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Research paper

Phosphorylated Cashew Nut Shell Liquid prepolymer modified kaolin as a reinforcing filler for natural rubber

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ABSTRACT

At least a partial substitution of carbon black/precipitated silica being used in the rubber industry with low cost *reinforcing fillers* based on china clay (kaolin) — a *non-replenishable natural resource* could lead to technical and economic viability. Low cost industrial byproducts/renewable natural resources such as Cashew Nut Shell Liquid (CNSL) or Rubber Seed Oil (RSO) or their derivatives may be used as *organo-modifiers* for kaolin to impart excellent compatibility with non-polar rubbers along with desired physico-mechanical properties for various applications. Results of the present study as obtained from XRD, TEM, SEM, TGA, CLD (chemical crosslink density) and tensile properties show that low dosages of kaolin modified with a solution of Phosphorylated Cashew Nut Shell Liquid prepolymer (PCNSL) in toluene could act as potential *nano-reinforcing fillers* for natural rubber (NR), as evidenced by improvements in filler dispersion, thermal stability and tensile properties of the vulcanizates.

1. Introduction

One of the major driving forces behind the recent upsurge of R&D work in the area of clay–rubber nanocomposites is their significant application potential in the rubber industry, particularly because of their unique combination of excellent physico-mechanical properties and improved processability. The significance of research in this area is quite evident from the plethora of related publications and patents coming up every year (Sengupta et al., 2007; Bergaya et al., 2011a,2011b; Das et al., 2011; Tan et al., 2012). Exceptional improvements in properties have been reported for various organo-montmorillonite/natural rubber (NR) nanocomposites (Arroyo et al., 2003; Lopez-Manchado et al., 2003, 2004; Li et al., 2008; Carli et al., 2011; Khanlari and Kokabi, 2011). The results of a study by Arroyo et al. (2003) show that the mechanical properties of NR with 10 parts per hundred rubber (phr) of octadecylamine modified montmorillonite are comparable to the compound with 40 phr of carbon black. Li et al. (2008) have reported that at concentrations below 5 phr exfoliated layers of organo-montmorillonite improve the tensile properties, tear strength, solvent resistance, thermal stability and gas barrier property of NR vulcanizates. Lopez-Manchado et al. (2003, 2004) have studied NR systems reinforced with octadecyl amine modified bentonite with and without a silane coupling agent, namely bis(triethoxysilylpropyl)tetrasulfan (TESPT). Khanlari and Kokabi (2011) have shown that an addition of 3 mass% of organomodified montmorillonite to NR improved its thermal stability, aging properties and flame resistance. Results of a recent study on NR nanocomposites filled with Cloisite 15A, a commercial organoclay indicate that 50 phr of silica can be replaced by 4 phr of the organoclay without affecting the properties of the final material even after aging (Carli et al., 2011).

A study by Gopi et al. (2011) indicates that 15 phr of carbon black in conventional styrene butadiene rubber (SBR)-carbon black based tire tread compounds can be replaced by 6 phr of organoclay (Cloisite 15A) as substantiated by improved performance characteristics. The dynamic properties of NR vulcanizates containing carbon black/clay hybrid filler were studied by Liu et al. (2010). It was shown that inclusion of organomodified clay could induce a stronger and more developed filler network, leading to lower tan value at broad temperature range as well as strain amplitude. Shan et al. (2011) have studied a series of organoclay/NR/SBR nanocomposites with organoclay content ranging from 1 to 7 phr and suggested their application prospects in the tire industry, based on improvements in physico-mechanical properties.

The reports as mentioned above on clay/rubber nanocomposites are mostly based on organomodified montmorillonites. There exist very few reports on the use of kaolin as a reinforcing filler for rubbers (González et al., 1989; Wu and Tian, 2013; Liu et al., 2008; Malicka-Soczka et al., 2010; Zhang et al., 2010; Preetha Nair and Joseph, 2012). A study by Wu and Tian (2013) on kaolin filled rubber compositions using NR, SBR, polybutadiene rubber (BR), nitrile rubber (NBR), ethylene propylene diene monomer rubber (EPDM), chloroprene rubber (CR) and methyl vinyl silicone rubber (MVQ) reports good mechanical properties and resistance to heat aging. A similar study had been made by Liu et al. (2008) in NR, SBR, BR and EPDM. This comparative study on the reinforcing effects of kaolin and precipitated silica in natural and synthetic rubbers showed that good interfacial interactions between the kaolin and the rubber chains imparted excellent

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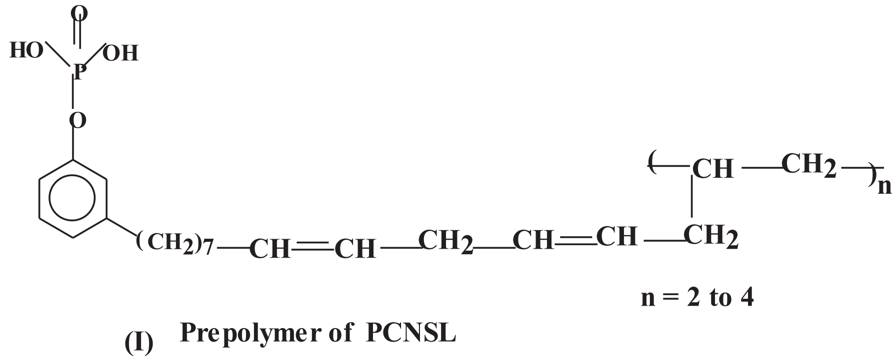

Fig. 1. Chemical structure of prepolymer of PCNSL.

processability, mechanical properties and thermal stability to the rubber composites. However, the dosage of filler ranged from 20 to 60 phr in both the above studies. Subsequently, Malicka-Soczka et al. (2010) have studied the effect of kaolin modified with various silane agents in SBR compositions. The vulcanizates containing 6.5 phr of the modified kaolins showed significant improvements in tensile strength, modulus, tear strength and elasticity. Zhang et al. (2010) have reported that highly filled NR/silane modified kaolin composites exhibited outstanding mechanical properties, excellent gas barrier properties and much higher thermal stability compared to pure NR. A recent study by Preetha Nair and Joseph (2012) on the reinforcement effect of unmodified and vinyl silane modified kaolins in NBR shows improved mechanical properties and thermal stability of the vulcanizates at concentrations of the fillers up to 15 phr.

A variety of long chain organomodifiers such as quaternary ammonium salts and polyethylene glycol have been used for the preparation of organoclays, most of which are based on petrochemical sources that are depleting rapidly (Betega de Paiva et al., 2008; He et al., 2010; Zampori et al., 2010; Mallakpour and Dinari, 2011; Rooj et al., 2012). Reports on the use of low cost renewable natural resource based organo-modifiers for clays are rather scanty. Rugmini and Menon (2008) have reported the synthesis and characterization of organomodified kaolins using sodium salt of Rubber Seed Oil (SRSO) and their suitability as reinforcing fillers in NR at very low dosages. In a related study, Yahaya et al. (2009) have reported that at concentrations less than 10 phr, kaolin modified with SRSO improves the tensile and tear properties, chemical crosslink density index and resistance to solvent swelling of NR vulcanizates. Also, Yahaya et al. (2012) have observed considerable improvements in tensile properties and tear strength of NR vulcanizates containing 5 phr of kaolin modified with sodium salt of tea seed oil.

The suitability of Phosphorylated Cashew Nut Shell Liquid prepolymer (PCNSL) as a low cost multifunctional additive for natural rubber compounding has been reported earlier (Menon et al., 2001). In the quest for developing low cost reinforcing fillers for the rubber industry, particularly based on renewable natural resources, PCNSL was used as an organo-modifier for kaolin and precipitated silica and the effect of the modified nanofillers in NR was studied, some results of which are presented in this paper.

Table 1
Composition of the mixes.

Mix code	NR1	NR5	NR10	PBT	PST	SRSO
Composition (phr)						
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Kaolin	–	8	–	–	–	–
Silica	–	–	8	–	–	–
PCNSL modified kaolin	–	–	–	8	–	–
PCNSL modified silica	–	–	–	–	8	–
SRSO modified kaolin	–	–	–	–	–	8
PCNSL	2	2	2	–	–	–
MBT	2	2	2	2	2	2
Sulfur	2	2	2	2	2	2

2. Experimental

2.1. Materials

Commercial grades of Rubber Seed Oil (RSO) and Cashew Nut Shell Liquid (CNSL) were obtained from M/s. Murugesan & Sons, Coimbatore and M/s. Adarsh Cashews, Sanoor, India, respectively. Natural rubber (grade, Ribbed Smoked Sheets, RSS-5) was purchased from the local market. Commercial grades of rubber chemicals such as zinc oxide (White seal; ACPL-P999), sulfur ('Rub-O-Sulf'), mercaptobenzothiazole (MBT, 'PILCURE') and stearic acid ('Lubstric'; Godrej Industries Ltd.) were obtained from M/s. Ceyenar Chemicals, Kottayam, India. Kaolin (grade-BCK) was supplied by M/s. English India Clays, Ltd., Thiruvananthapuram. Precipitated silica ('Ultrasil VN3' from 'INSILCO Ltd.', Gajraula, UP, India; specific surface area 180 m^2/g; density 0.277 g/cm^3) was obtained from M/s. Ceyenar Chemicals, Kottayam, India.

2.2. Methods

SRSO and SRSO modified kaolin were prepared as per the method reported earlier (Rugmini and Menon, 2008). SRSO was prepared by reacting 28 g of RSO with 100 mL of 20% NaOH in an ice bath with constant stirring for 12 h. The mixture was kept for one day. The pH of the final solution was maintained at 8–9. SRSO thus obtained was washed

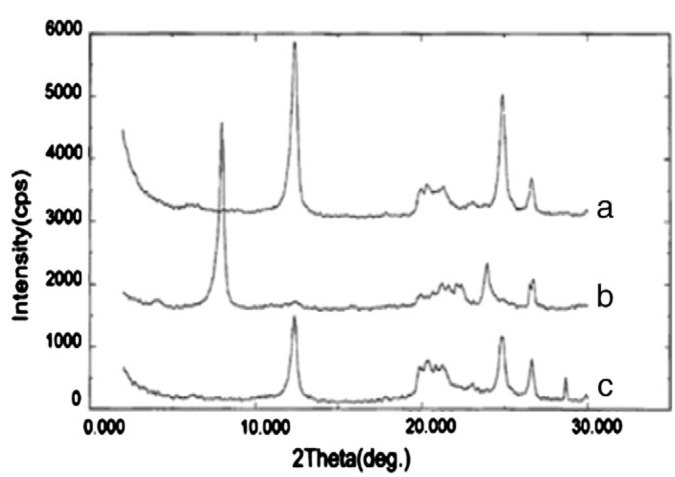

Fig. 2. XRD patterns — (a): unmodified kaolin, (b): SRSO modified kaolin and (c): PCNSL modified kaolin.