Ester-amide based on ricinoleic acid as a novel primary plasticizer for poly(vinyl chloride)

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ABSTRACT: Utilization of ricinoleic acid as a raw material for the synthesis of green plasticizer would offer an alternative to the phthalate plasticizers. Ester-amide of ricinoleic acid was synthesized by a two-step reaction with dibutyl amine and benzoic acid; and then utilized as primary plasticizer in PVC. Ester-amide plasticizer was added up to 40 phr in PVC; and the prepared PVC sheets were characterized for mechanical, X-ray diffraction, thermal, rheological, colorimetric, and exudation properties. Addition of the ester-amide plasticizer demonstrated good incorporation and plasticizing performance in PVC. Viscosity of PVC decreased with increased addition of ester-amide plasticizer. The dark color of the synthesized plasticizer could have constraints on its application areas; however, the prepared samples illustrated negligible weight loss in the exudation test, attributed to better compatibility between them brought about by the ester, tertiary amide and polarizable benzene ring in the ester-amide plasticizer with the C-Cl polar linkage in PVC. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41913.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the least stable and difficult to process commodity polymer. Large commercial utilization of it is attributed to the discovery of various additives like stabilizers, plasticizers, lubricants, processing aids, etc.[1] It is a third largely used commodity polymer after poly(ethylene) and poly (propylene).[2] PVC is used in wide range of applications like water supply and sewage pipes,[3] electric cables,[4] garments,[5] furniture,[6] healthcare products,[7] etc. Global demand for PVC was around 39 million tons per annum as of 2013; which accounts for 17 to 18% of the total polymer demand, having growth rate per year of about 5%.[8]

Of the various additives listed, plasticizers and stabilizers are the most important additives for PVC. Plasticizers are low molecular weight chemical compounds, which place themselves in between the PVC polymer chains thus increasing the intermolecular distance. This leads to decrease in the cohesive forces of attractions between the PVC polymer chains making the PVC polymer structure flexible and soft.[9] This phenomenon helps PVC overcome its innate limitations of rigidity, processing difficulty and thermal instability. There are near about 300 different varieties of plasticizers developed and reported for PVC. However, only 50 to 70 are commercially viable and available; which

are primarily phthalate and adipate based. Of the total quantity of plasticizer produced worldwide, about 75% is utilized by the PVC industry.[10] In order to make PVC process-able, plasticizers are added to an extent of 30 to 40 phr of the total weight of PVC.[11]

Plasticizers can be either a primary or a secondary plasticizer. Primary plasticizers are compatible with PVC over a broad concentration range and directly helps improve the flexibility and softness of the PVC. Secondary plasticizers have limited compatibility with the PVC polymer chains and thus do not help PVC become flexible or soft as required. However, when used in combination with primary plasticizer, they are capable of improving PVCs flexibility and softness.[12]

Phthalates are used as primary plasticizer in PVC due to its better compatibility with the PVC polymer chains. Better compatibility is caused due to interactions of the alkyl ester linkage of the phthalate with the polar PVC polymer chains.[13] Phthalates widely and commercially used as plasticizer for PVC are dioctyl phthalate (DOP),[14] dibutyl phthalate (DBP),[15] di(2-ethylhexyl) phthalate (DEHP),[16] and diisodecyl phthalate (DIDP).[17] However, these are low molecular weight chemical structures not bound to the PVC polymer structure and thus leach out of the PVC matrix over time and diffuse into air, water, soil food,

living organisms, etc.[18] These phthalate based plasticizers are reported to be toxic in nature and found to have adverse effect on the health of humans. They have been identified as reproductive and developmental toxicants and also probable carcinogens.[19] These plasticizers are restricted from use in children products in US and European Union. However, they are still unregulated and are largely used in children toys in countries like India and China; mainly due to the low cost and difficult availability-of-alternative concern.[20]

Extensive research is been carried out to develop phthalate free plasticizers which should be nontoxic in nature. Material that is largely utilized in developing this alternative phthalate-free plasticizer is vegetable oil directly or its chemical constituents.[21] Epoxidized soya bean oil is one of the very few oil based plasticizer being commercially used and having worldwide production of around 20,000 tons.[22] Recently, Chaudhary et al. investigated the effect of mix of bis(2-ethylhexyl) succinate and epoxidized soybean oil (ESBO) as bio-based coplasticizer for PVC. They were effectively able to add about 50% (w/w) of ESBO as a succinate replacement decreasing the volatility and thus its side effects.[23] Nihul et al. investigated the effect of epoxidized rice bran oil (ERBO) as coplasticizer for PVC. They synthesized ERBO with 82% oxirane content and were able to replace about 60% of the DOP, when used as secondary plasticizer for PVC.[24] Chavan and Gogate studied the effect of ultrasonication on the synthesis of epoxidized sunflower oil (ESNO) and synthesized ESNO with oxirane content of 91.1% to be used as a secondary plasticizer in addition to DOP.[25]

Recently, wide research is been undertaken in the synthesis of bio-based plasticizer from the esterification reaction of the fatty acids obtained from vegetable oil. Waskitoaji et al. investigated the synthesis of ester compounds via the esterification reaction between palm oils fatty acid (oleic acid) and various alcohols like 1,4-butanediol, iso-butanol, and 2-ethyl hexanol using concentrated sulfuric acid as the catalyst. Secondary plasticizer, iso-butyloleate obtained by the esterification reaction of oleic acid and iso-butanol was found to replace about 80% of DEHP.[26] Gan et al. synthesized a series of esters of palm stearin and palm olein by the process of alcoholyis using KOH as the catalyst and were further epoxidized by the method of peroxyformic and peroxyacetic acids. Of the ester series explored, epoxy butyl esters of palm olein were determined to be the best plasticier for PVC.[27] Benzyl ester of dehydrated castor oil (BEDCOFA) fatty acid were synthesized by Mehta et al. by reacting benzyl alcohol with fatty acid of dehydrated castor oil fatty acid. Prepared BEDCOFA was utilized as a secondary plasticizer with DOP and showed significant similarity in properties with DOP plasticized PVC sheets.[28] They also synthesized diester based on castor oil fatty by a two-step esterification process reacting castor oil fatty acid with benzyl alcohol and octanoic acid using dibutyltin dilaurate as the catalyst. Synthesized novel chemical compound was found to be suitable to be used a coplasticizer for PVC, replacing about 30% of DOP, with no much significant deviation from the DOP-plasticized PVC.[29]

Ricinoleic acid (RA) rich vegetable oils are of meticulous interest to the oleochemical industries.[30] RA is commercially obtained from the endosperm of castor-bean (Ricinus communis) in the form of triacylglycerol (castor oil).[31] India is a leading producer of castor oil (1104.8 kg/ha) and thus RA. Cost of castor oil produced in India is around 0.41 $ per pound.[32] RA has a chemical structure uniquely different from other fatty acids. It has a chemical structure consisting of two reactive functional groups (hydroxyl and carboxyl) along with a double bond.[33] RA is extensively utilized in synthesis of polyurethane and polyester resins. It has also been used as an additive in blends and composites in order to improve the performance properties of the material.[34]

In this research work, an attempt is made to utilize ester-amide of ricinoleic acid as a primary plasticizer for PVC. This novel ester-amide was synthesized by a two-step reaction of ricinoleic acid (RA) with dibutyl amine (DBA) and benzoic acid (BA) using 98% concentrated sulfuric acid as the catalyst. Synthesized ester-amide was then utilized as a primary plasticizer for PVC in different concentrations and the prepared sheets were evaluated for mechanical, thermal, rheological, crystallinity, and exudation properties.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC, Grade: K57, suspension resin, bulk density: ~0.53 g/cm^2, particle size: ~200 mesh, inherent viscosity: ~0.7 dL/g) was procured from Vansh Polyvinyl India Pvt. Ltd., Mumbai, India. Lead based one pack stabilizer was obtained from Ala Chemicals, Mumbai, India. Jayant Agro, Mumbai, India, supplied ricinoleic acid (RA). Dibutylamine (DBA), benzoic acid (BA) and 98% concentrated sulfuric acid were purchased from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. All chemicals were of analytical reagent grade and were used as obtained without any purification or modification.

Methods

Synthesis of Ester-Amide of Ricinoleic Acid. The two-step ester-amide reaction of RA was carried out with DBA and BA using 98% concentrated sulfuric acid as the catalyst. In the first step, RA was reacted with DBA in a 1:1 molar ratio without any addition of catalyst or solvent. Reaction was carried out in a four-necked reactor equipped with stirring arrangement, Dean-stark apparatus, thermocouple arrangement and nitrogen gas inlet system. The reactants were heated gradually from 170 to 180°C and stirred continuous at 1000 rpm, under nitrogen atmosphere. Acid and amine value of the reaction mixture was determined after every 30 min in order to monitor the progress of the reaction. Reaction was continued until the acid and amine value of the system decreased below 5 mg KOH/g sample, which required about 12 h. First step led to the preparation of DBA modified (or amide modified) RA. After the completion of reaction, the reaction mixture was cooled down below 100°C. In the second step, the reaction mixture was reacted with BA in the presence of 98% concentrated sulfuric acid (0.1% w/w of the BA added) as the catalyst[35] at 170 to 180°C. Reaction was monitored for acid value after every 30 min, in order to monitor the progress of reaction. Reaction was continued until the acid value of the system decreased below 5 mg KOH/g sample, which required another 12 h. No purification step was
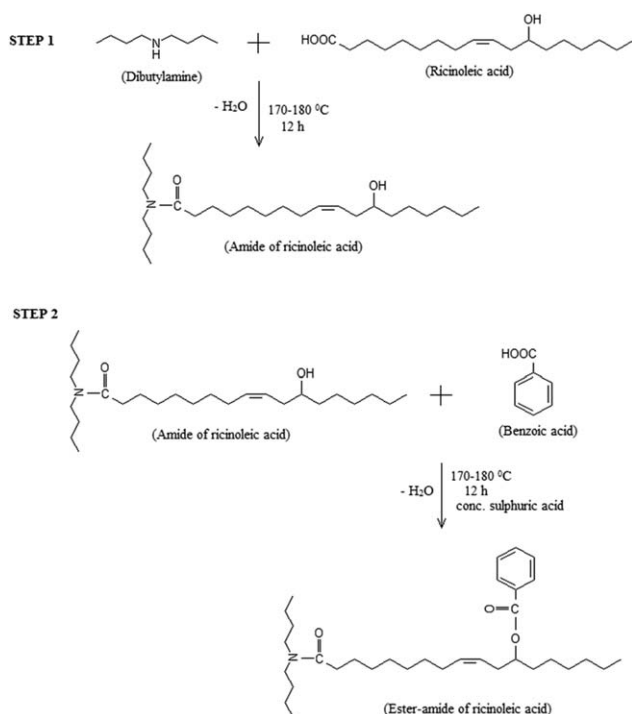
Figure 1. Reaction scheme for the synthesis of ester-amide plasticizer from ricinoleic acid, dibutyl amine, and benzoic acid.

performed on the final product. Reaction scheme for the synthesis of ester-amide plasticizer from RA is represented in Figure 1.

Yield of the synthesized ester-amide plasticizer was determined as per the following formula:

Yield of ester-amide plasticizer = (Weight of the ester-amide synthesized)/(Theoretical yield of the ester-amide).[35]

Preparation of PVC Sheets. Required quantity of PVC, one pack stabilizer and novel ester-amide plasticizer were dry blended in a high-speed mixer for 5 min to form a uniform mixture. Table I provides the information of the compositions prepared and their nomenclature. Melt blending was performed using a two-roll mill at 180°C for 20 to 30 min, until all the mixture is converted into a uniform molten mass. Material obtained from two-roll mill was predried in oven for 6 to 8 h to remove any adsorbed or absorbed moisture. Samples for testing were prepared by compression molding the molten mass using an upward stroke compression-molding machine. The upper and lower platen temperatures of the compression-molding machine were maintained as 180°C and 185°C, respectively, and 20 MPa pressure was applied. Pressure and heat was applied for 15 to 20 min during the compression stage, followed by cooling to room temperature requiring about 30 to 45 min. Sheet obtained (20 cm × 20 cm × 2 mm) was then cut to get samples for further testing. Cut samples were conditioned for 24 h before any test.

CHARACTERIZATIONS AND TESTING
Synthesized Ester-Amide of Ricinoleic Acid
Acid Value. Acid value was determined as per the procedure and calculations described in ASTM D974. Two grams of sam-

Table I. Prepared PVC/Ester-Amide Compositions and Their Nomenclature

Sr. No.	Sample name	PVC (g)	One pack stabilizer		Ester-amide plasticizer	
			phr	g	phr	g
1.	PVCC	500	5	25.0	0	0.0
2.	PVCP10	500	5	25.0	10	50.0
3.	PVCP20	500	5	25.0	20	100.0
4.	PVCP30	500	5	25.0	30	150.0
5.	PVCP40	500	0	25.0	40	200.0

ple was dissolved in 50 mL benzene-alcohol mixture using a 125 mL Erlenmeyer flask; and then a few drops of phenolphthalein indicator were added. Obtained solution was titrated against 0.5N alcoholic potassium hydroxide solution, until a faint pink color was observed which last for 30 s or more. The calculation of acid value is shown below:

Acid value = (56.1 × volume of alc. KOH × normality of alc. KOH)/(weight of sample)

Amine Value. Amine value was determined as per the procedure and calculations described in ASTM D2074-92. Two grams of sample was dissolved in 50 mL iso-propyl alcohol using a 125 mL Erlenmeyer flask; and then a few drops of bromocresol green indicator were added. The solution was titrated against, 0.5N standardized hydrochloric acid (HCl), until a yellowish green color was observed which remained for 30 s or more. The calculation of amine value is shown in below:

Amine value = (56.1 × volume of HCl × normality of HCl)/ (weight of sample)

Hydroxyl Value. Hydroxyl value was determined as per the procedure and calculations described in ASTM D1957. Five grams of sample was accurately weighed in a 250 mL Erlenmeyer flask; whereas other Erlenmeyer flask was not added with the sample and thus used as blank. Both the flasks were then added 20 mL of acetic anhydride—pyridine reagent (1:4 volume ratio) and attached with air condenser. Flasks were then immersed up to the liquid level in an oil bath maintained at 95 to 100°C. Flasks were swirled vigorously to bring about complete dissolution of the sample in the reagent. Flasks were heated continuously for 1 h to insure uniform reaction. Flasks were cooled to room temperature. Then, 10 mL water was added to the flasks through the air condenser. Flasks were again heated on oil bath for 15 min to hydrolyze the excess acetic anhydride reagent. Flasks were then cooled to room temperature and 25 mL neutralized alcohol (half through the condenser, which was removed afterwards) were added. Prepared mixture was stirred rigorously. Mixture was made ready for titration on addition of 1 mL phenolphthalein indicator and was titrated against 0.5N alcoholic potassium hydroxide to a faint pink color, which remains for 30 s or more. The calculation of hydroxyl value is shown below:

Hydroxyl value = [56.1 × normality of alc. KOH × (mL KOH blank − mL KOH sample)]/[weight of sample] − acid value.

Specific Gravity. Specific gravity (g/cm^3) of the synthesized ester-amide plasticizer was determined in accordance with ASTM D-891.

Rheological Analysis. A brookfield viscometer (Rheotec, spindle type: L2, rotation speed: 150 rpm) was utilized to determined the viscosities of dioctyl phthalate (DOP) and the synthesized ester-amide plasticizer. Analysis was performed at room temperature (~30°C). Samples were also subjected to rheological analysis to obtain a detailed flow behavior of the materials and thus compare them more appropriately.

Rheometer (MCR 101, Anton Paar, Austria) with a cone and plate assembly was used to investigate the rheological behavior of the synthesized ester-amide plasticizer and compare with that of DOP. Cone and plate (diameter: 35 mm, cone angle: 2°, spindle name: CP35-2-SN20784) were separated by a distance of 0.147 mm during the rheological investigation. The data investigation was performed using Rheoplus/32V3.40 software, supplied by the manufacturer. A temperature of 30 ± 0.5°C was maintained constant during the rheological analysis. Twenty-five viscosity/shear rate data points were obtained, at 6 points/decade, during the shearing of the samples from 0.1 s^{-1} up to a shear rate of 500 s^{-1}. Test was performed in the experimental time of 200 s.

In order to understand the thermal stability of the ester-amide plasticizer it was subjected to a test of viscosity (Pa s) versus temperature (°C). Temperature sweep involved heating at a rate of 2°C/min from 30 to 180°C. During the analysis shear rate was maintained constant at 0.1 s^{-1}. Results obtained for the synthesized ester-amide plasticizer were compared with that of the commercially available plasticizer for PVC, that is, dioctyl phthalate (DOP).

Fourier Transform-Infrared Spectroscopy (FT-IR). The FT-IR spectrum of the synthesized ester-amide plasticizer was recorded with a PerkinElmer, Spectrum GX equipment (USA). Solution of the ester-amide plasticizer (1–2 wt %) was prepared in chloroform and was scanned with a resolution of 2 cm^{-1} in the scan range of 450 to 4000 cm^{-1}. FT-IR of pure solvent was run prior to running the FT-IR of the samples, to use its peaks as baseline, so as to automatically subtract it from the samples peak.

Gardner Color Scale. The color of the ester-amide plasticizer was evaluated on the Gardner Color Scale as per the ASTM standard of D-1544-63.

Plasticizer Demand for PVC

The plasticizer demand for PVC of the synthesized ester-amide plasticizer was determined in accordance with the ASTM standard method of D1755 of evaluation of plasticizer absorption value. It is reported as the quantity of plasticizer (g) absorbed by 100 g of the PVC. This value was compared with that of the commercial PVC plasticizer i.e. DOP.

PVC Sheets Prepared by the Addition of Ester-Amide Plasticizer
Fourier Transform-Infrared Spectroscopy (FT-IR). The phenomenon of positive interaction between PVC and any type of plasticizer depends on the electronic delocation or bond weakening between the interacting groups or atoms.[36] FT-IR analysis can be utilized to understand the vigor of plasticizer-PVC interactions. Typically, if there are interactions happening between PVC an plasticizer, then the spectral peaks corresponding to PVC (C—Cl group) and plasticizer (ester and amide groups) are expected to shift to lower wavenumber frequencies.[37]

FT-IR spectra of the prepared PVC sheets, in transmission mode, was determined using a Bruker Alpha-P FT-IR spectrometer (Bruker Optic GmbH, Ettlingen, Germany). The obtained C—Cl, carbonyl and amide peaks were used to evaluate the miscibility of the plasticizer in PVC.

Mechanical Property. Tensile properties (tensile strength, tensile modulus, and percentage elongation at break) and flexural properties (flexural strength and flexural modulus) were measured at ambient condition using a Universal Testing Machine (LR-50K, Lloyds Instrument, UK), as per the ASTM procedures D 638 and D 790; whereas, the crosshead speed was maintained constant at 50 mm/min and 2.8 mm/min, respectively. Charpy impact strength was determined at ambient condition according to ASTM D 256, using impact tester (Avery Denison, UK) having striking velocity of 3.46 m/s, employing a 2.7 J striker.

Shore D Hardness. Shore D hardness of the prepared PVC sheets was determined in accordance with ASTM standard D2240 (test sample dimension: 2 cm × 2 cm × 0.2 cm). Samples were analyzed at fifteen different locations.

X-ray Diffraction Analysis. Prepared PVC sheets were subjected to X-ray diffraction analysis in order to determine the effect of ester-amide plasticizer addition on the crystallinity of PVC. X-ray diffraction analysis was performed using a Rigaku Miniflex (Japan) X-ray diffractometer. Samples were scanned in the scan range from 5° to 80° using a normal focus copper X-ray tube operated at 30 kV and 15 mA having wavelength of 1.54 Å. Scan speed was maintained at 3°/min. Data analysis was performed using the Jade 6.0 software supplied by the instrument manufacturer.

Percent crystallinity was calculated according to the equation given below:

% Crystallinity = (total area of crystalline peaks)/(total area of all peaks).[38]

Thermal Property. Effect of ester-amide plasticizer addition on the glass transition temperature of PVC was analyzed using a Differential Scanning Calorimetry (Q 100 DSC, TA instruments Ltd., India). Two consecutive heating scans were determined to minimize the influence of possible residual stresses in the material due to any specific thermal history. Scanning rate of 10°C/min was maintained for the heating cycle; whereas nitrogen gas purge rate was maintained at 50 mL/min. Glass transition temperature was determined from the second heating curve.

Rheological Analysis. Rheometer (MCR 101, Anton Paar, Austria) with a parallel plate assembly (PP35-SN20785, diameter: 35 mm) was used to investigate the rheological behavior of the ester-amide plasticizer added PVC sheets. Parallel plates were separated by a distance of 1 mm during the rheological
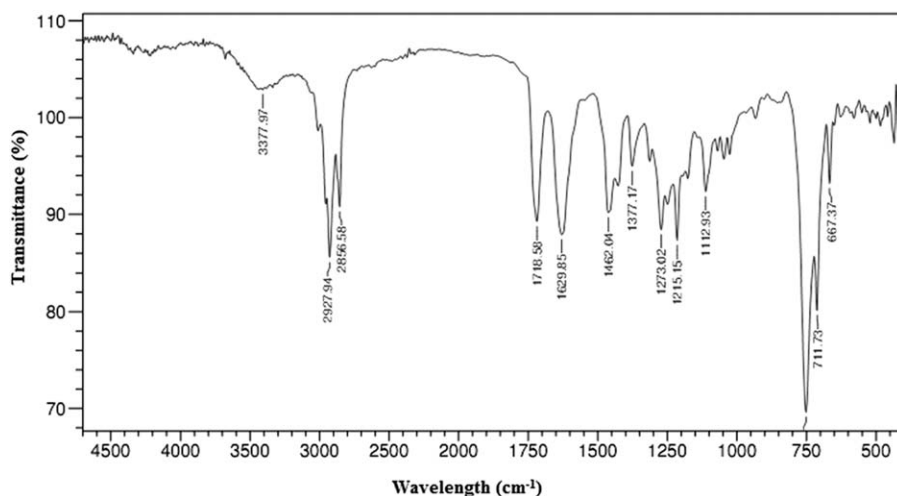
Figure 2. FT-IR spectrum obtained for the ester-amide plasticizer.

investigation. The data investigation was performed using Rheo-plus/32V3.40 software, supplied by the manufacturer. Before analysis, samples were thoroughly dried and conditioned at room temperature for 48 h.

Plot of viscosity (Pa s) versus shear rate (s^{-1}) was determined in the shear rate range from 0.1 s^{-1} to 1000 s^{-1}; and 20 viscosity/shear rate data points were obtained, at 6 points/decade in the experimental time of 200 s. Temperature was maintained constant at 180 ± 0.5°C during the rheological analysis.

Plots of loss modulus (G'') versus angular frequency (s^{-1}), storage modulus (G') versus angular frequency (s^{-1}), damping factor (tan $\delta = G''/G'$) versus angular frequency (s^{-1}) and complex viscosity (Pa s) versus angular frequency (s^{-1}) were determined in the angular frequencies from 0.5 s^{-1} to 500 s^{-1} at a constant temperature of 180°C. Shear strain was maintained constant at 5%. Sixteen data points were obtained at 5 points/decade.

The plot of viscosity (Pa s) versus time (s) was determined at a constant shear rate of 1 s^{-1} with temperature being maintained constant at 180°C. Hundred data points were measured in the total analysis time span of 1000 s at the frequency of 1 point/10 s. Whereas, the plot of damping factor (tan δ) versus time (s) was determined at 180°C, wherein shear strain and angular frequency were maintained constant at 5% and 10 s^{-1}, respectively. Here too the analysis was performed up to 1000 s and a total of 16 data points were determined.

Colorimetric Analysis. CIE L^*, a^*, b^*, and ΔE values for the PVC/ester-amide plasticizer compositions were determined using Color Spectrophotometer (Color Eye 7000, Optiview Light Quality Control 1.9, Gretag Macbeth, Germany). Illuminant used was D65. Observer was placed at 10°. Yellowness-C of the PVC samples was also determined as per ASTM D1925.

Exudation Test. Exudation of the synthesized ester-amide plasticizer and that of DOP from the PVC was evaluated by placing a sample of the plasticizer added PVC film between two pieces of tissue paper. The combined system (PVC film sample and tissue paper) was then placed at room temperature for 48 h.

Then, the tissue paper was separated from the PVC film and weighed to determined the extent of plasticizer exudation.

RESULTS AND DISCUSSION

Synthesized Ester-Amide of Ricinoleic Acid

Plasticizers are chemical compounds added in hard thermoplastic polymers with an aim to improve its flexibility, extensibility, process-ability, and impact resistance.[12] It also helps in decreasing the glass transition temperature and melt viscosity of the base polymer.[28]

The present work deals with the utilization of ester-amide of RA as a novel primary plasticizer for PVC. Plasticizer was synthesized by a two-step reaction of the RA with DBA and BA using 98% concentrated sulfuric acid as the catalyst. Synthesized ester-amide plasticizer was characterized for acid value, amine value, hydroxyl value, specific gravity, Brookfield viscosity, rheology, color, and PVC absorption value. Whereas the ester-amide plasticizer incorporated PVC sheets were investigated for mechanical, thermal, rheological, exudation, color, chemical resistance and crystallinity properties.

Acid, amine and hydroxyl values for the synthesized ester-amide plasticizer were determined to be 4.5, 4.3, and 11.7 mg KOH/g sample, respectively. Specific gravity of the plasticizer was measured to be 0.97; whereas, the color rating (Gardener color scale) of the product was determined to be 14 → 15. Viscosity of the ester-amide plasticizer and that of DOP, determined using Brookfield viscometer, were found to be 67 and 53 cps, respectively. Higher viscosity of the ester-amide plasticizer (molecular weight: 513.80 g/mol) is attributed to its higher molecular weight as compared with DOP (molecular weight: 390.56 g/mol); and also to the higher level of intermolecular forces of attraction caused due to the presence of tertiary amide linkage in addition to the ester linkage. Yield of the ester-amide plasticizer synthesized using the two step process was determined to be 84.5%; which is high enough to make the process economically viable.

FT-IR Analysis. FT-IR spectrum obtained for the ester-amide plasticizer is shown in Figure 2. Small band at 3377.97 cm^{-1} is
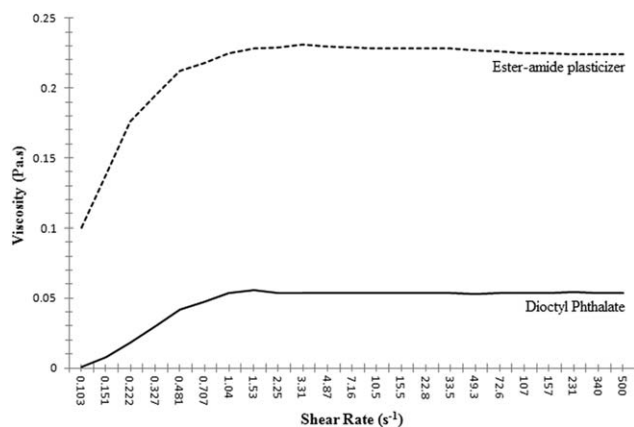
Figure 3. Plot of viscosity (Pa s) versus shear rate (s^{-1}) obtained for the ester-amide plasticizer and DOP.

attributed to the unreacted hydroxyl group ($-OH$) of RA. Bands at 2927.94 cm^{-1} and 2856.58 cm^{-1} were due to asymmetric and symmetric stretching of $-CH_2$ group present in the long chain of RA or that in the structure of DBA. A small peak at 1718.58 cm^{-1} corresponds to the ester linkage ($C=O$), formed by the reaction of RA with BA. Carbonyl band ($-CON<$) of ester-amide was observed at 1629.85 cm^{-1}, validating the reaction between RA and DBA. Band at 1462.04 cm^{-1} belonged to the stretching vibration of $C-N$. Peak observed at 1377.17 cm^{-1} was caused due to the $C-H$ bending mode of $-CH_2$; while the bending vibrations of methyl ($-CH_3$) group was confirmed by the peak at 1273.02 cm^{-1}. $C-O$ stretching peak was seen at 1215.15 cm^{-1}. $C-O-C$ stretching peak was obtained at 1112.93 cm^{-1}, confirming the reaction between RA and BA. The strong peak at 750 cm^{-1} corresponded to the $C-C$ deformation. Sharp peaks at 711.73 and 667.37 cm^{-1} are attributed to the vibrations of the $C-C$ linkage present in the benzene ring of BA. FT-IR analysis thus proves that the compound formed was an ester-amide.

Rheological Analysis. PVC and the additives added to it, including filler and plasticizer, are processed in multiple stages. These stages can be broadly classified into dry blending and melt blending. There are varied type of equipments used in the process of dry blending (high speed mixer, ribbon blender, tumbler, etc.) and melt blending (extrusion, two-roll mill, batch mixer, etc.). Each of this process applies varied level of shear rates and temperature on the material being processed. Brookfield viscometer provides viscosity information for the plasticizer at a particular shear rate and temperature. However, it is very essential to know the effect of varied shear rate and temperature on the ingredients to be added in PVC, including plasticizer. Rheological analysis will provide additional information regarding the way they will blend with PVC and the preventive measures to be taken. Thus, in this study synthesized ester-amide plasticizer and commercial PVC plasticizer (DOP) were subjected to rheological analysis in order to understand the effect of shear rate and temperature on their flow behavior.

Plot of viscosity (Pa s) versus shear rate (s^{-1}) obtained for the ester-amide plasticizer and DOP is shown in Figure 3. Viscosity of ester-amide plasticizer was found to be higher than that of

DOP; which is in corroboration with the viscosity determined using Brookfield viscometer. Viscosity of DOP increased from 0.1 s^{-1} to 1 s^{-1} and then remained strictly constant at higher shear rates; which denotes Newtonian behavior. Whereas, in case of the ester-amide plasticizer, viscosity increased from 0.1 s^{-1} to 1 s^{-1} followed by slight decrease at higher shear rates; thus, demonstrating non-Newtonian shear-thinning behavior. This might have caused due to its high molecular weight and also due to the increased level of intermolecular hydrogen bonding attributed to the presence of tertiary amide linkages in its molecular structure. Initial increase in viscosity, from 0.1 s^{-1} to 1 s^{-1} shear rate, for both DOP and the synthesized ester-amide, might have occurred due to the molecular acclimatization to the shearing phenomena. However, on being acclimatized to the shearing phenomenon, they displayed their actual flow behavior. Thus, it can be said that shear rate has effect on the flow behavior of the ester-amide plasticizer.

Effect of temperature on the flow behavior (viscosity) of the plasticizers is illustrated in Figure 4. Viscosity of both ester-amide plasticizer and DOP decreased with increase in temperature; however, the rate of decrease in the viscosity of ester-amide plasticizer was highly appreciable as that compared with DOP. This is attributed to the demonstration of non-Newtonian behavior by the ester-amide plasticizer. Interestingly, at temperatures above 100°C, viscosity of ester-amide plasticizer was comparable to that of DOP. Thus, it can be said that at processing temperature of PVC (~180°C), synthesized ester-amide plasticizer will have similar flow behavior as that of DOP; and could have similar ability to mix with PVC. Viscosity of ester-amide plasticizer was higher than that of DOP at temperatures below 100°C.

Plasticizer Demand for PVC. The plasticizer absorption value for ester-amide plasticizer and DOP were determined to be 42.8 and 53.4 g/100 g of PVC, respectively.

PVC Sheets Prepared by the Addition of Ester-Amide Plasticizer

FT-IR Analysis. FT-IR spectra obtained for the prepared PVC sheets are shown in Figure 5. Peak at 2911 cm^{-1} is due to the $-CH$ stretching. Peak at 560 cm^{-1} correspond to the vibrations
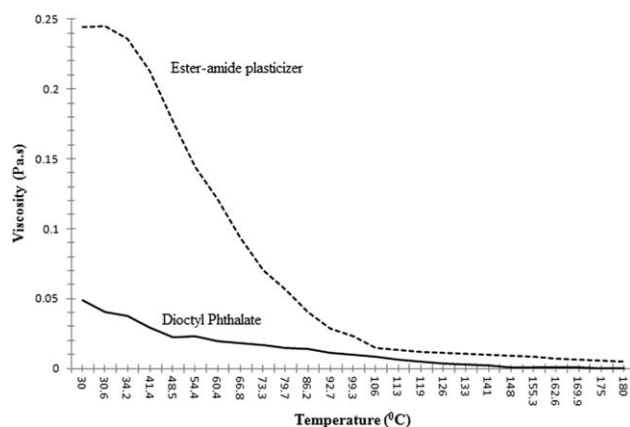

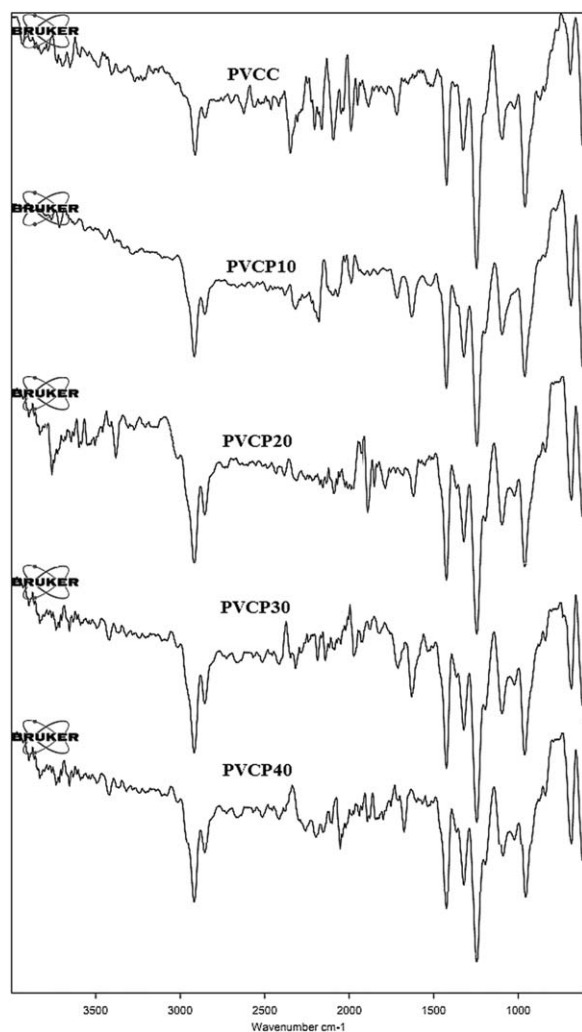**Figure 4.** Plot of viscosity (Pa s) versus temperature (°C) obtained for the ester-amide plasticizer and DOP.

Figure 5. FT-IR spectra obtained for the prepared PVC sheets.

of the —CH$_2$ groups, while, the peak at 1415 cm^{-1} is caused by the symmetric scissoring vibrations of the —CH$_2$ groups. PVC shows its characteristic peaks at 961 and 685 cm^{-1}. There are many other peaks observed, however, this are prominent and important peaks. Additional peaks were observed in PVCP10, PVCP20, PVCP30, and PVCP40 due to the addition of the ester-amide plasticizer. C=O linkage of plasticizer showed its characteristic peak at 1717 cm^{-1}. Whereas, the C—O stretching and C—N stretching vibration peaks are observed at 1215 and 1425 cm^{-1}, respectively.

Wavenumber of PVC characteristic peaks, C=O linkage, C—O stretching, and C—N stretching vibration shifted to higher values on addition of the ester-amide plasticizer in PVC (Table II). No appreciable change was observed in the wavenumber values of the other peaks mentioned above. Thus, it can be said that there are interactions happening between the added ester-amide plasticizer and the PVC polymer chains; and the intensity of this interaction increased with increased addition of the ester-amide plasticizer in PVC. Hence, the synthesized ester-amide plasticizer can be considered to be compatible with the PVC.[37] Similar results have been reported by Yin *et al.*[36] for the glucose ester-based bioplasticizer added PVC films.

Mechanical Property. PVC shows the presence of dipole-dipole interactions caused due to the electrostatic forces of attraction between the chlorine atom from one PVC polymer chain to that of the hydrogen atom of the another PVC polymer chain; making it a tough and hard material. Addition of plasticizer to PVC lowers its strength and modulus at the same time as its elongation is enhanced. This is attributed to the weakening of the PVC dipole-dipole interactions by the presence of the plasticizer, acting as spacers between the former links. Decreased modulus is one of the most important contributions from the plasticizer as this increases the flexibility of PVC material, extending its application area.

Tensile properties like tensile strength (MPa), tensile modulus (MPa), and elongation at break (%) are summarized in Figure 6(A); while flexural properties (flexural strength, MPa and flexural modulus, MPa) and impact strength (J/m) are shown in Figure 7. PVCC was determined to have tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, and impact strength values of 53.4 MPa, 2401.1 MPa, 3.4%, 93.1 MPa, 8554.1 MPa, and 15.9 J/m, respectively. Values of tensile strength, tensile modulus, flexural strength, and flexural modulus decreased; while, that of elongation at break and impact strength increased with increased addition of ester-amide as a primary plasticizer in PVC. The synthesized ester-amide plasticizer acted as spacer between the PVC polymer chains, decreasing its dipole-dipole interactions, thus increasing the mobility of the polymer chains. This increases the flexibility and softness of the PVC material. In addition, the ester-amide plasticizer was supposed to have better compatibility with PVC polymer chains due to the polarity induced by the presence of the ester, tertiary amide and polarizable benzene ring in its molecular structure (proven by the FT-IR analysis mentioned earlier). Thus, the ester-amide plasticizer is better able to

Table II. Effect of Ester-Amide Plasticizer Addition on the Wavenumber of Specific Peaks of PVC and Ester-Amide Plasticizer

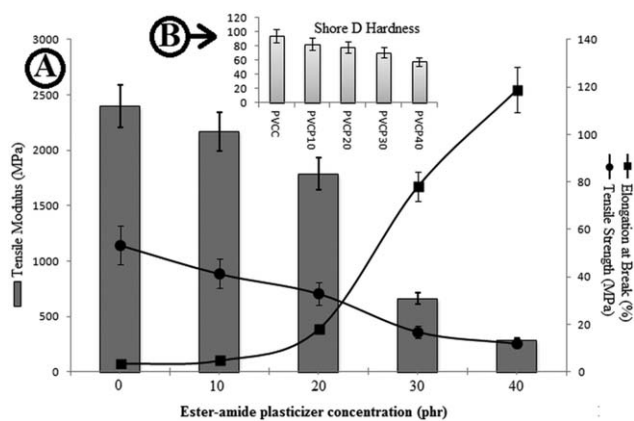| FT-IR peaks	Sample name					Trend
	PVCC	PVCP10	PVCP20	PVCP30	PVCP40	
Characteristic PVC peaks	961.00	962.65	963.37	965.01	966.12	Increased
	685.74	688.89	686.66	687.98	689.04	Increased
C=O linkage of plasticizer	–	1710.25	1711.55	1713.18	1738.80	Increased
C—O stretching	–	1215.15	1246.10	1249.19	1251.18	Increased
C—N stretching vibration	–	1425.69	1454.87	1462.04	1464.61	Increased

Figure 6. Summarization of (A) tensile strength, tensile modulus and elongation at break and (B) Shore D hardness values obtained for the PVC/ester-amide plasticizer sheets.
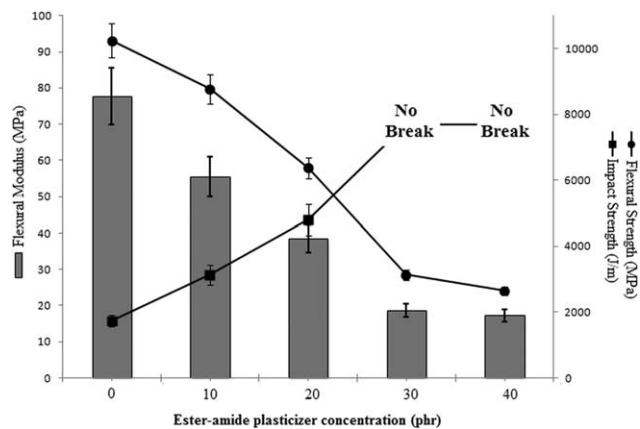

Figure 7. Summarization of flexural strength, flexural modulus, and impact strength values obtained for the PVC/ester-amide plasticizer sheets.

disperse into the PVC polymer matrix and place itself in between the PVC polymer chains. The distance between the PVC polymer chains increased with increased addition of ester-amide plasticizer, further decreasing its strength and modulus property; however, increasing the elongation and impact strength property. Similar trend in mechanical properties had been reported by Yin *et al.* for the PVC added with glucose hexanoate ester as primary plasticizer.[36] Obtained values are very much in correlation with the DOP added in similar concentration in PVC sheets.[39]

For PVCP40 (i.e. PVC loaded with 40 phr of ester-amide plasticizer) tensile strength, tensile modulus, flexural strength, and flexural modulus decreased by 77.8, 88.2, 74.2, and 77.9% respectively; whereas, elongation at break increased by about 35 times. However, samples of PVCP40 were very flexible and thus were not able to show break in the impact test. These changes in the mechanical properties are highly appreciable considering the quantity of ester-amide plasticizer added.

Shore D Hardness. Values of Shore D hardness obtained for the ester-amide plasticizer added PVC samples is summarized in Figure 6(B). PVCC was determined to have hardness value of 94; which decreased gradually with increased addition of ester-amide plasticizer in it. Hardness value decreased to 58 for PVCP40, which is a decrease of 38%. Ester-amide plasticizer dispersed uniformly in to the PVC polymer matrix due to the presence of polar groups like ester, tertiary amide, and polarizable benzene ring in its molecular structure. Thus, it was able to interact with the C—Cl polar linkage in the PVC backbone chain. This plasticizer acted as spacer between the PVC polymer chains decreasing the intensity of inter-molecular forces of attraction; which led to decrease in the number of polymer chains per unit area (i.e. packing density) and thus crystallinity. As a result PVC becomes softer and flexible on addition of ester-amide plasticizer. This is revealed in the hardness property; as softer the PVC becomes easier it is for the pin of the hardness tester to penetrate the surface.

X-ray Diffraction Analysis. X-ray diffractograms obtained for the PVCC and PVC/ester-amide plasticizer sheets is summarized

in Figure 8. Values of crystallinity are also reported in the figure at a place very close to the respective curve. No appreciable change was observed in the shape of the X-ray diffractograms; however, the change in the values of crystallinity was appreciable, on addition of ester-amide plasticizer in PVC. PVCC was determined to have crystallinity of 8.2%; which decreased up to 3.1% for PVCP40. Crystallinity of PVCP40 decreased by about 62%; which is a considerable decrease compared with the quantity of ester-amide plasticizer added. This analysis is in correlation with the mechanical properties investigated; and thus confirms the plasticization effect induced by ester-amide in PVC. Ester-amide plasticizer disperses uniformly in the PVC polymer matrix, due to better compatibility between them, and places itself in between the PVC polymer chains. This leads to decrease in the intermolecular forces of attraction between the PVC polymer chains, decreasing the molecular alignment and hence the crystallinity.

Thermal Property. Glass transition curves obtained for the prepared PVC/ester-amide formulations are illustrated in Figure 9. Single glass transition temperature (T_g) values indicate good miscibility of the plasticizer in to the PVC matrix. PVCC was found to have T_g of 85.1°C, which is in correlation with the T_g values for unplasticized PVC reported in literature.[39] T_g values for PVC decreased gradually on addition of ester-amide
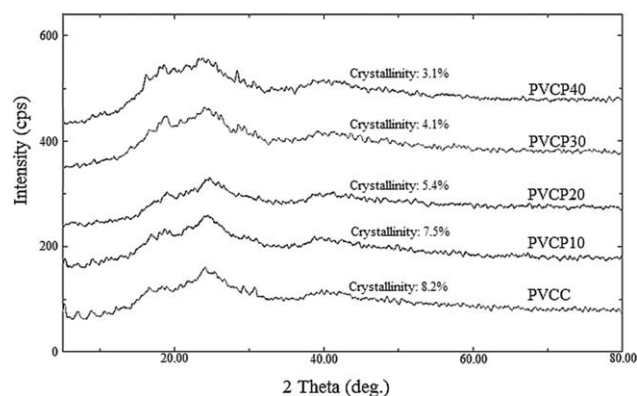

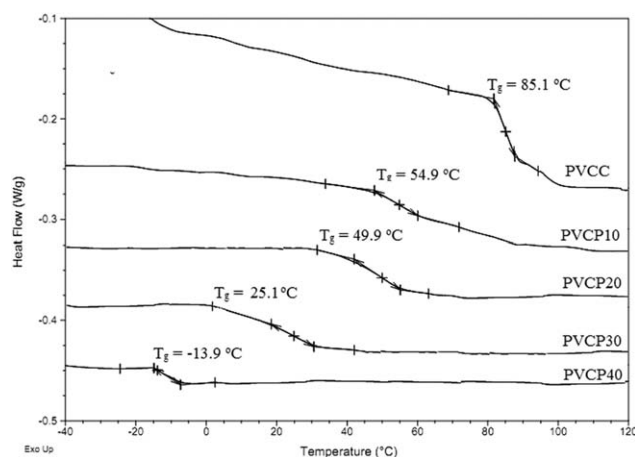**Figure 8.** X-ray diffractograms obtained for the PVCC and PVC/ester-amide plasticizer sheets.

Figure 9. Glass transition curves obtained for the prepared PVCC and PVC/ester-amide formulations.

Figure 10. Plot of viscosity (Pa s) versus shear rate (s^{-1}) obtained for the prepared PVCC and PVC/ester-amide plasticizer sheets.

plasticizer. T_g decreased to $-13.9°$C for PVCP40; which is a remarkable decrease of about 95°C on just 40 phr addition of ester-amide plasticizer. T_g for 40 phr DOP added PVC was reported to be about $-25°$C.[29] Value of T_g determined for PVCP40 is very close to that of 40 phr DOP added PVC. Thus, it can be said that ester-amide of RA has plasticization similar to that for DOP.

Decrease in the T_g of PVC is a clear indication of the plasticization phenomena happening in it due to the addition of ester-amide plasticizer. This trend observed in the values of T_g is in correlation with the mechanical and X-ray crystallinity properties mentioned above. This is attributed to the increased distance between the PVC polymer chains caused by the ester-amide plasticizer; because of which molecular alignment of the PVC polymer chains decreases, decreasing crystallinity. This is expressed by the decrease in the values of T_g. This corroborates the plasticization of hard and rigid PVC into soft and flexible material by the synthesized ester-amide. Similar trend in the values of T_g gave been reported by Yin *et al.* for the PVC added with glucose hexanoate ester as primary plasticizer.[36]

Rheological Analysis. Plot of viscosity (Pa s) versus shear rate (s^{-1}) obtained for the prepared PVC/ester-amide plasticizer systems is summarized in Figure 10. It was determined that viscosity of all the samples decreased with increase in shear rate, demonstrating shear thinning behavior.[40–42] However, viscosity of PVCC and PVCP10 decreased slightly with increase in shear rate attributed to their rigid, inflexible and hard structure. Ester-amide was utilized as a primary plasticizer for PVC in our study. This ester-amide plasticizer chairs itself in between the PVC polymer chains, decreasing the intermolecular forces of attraction between them (happening due to C—Cl dipole-dipole interactions), making the material soft and flexible. Thus, the rotating spindle of the rheometer easily shears the ester-amide plasticized PVC.

PVCC and PVCP10 demonstrated more or less constant viscosity over the entire shear rate range; however, the viscosity of PVCP10 was comparatively lower. Interestingly, samples of PVCP20, PCVP30 and PVCP40 displayed constant viscosity
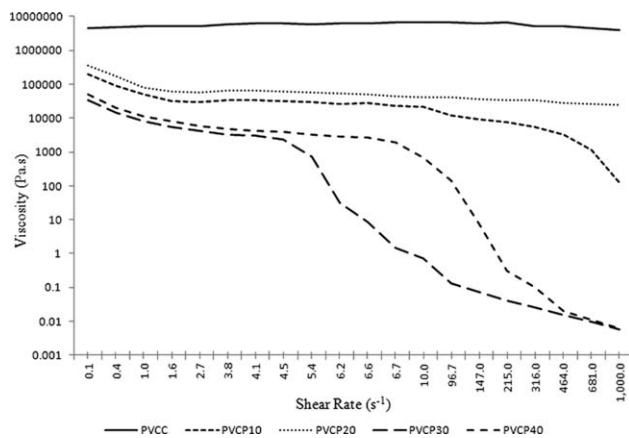
only up to a certain value of shear rate; above which viscosity decreased drastically due to the breakage of the molecular order of PVC. PVCP20 demonstrated constant viscosity up to the shear rate of about 100 s^{-1} and then revealed shear thinning phenomenon. This value of shear thinning point shifted to lower shear rates with increase in concentration of the ester-amide in the PVC polymer matrix; which is 7.5 and 4.5 s^{-1} for PVCP30 and PVCP40, respectively. This is caused by the easy shear thinning of PVC structure on addition of the ester-amide plasticizer due to the plasticization phenomenon. Viscosities of PVCP30 and PVCP40 converged to near about same viscosity value at very high shear rates (>500 s^{-1}) due to the complete rupture of their polymer structure by the shearing force exerted by the rheometer. This was not observed in case of PVCC, PVCP10, and PVCP20 as the concentration of the ester-amide plasticizer was not sufficient so as to plasticize the material, especially PVCC and PVCP10. However, at lower shear rate, samples demonstrated zero-shear viscosity; which shifted to lower values on addition of the ester amide plasticizer; and is attributed to the softness induced by the ester-amide in the PVC matrix.

Plot of storage modulus (MPa) versus angular frequency (s^{-1}), loss modulus (MPa) versus angular frequency (s^{-1}), damping factor (tan δ) versus angular frequency (s^{-1}) and complex viscosity (Pa s) versus angular frequency (s^{-1}) are illustrated in Figure 11(A–D), respectively. Values of both loss and storage modulus increased with increase in angular frequency. However, they decreased with increased addition of ester-amide plasticizer in PVC; but the rate of decrease in storage modulus was more as compared with that of loss modulus. Thus, PVC is expected to behave more as a viscous material, than elastic, on addition of the ester-amide plasticizer. The plot of damping factor versus angular frequency confirmed this observation. Damping factor is a ratio of loss modulus to storage modulus. Damping factor increased with increase in concentration of ester-amide plasticizer in the PVC matrix; suggesting PVC behaving more as a viscous material than elastic. This behavior is attributed to the plasticization effect induced by ester-amide in PVC. Molecules of ester-amide placed themselves in between the PVC polymer chains, increasing the interchain gap between them; thus,
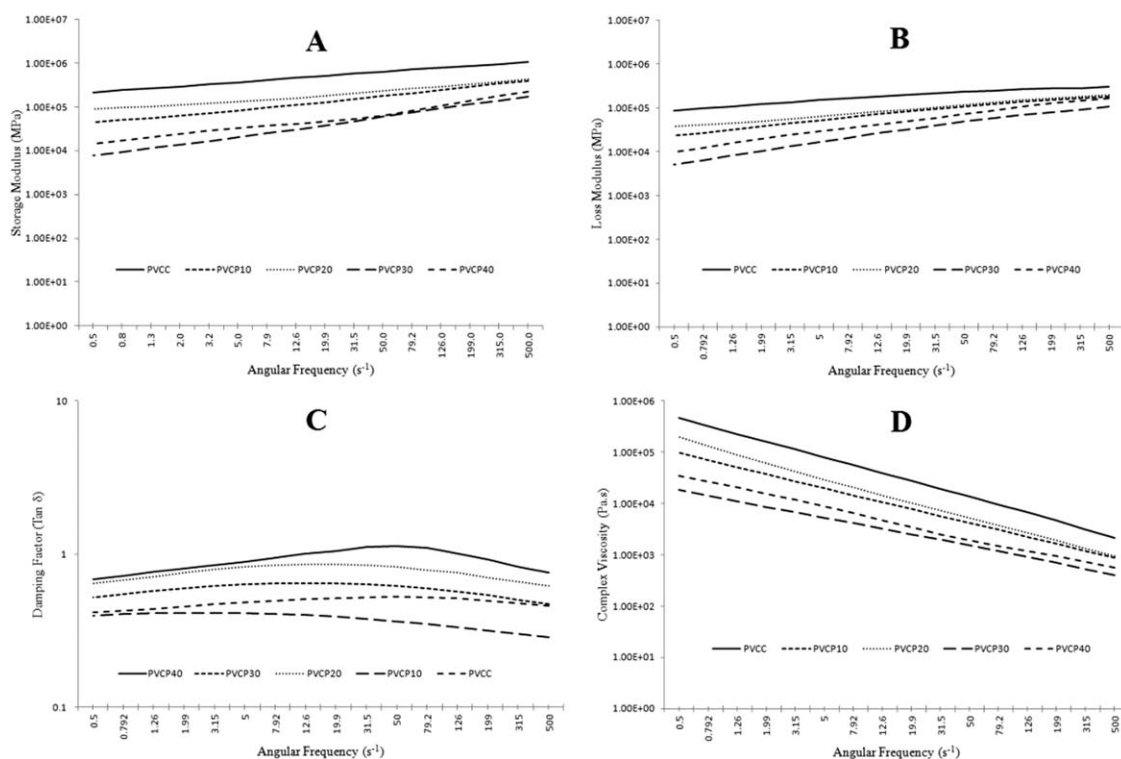
Figure 11. Plot of storage modulus (MPa) versus angular frequency (s^{-1}), loss modulus (MPa) versus angular frequency (s^{-1}), damping factor (tan δ) versus angular frequency (s^{-1}) and complex viscosity (Pa s) versus angular frequency (s^{-1}) are illustrated in A to D, respectively, for the prepared PVCC and PVC/ester-amide plasticizer sheets.

increasing flexibility. Secondly, values of damping factor decreased with increase in angular frequency for PVCC; suggesting the material to be more elastic in nature than viscous. This is attributed to the phenomenon of molecular entanglement and intermolecular forces of attraction occurring in unplasticized PVC. Damping factor increased slightly with increase in angular frequency for PVCP10, suggesting certain level of plasticization induced by a small quantity addition of the ester-amide plasticizer. However, the concentration of the ester-amide was not enough to bring about an appreciable increase in the flowability of PVC. However, damping factor increased up to a particular value of angular frequency for PVCP20, PVCP30, and PVCP40, and then remained nearly constant at higher angular frequencies. This behavior of change in the nature of damping factor with angular frequency intensified with increased addition of ester-amide in PVC. This phenomenon is attributed to the plasticization induced by ester-amide in PVC.

Complex viscosity of PVC decreased with increase in concentration of the ester-amide plasticizer; which is due to the plasticization effect. However, the values of the complex viscosity differed than that of the (apparent) viscosity determined in the viscosity versus shear rate test. Hence, the samples did not follow the Cox-Merz rule.[43]

Figure 12 shows the variation of viscosity as a function of time at 180°C and constant shear rate of 1 s^{-1} for the prepared PVC/ester-amide samples. Viscosity decreased with increase in time for all the PVCC and PVCP samples. Thus, the prepared PVC samples demonstrated thixotropic behavior. This can be

due to the reversible changes involving the breaking and reforming of the PVC/ester-amide molecular aggregates.[41,42] The breaking and reforming became easy with increase in the ester-amide concentration in PVC. This was attributed to the decrease in the intermolecular forces of attraction in the PVC polymer chains caused by the placing of the ester-amide molecule in between them. Thus, viscosity decreased with increased concentration of ester-amide in PVC.

Colorimetric Analysis. Graph of reflectance versus wavelength (410–750 μm) determined using color spectrophotometer for
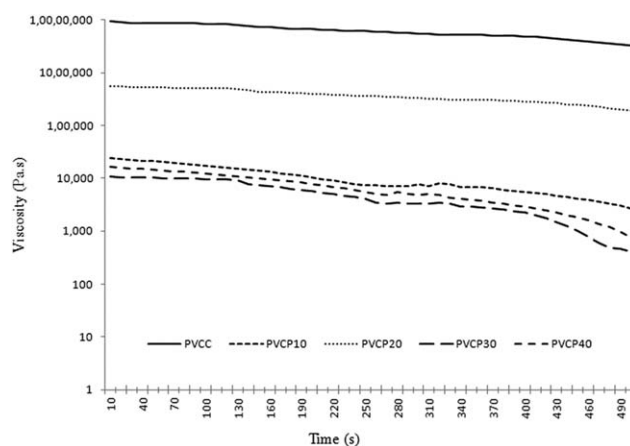

Figure 12. Plot of viscosity (Pa s) versus time (s), at 180°C and constant shear rate of 1 s^{-1}, for the prepared PVCC and PVC/ester-amide sheets.
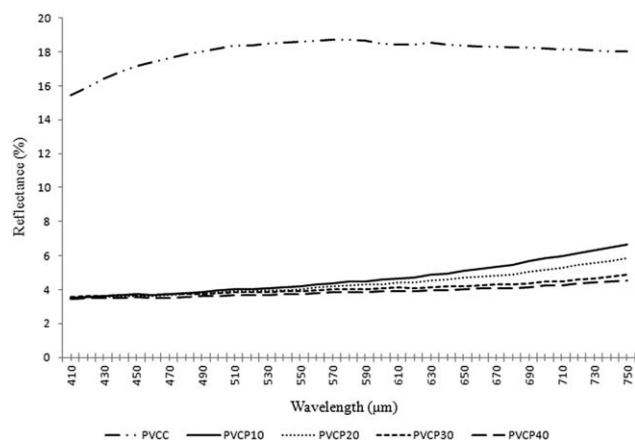
Figure 13. Graph of reflectance versus wavelength (410–750 μm) determined using color spectrophotometer for the prepared PVCC and PVC/ester-amide plasticizer sheets.

Table III. Colorimetric Analysis of the Prepared PVC/Ester-Amide Sheets

Sample name	L^*	a^*	b^*	ΔE	Yellowness index
PVCC	50	0.11	3.19	50.11	50.00
PVCP10	24.52	0.51	2.83	24.73	24.52
PVCP20	23.97	0.52	2.63	24.14	23.97
PVCP30	23.48	1.12	1.58	23.54	23.48
PVCP40	22.88	1.55	1.49	22.38	22.88

the prepared PVC/ester-amide samples is shown in Figure 13. Whereas, the values of L^*, a^*, b^*, ΔE, and yellowness index are listed in Table III. PVCC had higher reflectance than ester-amide added PVC samples in any of the wavelength region selected. Reflectance of PVC shifted to lower level on addition of ester-amide plasticizer; indicating PVC getting darker and thus more absorptive on addition of the ester-amide. However, the ester-amide added PVC samples demonstrated higher reflectance values in the wavelength region from 610 to 750 μm as that compared with lower wavelength region (410–610 μm); indicating the samples getting red colored on addition of ester-amide. PVCC denoted lower reflectance in the wavelength region of 410 to 490 μm; whereas, at higher wavelengths reflectance was near about constant. RA is a dark red colored chemical compound, which on undergoing amidation and esterification reaction with DBA and BA, respectively, becomes even darker red in appearance; which could have caused this lower reflectance in the PVCP samples as compared with PVCC and higher reflectance in the PVCP samples in the 610 to 750 μm wavelength range.

Values of L^*, b^*, ΔE, and yellowness index decreased; whereas, that of a^* increased on addition of the ester-amide plasticizer in PVC. Thus, PVC became blackish, bluish and reddish on addition of the ester-amide in PVC. Importantly, L^*, a^*, b^*, ΔE, and yellowness index decreased appreciably for PVCP10 as compared with PVCC; however remained nearly constant on higher addition of the ester-amide plasticizer. Thus, it can be said that even a small addition (i.e. 10 phr) of the ester-amide plasticizer in PVC

matrix makes it remarkably dark reddish-blue in color. Therefore, the coloration phenomena of this plasticizer can have constraints on the applications in which it could be used. They would be a preferable choice for applications where dark colored pigments are to be employed. Photo of the prepared PVCC and PVC/ester-amide plasticizer added sheets is shown in Figure 14.

Exudation Test. Average exudation of the synthesized ester-amide plasticizer and that of the conventional PVC plasticizer DOP, from the PVC sheets was in the range of 0.1 to 0.5% as can be seen from Figure 15. PVC/ester-amide samples did not show any significant weight loss during the investigational period and the obtained values are at par with that obtained for DOP. This must have been due to the better compatibility of ester-amide plasticizer with PVC polymer chains.

CONCLUSION

Ester-amide of ricinoleic acid (RA) was synthesized by a two-step reaction of RA with dibutyl amine and benzoic acid using 98% concentrated sulfuric acid as the catalyst. Synthesized ester-amide of RA demonstrated higher viscosity than DOP attributed to higher level of intermolecular forces of attraction. Structure of the ester-amide was confirmed by FT-IR analysis. However, the plasticizer was found to be dark red colored. Synthesized plasticizer was determined to have PVC absorption value of 42.8. This synthesized ester-amide of RA was then utilized as primary plasticizer in PVC, with an aim to introduce a new green plasticizer as an alternative for the traditional phthalate based plasticizers. Concentration of the ester-amide plasticizer was varied as 10, 20, 30, and 40 phr in PVC. PVCP40 demonstrated decrease in tensile strength, tensile modulus, flexural strength, flexural modulus and crystallinity by 77.8, 88.2, 74.2, 77.9, and 62%, respectively; whereas, elongation at break increased by about 35 times; which is highly appreciable compared with the quantity of ester-amide added. T_g for PVCP40 decreased to about −13.5°C, comparative to −25° for 40 phr DOP added PVC. Viscosity of PVC decreased

Figure 14. Photos of the prepared PVCC and PVC/ester-amide plasticizer sheets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
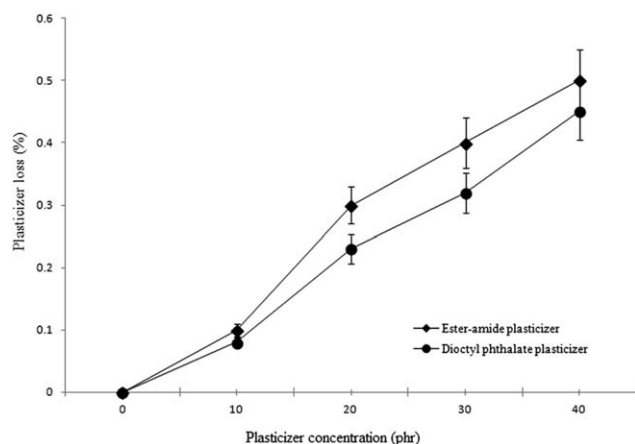
Figure 15. Exudation test results obtained for PVC/ester-amide and PVC/DOP plasticizer sheets.

with increased addition of ester-amide plasticizer in it, demonstrating non-Newtonian shear thinning behavior. PVC/ester-amide samples illustrated thixotropic behavior. The dark color of the samples obtained on addition of the ester-amide of RA in PVC could have constraints on its applications; however, the exudation test revealed the migration stability of the ester-amide plasticizer in PVC.

ACKNOWLEDGMENTS

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