. R. Adv Pharmacol Toxicol 2003, 1, 45.
10. Pal, P. K.; De, S. D. Rubber Chem Technol 1983, 55, 1370.