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Effect of Amphiphilic Polymer Modified Graphene Surfactant on the Thermal, Viscoelastic and Tensile Properties of Nitrile Latex Nanocomposites

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ABSTRACT

Carboxylated butadiene-nitrile latex (CBNL) elastomers possess several unique characteristics including excellent abrasion resistance and oil resistance. They are used in a wide variety of commercial and Defense applications. In this work, the effect of a newly developed graphene surfactant (GOS) on the thermal, mechanical and viscoelastic properties of vulcanized latex nanocomposites was studied. The latex was synthesized by emulsion polymerization and the vulcanized film without any filler had a tensile strength (TS) of 2.40 MPa and strain at break of 107%. Graphite filler (8 wt%) in combination with 2.6 wt% of GOS, added to the latex, increased the TS to 5.2 MPa and to 7.5 MPa with 10 wt% of the GOS, while the elongation at break was reduced to 48% and 30% for the latex nanocomposites, respectively. The vulcanized film without any graphite, but with 2.8 wt% of GOS had a TS of 7.8 MPa and a marginally increased elongation at break (88%), as compared to the graphite filled composites. The nanocomposites with graphite and GOS also showed higher damping characteristics, as indicated by the width of the tan δ peak, spanning over a broad temperature range of 100 °C for the sample with 2.6 wt% GOS and 8 wt% graphite. In summary, the work reports the development of potentially valuable damping materials from carboxylated nitrile latex using an amphiphilic polymer modified graphene surfactant in combination with graphite.

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Amphiphilic polymer modified graphene; carboxylated nitrile latex; nanocomposites; thermomechanical properties

Introduction

Layered fillers, like clay and graphene, are important functional fillers to improve the technical properties of elastomeric polymers.[1–8] The final composite properties are also influenced by the blending technique used for its preparation. Though mechanical blending is a direct method to prepare a composite, it is often accompanied by aggregation of the nanoparticles.[5,6] In solution blending, the aggregation is not significant but residual solvent removal is difficult, which affects the elastomer composite properties. The latex blending methods are one of the simplest and most efficient methods to

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prepare polymer nanocomposites, where nanoparticle aggregation is prevented and the optimum composite properties are realized at low filler loadings.[7–9]

Carboxylated nitrile elastomers (XNBR) are terpolymers of acrylonitrile and butadiene with small amounts of an acid termonomer. The elastomer properties are improved by the incorporation of carboxylic acid groups in the NBR backbone, resulting in products having increased strength, modulus, and abrasion resistance. In particular, the presence of chemically active functional groups (e.g., –COOH) in XNBR increases the inter- and intra-molecular interactions and its interaction with functionalized fillers, thereby improving the polymer's properties. Graphene has been one of the fascinating 2D nanomaterials discovered during the last decade; it is composed of sp2 hybridized carbon atoms arranged in a hexagonal lattice and can be conveniently prepared from graphite. It is the thinnest material compared to all other allotropes of carbon (graphite, CNTs, CF, fullerenes, etc.). The high specific surface area and aspect ratio, Young's modulus, fracture strength, and thermal conductivity of graphene makes it an attractive material for composite applications.[10–14] Unlike conventional fillers, the mechanical properties of a composite are improved with low concentrations of graphene.[1,4] We know of only a few studies in the literature that have addressed the effect of graphene and graphene oxide (GO) on the properties of XNBR.[12,14–17] Dry nitrile rubber composites with high concentration (25 phr) of graphene nano platelets have been reported by Yuan et al.[16] showing improved damping properties. Yang et al.[18] have reported XNBR/expanded graphite (EG) nanocomposites prepared via latex blending had improved mechanical gas-barrier properties and electrical conductivity. Wang et al.[17] studied GO–XNBR composites through latex blending, achieving composites with greatly improved mechanical properties and thermal conductivity. Similarly, Kang et al.[12] have studied the effect of adding GO to XNBR matrices using a latex co-coagulation method and observed enhanced interaction between the filler and the matrix.

Unmodified graphite and graphene do not possess any polar groups, which makes it difficult for any organic molecules or monomers to be loaded on their surfaces, to facilitate their dispersion in a polymer like XNBR. Thus, functionalized graphene has been widely studied for the synthesis of polymer nanocomposites e.g.[19–24] The functionalization has been achieved through covalent and non-covalent approaches.[23] For example, graphene functionalized using humic acid (FG) was incorporated into XNBR rubber to prepare XNBR/FG composites.[22] Compared to pure XNBR, incorporation of 3 phr (parts per hundred rubber) of FG improved the tensile strength of the composite by twofold. The elastic modulus and thermal conductivity of an elastomeric block copolymer blended with polyethylene (PE) modified graphene brush polymer showed improvement.[21] Recently, we reported the synthesis of comb-like polymer/graphene nanocomposites in which the monomer was pentadecylphenylmethacrylate (PDPMA), the monomer used in the present study, and their excellent adhesion properties.[25] The amphiphilic modification of the GO by a comb-like polymer yielded a novel graphene surfactant which acted as both a reinforcing agent and surfactant in polystyrene.[26] In the work described here we studied the effect of adding this novel surfactant to nitrile latex graphene nanocomposites. The effects on the tensile, thermal decomposition, surface properties and the morphology were studied and are described.

2. Experimental

2.1. Materials

The monomers, 1,3-butadiene, acrylonitrile and methacrylic acid were procured from Sigma-Aldrich Chemicals Pvt. Ltd.(India). The surfactant, sodium dodecyl sulfate (SDS) and chain transfer agent, n-dodecyl mercaptan (DDM), were supplied by Alfa-Aesar, Division, Johnson Mathey Chemicals India Pvt. Ltd. (India). Methacrylic acid was purchased from Fluka Chemie GmbH (Germany). Sodium hydroxide pellets (NaOH), sodium persulphate ($Na_2S_2O_8$) and sodium metabisulphite ($Na_2S_2O_5$) were obtained from S.D Fine-Chemicals Ltd. (India). The synthesis of the amphiphilic polymer modified graphene surfactant (GOS) was carried out by the procedure reported by us recently.[25,26] In brief, the procedure for surfactant preparation involved performing atom transfer radical polymerization (ATRP) of pentadecylphenyl methacrylate (PDPMA) monomer using a graphene based initiator for the polymerization synthesized by us starting from graphite.[25] The PDPMA grafted product was subsequently sulfonated and made alkaline to obtain the GOS. The synthesis and aggregation behavior of this surfactant has been studied and reported in detail by our group.[26] The antioxidant, Agidol-2, was kindly supplied by J.S.C Sterlitamak Petrochemical Plant, Russia. Zinc oxide, sulfur and accelerator (TMTD-tetramethyl thiuram disulfide) were procured from Asiatic Rubber Industries, India. Graphite black powder with carbon content 99.9% and particle size of about 300 nm was purchased from the Rangoon Mill Store, India.

2.2. Emulsion polymerization

XNBR was prepared from acrylonitrile, butadiene and acrylic acid via emulsion polymerization in a 1 L pressure reactor as per the recipe given in Table 1, following a literature procedure.[27] In a typical process the reactor was charged with water, emulsifier and a portion of the monomers. A buffer, such as sodium hydroxide, was dissolved in the aqueous phase to moderate the pH against any large changes. The reactor was clamped after addition of all the ingredients except butadiene and then purged with N_2 gas for 30 min. The butadiene monomer was then added and pressurized the reactor to 15 bar using N_2 gas; the contents were heated to 50 °C and the agitator speed was maintained at 200 rpm. The polymerization, initiated using a persulfate/metabisulphite

Table 1. Composition used for the polymerization and characteristics of the nitrile latex (CNBL) sample studied.

Ingredient	Weight (g)
Butadiene	54
Acrylonitrile	36
Methacrylic acid	3
Surfactant (anionic)	5
Chain transfer agent	1
$Na_2S_2O_8$ (sodium persulphate)	3
$Na_2S_2O_5$ (sodium metabisulphite)	2.5
NaOH	1.5
Water	220 g
Solids	28%
Particle size	214 nm
Polydispersity	0.2

initiator system, was continued for 24 hours at 50 °C with stirring. Then the heating was cut off to cool the contents to room temperature and the reactor pressure was released. The latex, (termed CNBL), collected from the drain valve, was filtered and characterized for solid content and particle size, as given in Table 1.

2.3. Nanocomposite preparation

The suspensions for the nanocomposite films were prepared in a beaker using the following recipe: CNB Latex −10 g; ZnO dispersion (0.5 g of 50% dispersion; 50% dispersion means 50 g ZnO was dispersed in 100 ml water, as supplied by the Asiatic Rubber Industries (see materials section); sulfur dispersion – 0.2 g of 50% dispersion; tetramethylthiuram disulfide 0.1 g of 50% dispersion; graphite powder (8 wt%) (all dispersions were prepared in water). It was then mixed well by sonication for 2 minutes and then with a glass rod. The compounded latex was cast in a Petri dish, dried at RT for 1 day and then cured at 150 °C for 1 hour in a hot air oven to form a film 0.2 mm thick. Test specimens (size 10 cm × 1 cm × 0.02 cm) were cut from the cured films for tensile, contact angle and DMA measurements.

2.4. Characterization

Particle sizes of the CNBL were measured by dynamic light scattering with a Nanosizer from Malvern Panalytical Ltd, UK. The solid content and conversion were determined using gravimetric methods.

Tensile tests were carried out using a UTM (Dak System Inc, India, Series 7200) at room temperature (RT). The strain rate was 50 mm/min and the gauge length was 50 mm with a cross-section area of 0.6–0.7 sq.mm. At least five specimens from each sample were tested and the average values are listed. From the recorded stress/strain curves, the tensile strength (TS) and elongation at break were determined.

Thermal stability studies were performed using a TGA from TA Instruments, Inc. (USA) model: Q500. The tests were run using 3–5 mg samples at 10 °C/min, from RT to 800 °C under N_2 atmosphere.

The viscoelastic properties, including storage modulus (E'), loss modulus (E") and dynamic loss factor (tan δ), were measured as a function of temperature using a DMA instrument (Model: Q800) also from TA Instruments, Inc. (USA). The measurements were performed at a frequency of 1 Hz and heating rate of 10 °C/min in the temperature range from −50 °C to 250 °C.

Morphology characterization was performed using a JEOL 7610FS-3000 N machine from Japan Electron Optics Laboratory, Japan. The film sample was mounted on steel studs with a double sided tape, the free surface sputtered with gold and then analyzed. The water contact angle was measured on a goniometer from Kruess Instruments GmbH, Germany.

3. Results and discussion

The present work reports the effect of a newly developed amphiphilic polymer modified graphene surfactant (GOS) on the technical properties of nitrile latex nanocomposites. The GOS structure is shown schematically in Figure 1. The 15 carbon alkyl chain

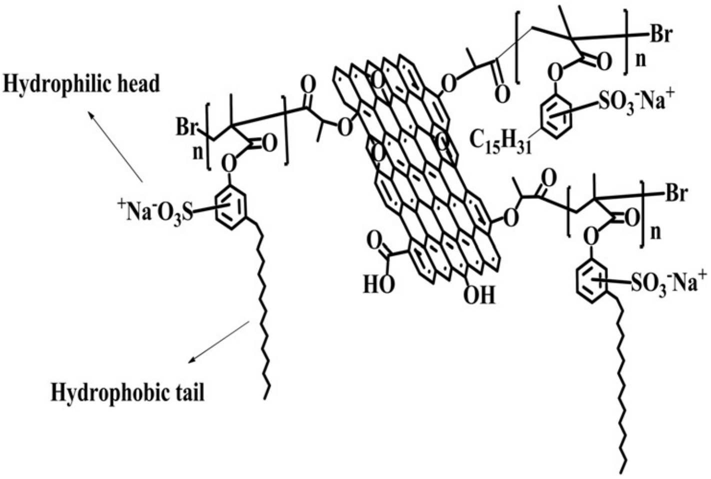

Figure 1. Schematic of the amphiphilic polymer modified graphene surfactant (GOS).

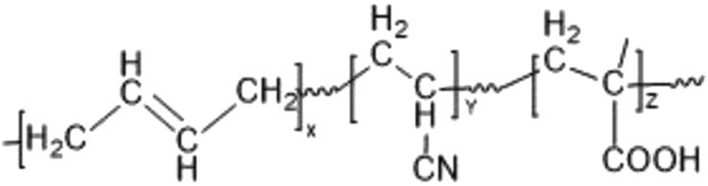

Figure 2. Repeat unit structure of carboxylated butadiene nitrile latex (CBNL).

present in the monomer is shown as a tail and it imparts a plasticizing and hydrophobic characteristic to the polymer. Its synthesis, structure characterization and micellization properties were reported by us previously.[26] The nitrile latex used in the present work was synthesized using a semi-batch emulsion polymerization process. Butadiene (x), acrylonitrile (y) and a small amount of an acid co-monomer methacrylic acid (z) in the ratio 58:39:3, were used in the emulsion polymerization. A schematic of the terpolymer structure is shown in Figure 2, with x, y and z indicated.

The composites were prepared, adding the same concentration of graphite (8 wt%) and other compounding ingredients to the nitrile latex in a 100 ml beaker as per the recipe given in the experimental (Section 2.3, nanocomposite preparation). The contents were mixed with a glass rod for 5 minutes and then sonicated for 2 minutes. The compounded latex was cast into a Teflon Petri dish, dried at RT for 24 hours and vulcanized by heating to 150 °C for 60 min. The vulcanized nanocomposite films were characterized for stress-strain behavior, thermal stability, viscoelasticity, morphology and surface properties. The properties of the vulcanized CNBL films with graphite filler, without any filler but only GOS and using graphite in the presence of the graphene surfactant GOS were studied.

3.1. Effect of the amphiphilic polymer modified graphene surfactant (GOS) on the composites stress-strain behavior

The measurement of the stress-strain behavior under a tensile force is useful to study the influence of additives on a composite's properties. Various carbon nanomaterials,

Table 2. Effect of graphene surfactant (GOS) on the tensile properties of nitrile latex nanocomposite films.

Sample code	Tensile strength (MPa)	Elongation at break (%)	additives
CNBL-F1	2.40	96	curatives, no graphite
CNBL-F2	3.30	50	Curatives + 8% graphite
CNBL-F3	5.19	48	8% graphite + 2.6 wt% GOS
CNBL-F4	7.50	29	8% graphite +9.6 wt% GOS.
CNBL-F5	7.80	88	2.8 wt% GOS

Note: Curatives include ZnO, accelerator, sulfur and antioxidant.
GOS – graphene oxide surfactant.

like carbon nanotubes, graphite and graphene, have been widely studied as fillers in elastomeric nanocomposites. Realizing the full properties of nitrile latex nanocomposites would depend on the state of filler dispersion in the resulting nanocomposites. Recent studies have shown that for the same filler content, considerable improvement in mechanical properties can be achieved using CNT and graphene in comparison to the conventional carbon black fillers.[14,23] The effect is mainly attributed to the high aspect ratio of the nanofillers and the strong polymer-filler interactions.[14,23]

In this work, to facilitate improved filler dispersion, the effect of a newly synthesized amphiphilic polymer modified graphene surfactant (GOS) was studied. The nanocomposites were prepared with varying concentrations of the GOS. The effect on the tensile properties is summarized in Table 2, with the compositions and labels of the various studied films also listed. The vulcanized latex film without any filler (CNBL-F1) had a TS of 2.4 MPa, with 96% elongation at break.

The tensile strength increased to 3.3 MPa with all the curatives and graphite filler (8 wt%) but the elongation at break decreased to nearly half (CNBL-F2). The addition of 2.6 wt% GOS along with 8 wt% graphite (CNBL-F3) increased the TS to 5.2 MPa, i.e., more than twice the value of the cured film without graphite, but nearly the same elongation at break as for CNBL-F2. Further increase of the graphene surfactant concentration to 9.6wt% increased the TS to 7.5 MPa but the elongation at break decreased to 29% (CNBL-F4). The sample with 2.8 wt% GOS alone (CNBL-F5), without any graphite, exhibited the highest TS, 7.8 MPa, and had an elongation at break of 88%. Thus, the observed results confirmed the dual role of the GOS as a surfactant and reinforcing agent (the surfactant properties have been reported previously[26]). In this work, also, the uniformity of the dispersion (as observed from the appearance of the mixed nanocomposite dispersion (not shown here) was better in samples with added graphene surfactant. The CNBL-F2 film without any GOS was rough to the touch with finger after drying and curing, while the CNBL-F3 and CNBL-F4 films with GOS were soft and smooth to the touch. It is noted that, at small concentrations, (2.6wt%), the graphene surfactant not only facilitated dispersion of the graphite in the latex film but also improved the film formation and, thereby, the film properties, if the effects of GOS in the presence of graphite are considered. The observed enhancement in tensile properties is attributed to the increased interaction between the filler and the latex polymer. However, GOS alone (CNBL-F5) gave a much larger improvement in tensile strength and nearly equal elongation at break as for the CNBL-F1 film with no graphite, suggesting that adding GOS alone could yield the desired improvement in properties.

The following considerations might help to understand this effect. The graphene surfactant contains polar sulfonate groups, a 15-carbon alkyl chain in the meta position of

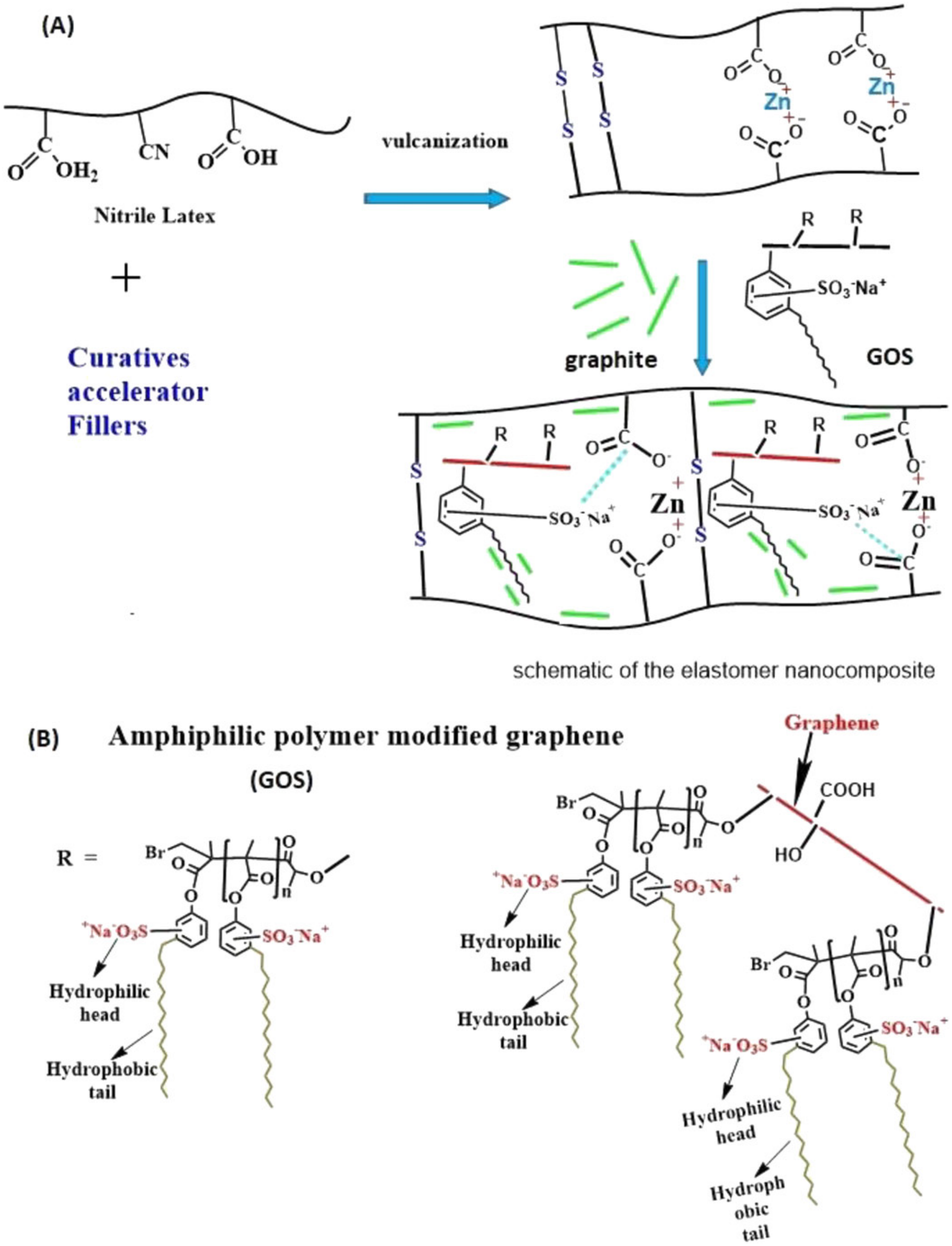

Figure 3. Schematic of the nanocomposite preparation using CBNL and the various additives, highlighting the possible interactions between the different additives.

the surfactant moieties and a relatively hydrophobic graphene domain (cf. Figure 1). On the other hand, the nitrile latex polymer contains polar carboxyl and nitrile groups along with hydrophobic butadiene as the major component. Effectively, this could facilitate interaction between the carbon filler and the polar groups on the nitrile elastomer.

The metal oxide (ZnO) in cure system could also participate in these interactions, forming a bridge type structure, as shown schematically in Figure 3. Generally, the incorporation of non-polar graphite filler in a latex polymer is difficult. The covalent modification of graphene oxide (GO) with amphiphilic polymers thus improved the surfactant properties of the graphene and permitted enhanced interactions.[22,26] While the increasing TS of F1- F4 could be explained by the increasing interaction between graphite filler, surfactant and the carboxylated nitrile polymer, the effect was different in the case of F5. Here, apart from the polar interaction between carboxyl and sulfonate groups, the reinforcing effect of the graphene appears to be operating. This could be because the polymer grafted monolayer graphene (GOS) has better reinforcing effect in the absence of graphite, as suggested by studies with other systems.[25,28] In the presence of graphite a higher concentration of GOS was needed for the increased strength, but we note the effect was less than that of GOS alone.

3.2. Dynamic mechanical properties

Dynamic mechanical analysis (DMA) constitutes a convenient tool for determination of important viscoelastic properties of polymer composites, including glass transition temperature, elastic and loss moduli and damping behavior.[28,29] In this work, DMA was used to study the effect of the GOS on the viscoelastic properties of the various nanocomposite systems. The analysis was done at a constant frequency of 1 Hz over the temperature range −50 °C to 250 °C. The variations in storage moduli of the neat nitrile latex film without any filler and the various nanocomposites are compared in Figure 4A. Among the different samples, the latex film without any graphite (F1) possessed an initially (at −50 °C) high storage modulus, which decreased rapidly with increasing temperature, the decrease starting at about −21 °C. The temperature was determined from point of intersection of two extrapolated lines. With the addition of graphite (F2), the initial E' values were lower but the modulus decrease was seen starting at a higher temperature of 24 °C. The lowest modulus at −50 °C was observed for sample F3 with 8 wt% graphite and 2.6 wt% of GOS that decreased further above 31 °C. Further increase of GOS concentration (F4) nearly doubled the modulus and the reduction in modulus started at a slightly lower temperature of 25 °C. The reduction in temperature at which E' decrease starts could be due to the plasticizing action by the dangling alkyl chains at the high concentration (9.6 wt%) of the GOS. Thus, a combination of GOS and graphite improved the overall properties and service temperature of the nanocomposites. With GOS alone (F5) the modulus exhibited a stepwise reduction, before the major decrease starting at 25 °C. The change in modulus indicated a change in the rigidity and ultimately, the strength of the sample. At the highest concentration of GOS used (F4) along with 8 wt% graphite, the storage modulus almost doubled as compared to the neat nitrile latex film (from 2500 MPa to 4500 MPa). The improvement in storage modulus at low temperatures suggests that, at higher concentrations, GOS acted as an effective reinforcement in the polymer matrix by transferring the load from the polymer to the 2D filler graphene. At the lowest concentration of GOS (CNBL-F3) along with graphite the storage modulus was lowest compared to that of the neat nitrile latex, suggesting a

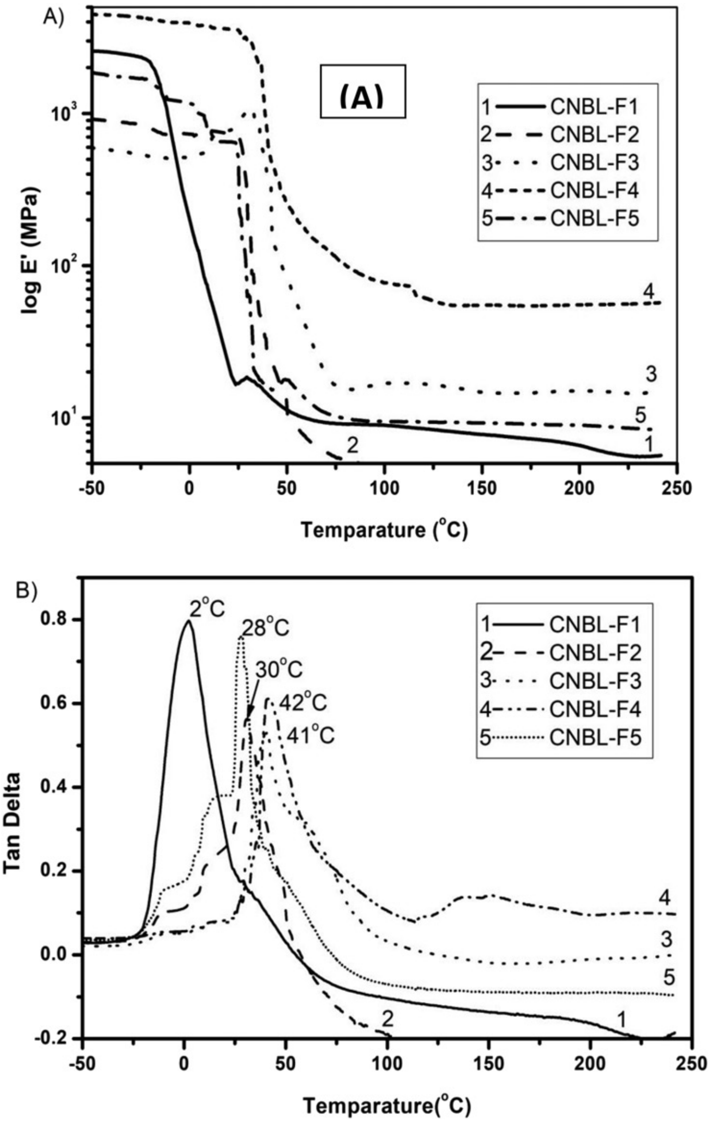

Figure 4. Dynamic mechanical plots showing variations in (A) storage modulus and (B) tan delta with temperature for varying concentration of the graphene surfactant and graphite.

plasticizing action of the alkyl chains present in the comb-like polymer modified graphene surfactant,[25] but the value increased at ambient temperature.

The tan δ curves shown in Figure 4B confirm the graphene surfactant effect on the glass transition temperature of the nitrile latex composites. The temperature at the maximum of the tan δ curve was taken as the glass transition temperature. As expected, the neat latex film was soft at room temperature with a Tg value corresponding to 2 °C. The Tg values of the samples with GOS and graphite increased with increasing GOS concentration, indicating a stiffening effect due to the increased interaction between the filler and the elastomer but the increase was only marginal, from 2.6 to 9.6 wt% and the effect on Tg appeared to be due to the graphite (Table 3). The shift in the transition

Table 3. Effect of amphiphilic polymer modified graphene surfactant (GOS) on the glass transition and damping behavior of nitrile latex nanocomposites.

Sample code	Tg (°C)	Tan δ range (°C)	Tan δ width (°C)
CNBL-F1	2	−18 to 27	40
CNBL-F2	30	−18 to 50	60
CNBL-F3	41	−18 to 87	100
CNBL-F4	42	25 to 113	90
CNBL-F5	28	−22 to 62	80

temperature towards higher temperature indicates that GOS might be at the interphase between the latex and the filler, which would occur due to interaction between the rubber chains and the fillers, as indicated in Figure 3. Interestingly these fillers improved the elastic property of the composites in the Tg region (indicated by the higher storage modulus values). The glass transition temperatures of the nanocomposites and the tan δ peak full temperature width (start temperature – end temperature = measure of the damping) are further summarized in Table 3. The results showed an excellent improvement in damping characteristics of the GOS modified film (CNBL-F3) over a broad temperature range of 100 °C, as compared to 40 °C for the film without any GOS (CNBL-F2). To the best of our knowledge, this is the first report showing an improvement in damping characteristics of nitrile latex nanocomposites using a functional graphene additive. Previously, we found the same surfactant (GOS) alone suitable for the preparation of polystyrene nanocomposites with improved properties.[26]

3.3. Thermogravimetric analysis (TGA)

TGA provides important information about the effect of formulation variables on the thermal stability of nanocomposites. The important thermal decomposition parameters, T_{10}, T_{50}, T_{max} and the residue remaining at 800 °C of the latex nanocomposites, are tabulated in Table 4 with representative thermograms of CNBL-F2 (only graphite) and F3 (graphite and GOS) compared in Figures 5A and B, respectively. The results showed that the addition of GOS was beneficial to improve the overall decomposition profile and the product exhibited uniform decomposition (Figure 5B, single step in F3). In the case of F5, where no graphite filler was used, the char yield was the lowest. The vulcanization decreased the T_{10} slightly in F1 but showed higher T_{50} and T_{max}. The cured films with GOS and graphite showed increasing T_{50}, in going from F2 to F4. The addition of GOS alone (F5) caused a large decrease in T_{10}. However, T_{max} values showed a marginal increase from F1 to F5 though the difference was not large. In other words, the addition of graphite with curatives and ZnO successively increased the T_{max} as the GOS concentration was increased from 0 to 9.6 wt%. The maximum T_{50} was observed in F4 with 9.6 wt % GOS and 8 wt% graphite but a two step decomposition was observed, the peak values at 460 and 477 °C. Among the GOS modified samples, the char residue was found to increase with GOS addition, probably due to the carbon content of the graphene also contributing to the char yield. The TGA studies, thus, demonstrate that the incorporation of GOS in our nitrile latex polymer matrix increased the thermal stability (T_{max}) when used along with graphite. With GOS alone (F5), even though T_{max} was higher, the T_{10} was low indicating fast initial decomposition during the heating.

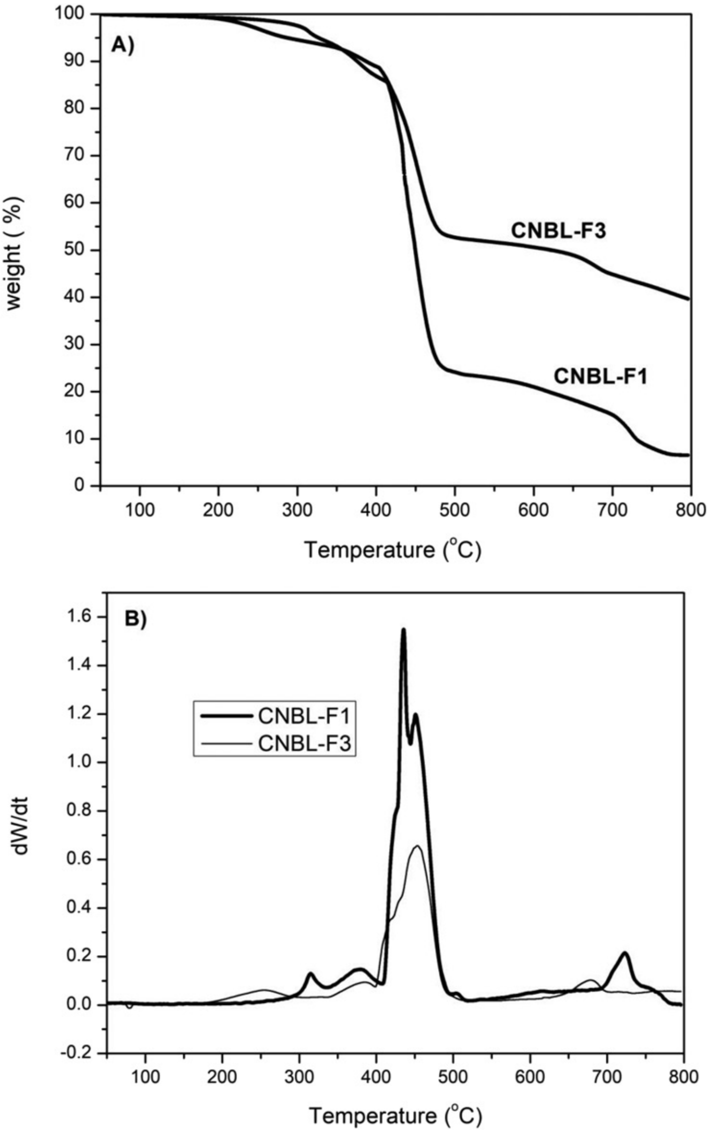

Figure 5. Thermogravimetric analysis curves of CNBL F2 and ad CNBL F3 showing (A) weight loss and (B) the derivative plots.

Table 4. Effect of graphene surfactant (GOS) on thermal properties of the nitrile latex nanocomposites.

Sample code	composition	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)	Residue (%) at 800 (°C)
CNBL	neat film	376	449	436,452	15
CNBL-F1	cured film	357	463	466	21
CNBL-F2	Cured with 8% graphite	381	475	470	33
CNBL-F3	Cured with 8% graphite +2.6 wt% GOS.	324	478	472	33
CNBL-F4	Cured with 8% graphite +9.6 wt% GOS.	378	503	460,477	35
CNBL-F5	Cured with 2.8 wt% GOS.	260	465	474	18

T_{10} – temperature at 10% weight loss; T_{max} – peak decomposition temperature.
T_{50} – temperature at 50% weight loss.

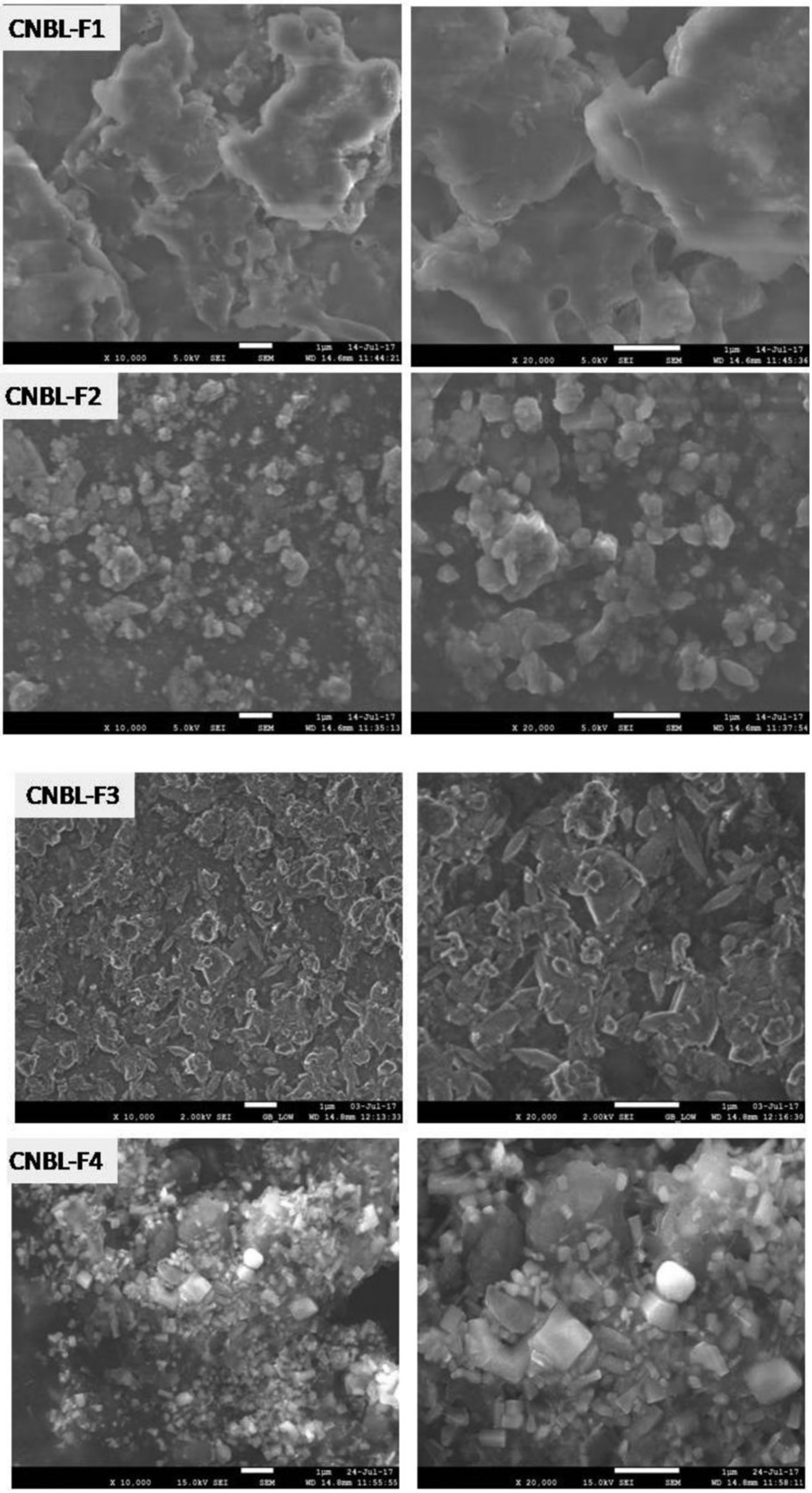

Figure 6. SEM images of the dried, free surfaces of nitrile graphite nanocomposites showing effect of graphene surfactant (GOS) modification on the morphology of the films (see Table 2 for composition details).

Table 5. Water contact angle value of graphene surfactant (GOS) modified nitrile latex nanocomposite films.

Sample code	Composition	Contact angle
CNBL-F1	cured film	40°
CNBL-F2	Cured with 8% graphite	72.3°
CNBL-F3	cured with 8% graphite +2.6 wt% GOS	42.6°
CNBL-F4	Cured with 8% graphite +9.6 wt% GOS	36.7°
CNBL-F5	Cured with 2.8 wt% GOS.	51.6°

3.4. Morphology

Figure 6 shows the SEM images of the surface of the nitrile latex nanocomposite as-prepared films. The morphology of unfilled nitrile latex film (CNBL-F1), the nitrile latex films with 8 wt% graphite (CNBL-F2) and latex film with two different concentrations of GOS (CNBL-F3 & CNBL-F4), each at two different magnifications, are shown. A large particulate texture was seen for the latex film without any filler or graphene surfactant (CNBL-F1), suggesting deformed latex particles because of film formation. The morphology of CNBL-F2, with 8 wt% graphite filler, showed small particles, but with some aggregated filler particles being seen and the latex particles seen with CNBL-F1 were no longer seen. CNBL-F3, with GOS and graphite, showed a more homogenous distribution and shape of the particles than in F2. In CNBL-F4, with a high concentration of GOS, the white particles were attributed to aggregates of the GOS and the graphite filler particles covered by the GOS within the nitrile latex. The more homogeneous appearance of F3 than F2 is suggested to result from increased interfacial bonding between the filler and the matrix polymer via the GOS. As shown in Figure 3, the polar groups as well as the hydrophobic graphene domains of the GOS facilitated better interaction between the graphite filler and the carboxyl groups on the nitrile elastomer and thereby improved the mechanical properties. But F4 showed a much worse morphology, probably because of the high concentration of GOS, resulting in some separate aggregations of polar surfactant moieties (the white particles).

3.5. Surface properties

Hydrophobic film surfaces, resisting water penetration into their texture and, simultaneously, the films offering additional functionality, like good damping performance and high temperature stability, have been reported to be important for a multitude of applications.[30–32] The wettability of graphene coated surfaces is generally measured by the water contact angle. Shin et al. reported a water contact angle value of 92° for single, bi-and multi-layer graphene particles.[32] However, to the best of our knowledge, the surface properties of latex nanocomposites with amphiphilic polymer modified graphene derivatives have not been reported to date. To study the effect of GOS on the hydrophobic/hydrophilic characteristics of the nanocomposite measurements of the water contact angle were performed on the films. The results are summarized in Table 5. The results, in general, suggest a decrease in the hydrophobicity of the graphite containing film on adding the hydrophilic GOS (from F2 to F4). The value for F5 was marginally higher than that of F1, probably due to the contribution by the graphene domains to the hydrophobicity.

4. Conclusions

The influences of a polymer modified graphene surfactant (GOS) on the properties of the nitrile latex nanocomposite films have been reported. The study showed that the filler graphite, along with the GOS, increased the tensile strength and modulus but decreased the elongation at break. For actual applications it is desirable to have a balance of properties depending on the required application. In optimizing the product properties it would be advantageous to use a GOS along with graphite or just GOS, as it improved the film tensile properties, without affecting the thermal stability and strength. The addition of GOS also improved the film formation (resulting in a smooth feel of the films to touch) apart from the film properties, when used at a low concentration. The TGA results show an improved thermal decomposition profile of the GOS modified samples. Dynamic mechanical analysis revealed the improved damping characteristics of the nitrile latex nanocomposites, suggesting their utility in damping applications. The effect of GOS on the surface properties and morphology was also studied. In summary, the amphiphilic GOS along with graphite, or GOS alone, could function as an important multifunctional additive for nitrile latex and, presumably, other elastomer nanocomposites.

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