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LESSONS OF MECHANICAL PROPERTIES, CURE KINETICS AND RHEOLOGY OF NANOCLAY/VINYL ESTER RESIN COMPOSITES

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ABSTRACT

In this work, the result of quaternary ammonium ion salt containing nanoclay content (1-5 wt%) on section morphology, rheology, cure mechanics and mechanical properties of the vinyl organic compound rosin (VER) based mostly nanocomposites was studied. The morphological characterization as well as d-spacing measure, research observation and phase-height image process were performed on the ready nanocomposites mistreatment little angel X-ray scattering (SAXS), transmission microscopy (TEM) and atomic force microscopy (AFM). consistent with the results obtained from these techniques, it absolutely was terminated that AN intercalated morphology existed for all the nanocomposites. The kinetic ANalyses of the equal natural process followed by storage modulus obtained from the rheometry experiments is shown to be an emotional rheologic characteristic to research the cure behavior of VER/clay nanocomposites. additionally, the foremost necessary finding concerning the result of nanoclay on the crosslinking behavior of VER systems lays on the surface assimilation and physisorption of the reacting monomers and leader molecules on the nanoclay platelets surface that is found to be accountable for the retardation of the cure reaction caused by organoclay. Eventually, the mechanical characterizations were performed through the tensile, flexural and impact analysis tests. during this case, a substantial improvement of the majority mechanical responses like tensile and flexural strengths and conjointly the corresponding moduli were determined for the nanocomposites.

1. INTRODUCTION

POLYMER nanocomposites particularly bolstered with stratified silicates has recently found an excellent interest. this might be addressed to their potential in providing a comprehensible improvement of physical, mechanical and chemical properties with even terribly low salt content [1]. This superior level of enhancements is obtained attributable to the high surface-to volume quantitative relation which ends up into their high surface activity [2]. However, the most key to achieve these enhancements is that the accomplishment of a high dispersion state, exfoliation and/or embolism in nanoclay layers inside the chemical compound matrix [3]. notwithstanding, the dispersion of nanoparticles inside compound matrix attributable to high-energy deliquescent surfaces of stratified silicates is kind of tough [4]. Therefore, the nanoclay surface is typically changed with AN organic chemical agent so as to create the bed area sufficiently hydrophobic for increasing the polymer-clay interactions [5]. despite the fact that, polymer/layered salt nanocomposites are wide studied [6-8], there's abundant less info offered on the thermosetting chemical compound based mostly nanocomposites containing nanoclay. within the field of chemical compound rosin nanocomposites, many studies are dedicated to the epoxy [9], polyester [10] and polyimide [11] nanocomposites containing nanoclay. Among these thermosetting materials, vinyl organic compound resins (VERs) area unit wide employed in marine and business applications because of their distinctive properties like acceptable chemical resistance, thermal stability, mechanical strength, low weight and low value [12-14]. Yebassa et al. investigated the result of process parameters on the with chemicals functionalized clay/VER nanocomposites [15]. They prompt that the addition of cinnamene as a comonomer and high-intensity supersonic mix produces vinyl organic compound nanocomposites with the best degree of clay exfoliation. Moreover, the correlation between morphology and mechanical properties of VER based mostly nanocomposites containing nanoclay has been highlighted by Gefu and his colleagues [16]. They showed that partly or nearly totally exfoliated nanoclay morphology enhances the mechanical and thermal properties of nanocomposites compared to the pure VER. moreover, the elastic properties of VER/clay nanocomposites are intensively investigated by Drozdov and his coworkers [17]. They found that the response to the uniaxial tensile stress is powerfully elastic, whereas increasing the clay content leads to a severe decrease of plastic strains determined in pure rosin. additionally, Shah et al. [18] have rumored that the equilibrium wet content, the glass transition temperature (Tg) and also the modulus of elasticity of VER/montmorillonite clay nanocomposites were above the neat rosin.

In spite of the actual fact that the chemical reactions involve the cure method that may for the most part have an effect on the physical, mechanical and thermal behavior of the cured systems [19], investigations regarding the parameters that rule the mechanism and rates (kinetics) of VER/montmorillonite systems cure behavior area unit lacking within the open literature. To the most effective of our information, the strategies used up to now to follow the cure reaction of VER nanocomposites area unit solely restricted to differential scanning measuring (DSC) [13,20] and Fourier rework infrared spectroscopic analysis (FTIR) [14]. However, DSC technique solely provides the general cure mechanics by measure the speed of made heat and needs assumptions regarding the enthalpies of elementary reactions [21]. Moreover, FTIR cannot typically find the increasing consumption of reactive teams at final natural process stages [21]. Therefore, one may utilize rheologic strategies to research the {curing|hardening|solidifying|solidification|set|natural method|natural action|action|activity} process a lot of with success so as to beat these impediments. The techniques not solely area unit crucial for optimisation of the process cycle, however can also be applied to attain a elementary understanding the cross-linking between mechanics and also the mechanical behavior of the system [22]. additionally, nano-structural morphological info is critical for AN in-depth understanding of the correlation between solid state structure once the {curing|hardening|solidifying|solidification|set|natural method|natural action|action|activity} process and different nanocomposites properties like mechanical behavior. Generally, 2 characterization techniques area unit employed in the investigation of polymer/clay nanocomposites morphology, specifically diffraction (XRD) and transmission microscopy (TEM). Despite XRD is most helpful technique for measurements of the nanoclay layers d-spacing, it can't be the sole technique to adequately describe the nanoscale distribution of the stratified salt in nanocomposites. Therefore, XRD results ought to be combined with TEM analyses so as to present a lucid image of actual dispersion of the nanoclay inside the matrix [18]. On the opposite hand, atomic force research (AFM) has recently become a a lot of powerful technique for researchers to quantify a range of surface topographies in nanometre scale. Therefore, XRD, TEM and AFM area unit the complimentary techniques for morphological characterization during this work. The objectives of this work include: analysis the result of nanoclay content on the cure mechanics of VER/clay nanocomposite mistreatment rheologic measurement; and conjointly the investigation of morphological structures by SAXS, TEM and AFM. additionally, tensile, flexural and impact experiments were performed to judge the result of nanoclay addition on the mechanical properties of VER matrix.

2. EXPERIMENTAL

A. Materials

VER (DERAKANE 470-30) with thirty third of cinnamene compound was purchased from Dow Chemical Co. (USA). we have a tendency to used Cloisite 30B (C30B) that was a montmorillonite clay organically changed with a quaternary ammonium ion salt (MT2EtOH: alkyl group, tallow, bis-2-hydroxyethyl, quaternary ammonium). bleach (BPO), as a thermal leader was provided from Fluka and used as received.

B. Sample preparation At the start, nanoparticles were dried to get rid of the wet absorbed by Montmorillonite. Vinyl organic compound rosin was then mixed with one, three and five skyscraper of C30B employing a high shear rotor-stator homogenizer. The mixture obtained through this technique was stable for many hours. Finally, BPO (1.5 wt%) was additional to the mixtures and also the compound was stirred for fifteen min. The solutions containing one, three and five skyscraper of organoclay were labeled as VER-1%OC, VER-3%OC and VER-5%OC, severally and every of them was equipped with glass stoppers sealed with polymer grease hold on at -10 °C so as to forestall the evaporation of cinnamene and to avoid any premature natural process.

C. Characterization strategies SAXS studies were preformed on a Hecus S3-Micro focus rotating ANode generator with an fast voltage of forty KV/30 mA. the info was collected on phosphor image plates at a sample-to-film distance of forty cm. Ultra-thin sections were ready by employing a Leica EM FCS cryoultra scientific instrument equipped with a diamond knife. TEM pictures of VER/clay nanocomposites were obtained at one hundred twenty kilovolt, underneath low-dose conditions, with a Philips 400T microscope. AFM research was performed employing a Dualscope/ Rasterscope C26, DME with AC Probe and metal coating Cantilever. All measurements were created at close temperature. Moreover, intermediate to onerous sound mode was used to reveal smart distinction in each height and section pictures. rheologic studies were conducted on a Rheoplus MCR300 rheometer (TA Instruments opposition., Delaware) mistreatment the parallel plate mode. The time sweep tests were allotted at totally different constant temperatures (80 °C, 90 °C, and ninety five °C) and a continuing shear frequency (1 Hz). so as to record the rheologic characteristic functions within the linear elastic vary, a continuing strain rate of 100 percent was applied for all the experiments. Tensile tests were performed to check the mechanical properties of pure VER and VER/clay nanocomposite samples with the employment of a Universal Testing Machine, Model LR ten K, consistent with the ASTM D638 at a cross head speed of a hundred metric linear unit/min and a riveting length of one hundred fifty mm.

Flexural take a look at were performed on identical machine mistreatment the 3-point bending technique consistent with ASTM D790-99. The specimen dimensions were twelve7 metric linear unit (L) x 12.7 metric linear unit (W) and had three.2 metric linear unit thickness and a crosshead speed two|of two} mm/min was applied for all the experiments. Impact tests on notched specimens were allotted mistreatment XCJ-500 Impact Tester (pendulum type) supported ASTMD256. All the results were rumored because the average of 5 experiments for every testing technique.

3. RESULTS AND DISCUSSION

A. Morphological characterization D-spacing measurements (SAXS) so as to judge the extent of intercalation/exfoliation of the organically changed montmorillonite particles inside the VER matrix, SAXS measurements were performed whose results area unit given in Fig. 1. it's famed that the position of peak provides info on the bed areas between the salt layers through the link between the basal plane.

However, the existence of C30B particles within the nanocomposites with higher clay concentrations was confirmed by the extra scattering determined in their SAXS spectra. during this case, the corresponding optical phenomenon peaks appeared at zero.25 and 0.27 Å-1 for the samples containing three and five skyscraper clay content that assign to bed spacing of two.50 and 2.32 nm, severally. Therefore, it may be understood from the height position that AN intercalated morphology is gift within the 2 latter samples containing higher clay content. Moreover, the wideness of the height appeared for the nanocomposites of three skyscraper nanoclay content, may even be AN proof of the native clay disorder that is thought as partial exfoliated morphology. notwithstanding, consistent with Klug et al. [24], peak broadening may be developed by the defects, lattice strain and finite distribution of clay stack sizes. Hence, any investigations area unit needed to verify the SAXS observations for deeper understanding of the results. Moreover, as given in Table one, the bed spacing decreases because the clay content will increase within the nanocomposites. This observation may be partially attributed to the actual fact that the low loadings of C30B within the nanocomposites enable comparatively a lot of VER chains to penetrate into the clay gallery. Moreover, the overall distances between the neighboring clay clusters area unit abundant larger at low concentrations of the nanoclay. Consequently, because the gallery of the C30B expands, interaction between the close clusters ought to still be abundant smaller, and also the growth of the gallery may be continued a lot of freely as rumored antecedently [25].

B. Research Observation

(TEM) TEM characterization technique was performed to interpret a lot of exactly the morphological options discovered through SAXS studies. Fig. a pair of shows the TEM pictures of VER nanocomposites containing one, three and five skyscraper of C30B. consistent with Morgan et al. [26] the shortage of peak obtained throughout X-ray analysis significantly in comparatively little angels just states that no peak was detected throughout spectroscopic analysis whereas it doesn't prove whether or not the exfoliated clay platelets exist within the nanocomposite or not. Although, there area unit many numbers of exfoliated single nanoclay layers gift within the VER matrix within the sample containing one skyscraper nanoclay loading, it's onerous to create a conclusion on the exfoliation of such a sample (Fig. 2(A)). Moreover, the TEM image for the nanocomposite containing three skyscraper nanoclay shows that though intercalated multilayer crystallites area unit determined, single exfoliated organoclay layers were conjointly current (Fig. 2(B)). Hence, one may recommend a mixed morphology of intercalated and partly exfoliated structures for such a sample. However, the TEM analyses unconcealed that the VER nanocomposite containing five skyscraper organoclay may solely be selected as intercalated structure (Fig. 2(C)). consequently, it's inferred that the dispersion of the C30B platelets inside the VER matrix is satisfactory and also the TEM results corresponds well with the SAXS optical phenomenon pattern info.

C. Section And Height Image Process (AFM) using AFM technique to spot high-resolution height pictures, a a lot of comprehensive understanding of structure-function relationships may be achieved besides some blessings over TEM [27]. Representative AFM height and section pictures of the nanocomposites containing one, three and five skyscraper of C30B content with totally different magnifications area unit shown in Figs. 3, 4 and 5, severally. sound mode AFM that was applied here; has the advantage of being non-destructive to the nanocomposite sheets surface compared to contact mode AFM. moreover, sound mode AFM is sufficiently sensitive to little modulus variations between 2 phases and thence it may be used to research the surface of fabric in a very nanometre scale. though solely a number of little areas of every sample were analyzed, it's determined from AFM pictures (phase and height) that clay discreet phases (dark spots in Figs. 3 and 5, bright spot in Fig.4) area unit quite often distributed within the continuous VER section while not aggregation for all the nanoclay contents. This may be because of the presence of the quaternary ammonium ion salt on the C30B surface that increased the compatibility between the organoclay and also the VER chains. consequently, this can be in conjunction with SAXS and TEM studies; but, flipping of the section distinction

determined in nanocomposite with three skyscraper nanoclay could also be addressed to the switch of AFM tip and sample interactions from the attraction to repulsion or vice-versa [29].

Upon shut examination of the VER/clay nanocomposites AFM section image analysis, one will verify the clay domains sizes on the average area unit one.21, 2.54 and 3.71 nm for nanocomposites with one, three and five skyscraper clay content, severally. These results purpose to the increment of average size of nanoparticles with increasing the clay weight content. evidently, dispersion method quantity} economical at high amount of clay concentration. additionally, the variations in surface topography may be determined quantitatively by reserves and Sq parameters that represent mean and root mean sq. surface roughness, severally. Before the roughness measure begins, the peak pictures were planar mistreatment first-order flattening. This eliminates image artifacts which could result in a vertical offset between the scan lines. Numerical values of reserves and Sq parameters and their variations area unit given in Table one. the foremost fascinating purpose regarding the reserves information was the increment of the mean roughness worth of the VER/clay nanocomposites upon increasing the clay content. this might be taken in terms of a poor dispersion of the nanoparticles within the nanocomposites with high clay concentration that is well per the SAXS and TEM results. moreover, the worth of (Sa-Sq) for nanocomposite with five skyscraper clay loading is above those full of one and three skyscraper clay content evidently. this might ensure the presence of a bigger undulation within the effective surface height of VER based mostly nanocomposites containing high quantity of clay loadings [30]

4. RHEOLOGIC CHARACTERIZATION

A. equal cure behavior one in all the foremost objectives of this work is to check the result of nanoclay on the cure behavior of the VER based mostly nanocomposites. Therefore, rheologic characterization as a sensitive technique to the state of natural process was performed to elucidate the role of nanoclay on natural process mechanism. Fig. six illustrates the equal time dependent storage modulus of the VER/clay nanocomposites which of neat VER at varied natural process temperatures. As delineated , G′ remains constant before the onset of curing; once the cross-linking method begins, a motivating increase in G′ the least bit the experiment temperatures happens. The characteristic parameters like G′∞ (the values of the storage modulus of the maximally cross-linked polymer), the onset of natural process (the time at that G′ increases) and also the whole natural process time were determined from the curves as listed in Table a pair of. It may be clearly understood that for the samples with identical organoclay loadings, the onset of natural process and natural process time decreases with increasing the temperature. This may be attributed to the supply of a lot of thermal energy for the natural process reaction at higher natural process temperatures. However, it may be understood that the organoclay nanoparticles area unit acting as inhibitors concerning to the cure reaction times. it'd be attributable to the actual fact that the organoclay will capture the reacting monomers and with chemicals absorb them to their surface. Thereby, the natural process reaction is hampered or perhaps stifled. Also, another mechanism of retardation could also be because of the physically action of the reactants on the surface of clay galleries that affects the ratio and results into some sterical hindrance reference to the forming network [31]. These phenomena that area unit stated as “chemisorption” and “physisorption” may conjointly cause the retardation in decomposition of the BPO used as leader and thence result into the delay in onset of curing process [32]. Moreover, the reaction between the nanoclay and VER chains ends up in a lot of restricted motion of the chains that any decelerates the cure reaction [33]. temperature. the rise within the natural process temperature favors the molecular quality that successively causes the rheometer detectors to indicate lower storage modulus. Moreover, it's price mentioning here that G′∞ of the neat VER systems will increase with the addition of C30B. this may be allotted to the presence of well distributed salt layers within the VER matrix that decreases the chemical compound chain quality.

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