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Correlation between Rheological and Adhesion Properties of Polyamide Hot Melt Adhesive Synthesized from Dimer Acid (Dilinoleic acid) and Ethylene Diamine

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ABSTRACT

The temperature at which hot melt adhesives (HMAs) are applied is very important to be known, as it will strongly affect the rheology of the material, ultimately affecting the adhesion properties. In this study polyamide HMA was synthesized using high purity polymerized fatty acid (dimer acid or dilinoleic acid) and ethylenediamine, and characterized for mechanical, thermal, adhesion and rheological properties. Adhesion joint formation (lap and T-peel) and rheological characterization were performed at varied temperatures – 140, 155, 170, 185 and 200°C to understand the effect of temperature on the properties mentioned and also to correlate them. From the correlative study it was found that 170°C is the best temperature to apply this adhesive. However, it cannot be generalized for other HMAs as it depends on many factors like: molecular weight of the adhesive, molecular weight distribution, type of glue gun, additives added, raw material used to prepare the HMA etc. Too low temperature leads to improper wetting of the substrates, while too high temperature leads to the formation of cross-links in the adhesive leading to optimized temperature of 170°C.

Keywords: *hot melt adhesive, polyamide, rheology, temperature*.

1. INTRODUCTION

Hot-melt adhesives (HMA) are solid adhesives which get converted to a molten liquid state on heating, and applied on to substrates; whereas sets up the bond on cooling [1]. HMAs are solid at temperatures below 80°C. Typical application temperatures are 150-200 °C [2]. Degree of tackiness of the HMA depends on the formulation. Conventional HMAs cool to harden and form bond, and do not undergo chemical cross-linking. HMAs have an open time from few seconds to few minutes [1]. Materials largely used as HMAs are ethylene and vinyl acetate copolymers (EVA), polyvinyl acetates (PVAc), polyethylene (PE), amorphous polypropylene (PP), block copolymers (styrene butadiene rubber, SBR), polyamides (PA) and polyester (PEster) [2].

The key advantage of HMA is their ability of being able to pre-apply e.g. as powder or adhesive spheres, in melt liquid form, as dispersion or as an adhesive foil. Thus, the joining procedure is not required to be carried out directly after applying the adhesive to the substrate; but can happen at any time later on [3]. HMAs are largely used in the manufacture of durable goods, such as in shoe assembly, kitchen and bathroom cabinets, telecommunication cable repair sleeves, and window assembly [4].

The use of polyamides in HMAs was found as early as 1959 [5]. Leoni et al. synthesized polyamide HMA using ethylenediamine, propylenediamine and polymerized fatty acid (PFA) composition containing 97% dimer acid [6]. PFA was reacted with 50 mole% ethylenediamine and 50 mole % propylenediamine. The prepared polyamide HMA had a softening point of 100°C, tensile strength of 8.5 MPa and T-peel strength 1.2 N/mm. Rossini and Meda studied the synthesis of polyamide HMA using PFA composition containing 15% trimer acid, 82% dimer acid and 3 % linoleic acid [7]. Other raw materials used were adipic acid, ethylenediamine and piperazine. Formulation contained 44 mole % PFA, 6 mole % adipic acid, 30.75 mole % ethylenediamine and 19.25 mole % piperazine. Acids and bases were reacted in 1:1 molar ratio. The HMA synthesized had a softening point of 101°C, T-peel strength of 0.72 N/mm and tensile strength of 3.7 MPa. Chen et al. studied the synthesis of polyamides using PFA consisting of 97% dimer acid, reporting mechanical, adhesion and thermal properties [8]. They studied the effect of PFA content and

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piperazine content on the properties of polyamide HMA and found that as the piperazine content increased or PFA content increased, softening point, glass transition temperature, heat of fusion, tensile strength, Shore D hardness, lap shear strength and T-peel strength of the hot melt adhesive decrease, while elongation at break increases. The synthesis of polyamide HMA using PFA (~23 % trimer acid, ~75 % dimer acid and ~3 % linoleic acid), sebacic acid, ethylenediamine and piperazine was studied by Kadam et al. [9]. As the mole percentage of ethylenediamine in the polyamide increased, amorphicity decreased, whereas T_f, H_f, T_c, H_c, T_s, T_g, tensile strength, hardness, LSS, TPS and viscosity increased. Chabert et al. prepared a novel hot melt adhesive by blending a commercial polyamide resin with a semi-crystalline supramolecular polymer in 1:1 ratio (weight basis) [10]. The supramolecular polymer played a dual role in affecting the properties and processability of the polyamide resin as an hot melt adhesive: acted as a reinforcing agent at room temperature and as a plasticizer at higher temperature. The blend material had 6 times higher peel strength than the base polyamide resin. Wang et al. synthesized poly (4, 4′-diphenylsulfone dimeramide) and poly(4, 4′-diphenyl dimeramide) using PFA containing 98% dimer acid and aromatic diamines. The prepared polyamides were found to have melting temperature in between 140 to 180 °C and very good mechanical strength [11]. Kadam and Mhaske investigated the effect of PFA purity on the properties of polyamide HMA synthesized using ethylenediamine. They determined no such appreciable change in the adhesion and mechanical property on using lower purity dimer acid in place of high purity dimer acid [12]. Polyamide HMA synthesized using PFA consisting 97% dilinoleic acid and ethylenediamine, are the very first type of polyamide HMAs; synthesized by Bradley in 1945 [13].

Gibert et al. investigated the rheological properties of industrial EVA and its copolymer based hot melt adhesives over a wide frequency range using time-temperature equivalence [14]. Park et al. determined rheological behavior of EVA based hot melt adhesive containing varied composition of vinyl acetate and blended with varied concentration of aromatic hydrocarbon resin using a Brookfield viscometer [15]. Whereas, Marin et al. determined complex shear modulus of a series of EVA/resin blends has been measured in a broad range of frequencies and temperatures [16]. However, it was found from the literature that there is no detailed analyses regarding the correlation between rheological and adhesion properties of the polyamide based hot melt adhesives. HMAs' are applied using a glue gun at a particular temperature and kept in the gun for a particular time and applied at a particular flow rate. Time, temperature and shearing all affect the flow behavior of this hot melts. Thus, we take this opportunity to determine the effect of these parameters on the rheological behavior of a simple HMA prepared from higher purity PFA and ethylenediamine and correlate it with the adhesion properties. This flow behavior will vary depending on the composition (tackifier, plasticizer, filler and other additives) of the HMA and its chemical structure. Thus, it is required to be analyzed for every such material. Prepared HMA was also characterized for mechanical, thermal, FTIR, acid value and amine value properties.

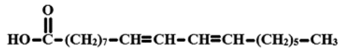
2. EXPERIMENTAL

2.1. Materials

Unidyme 18 (composition: linoleic acid ~1%, dimer acid ~98%, trimer acid ~1%) with an acid value of 198 mg KOH/g was obtained from Arizona Chemicals, Mumbai, India. Ethylenediamine was obtained from Ankita Chemicals, Mumbai, India. All chemical compounds were used as obtained without any modification or purification.

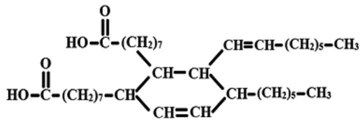
2.2. Preparation of HMA

The molecular structure of the reactants used in the preparation of the HMA is shown in Figure 1 (a-d); whereas their molecular weights are reported in Table 1. In order to obtain high molecular weight polymeric chains, acids and amine were reacted in 1:1 molar ratio.

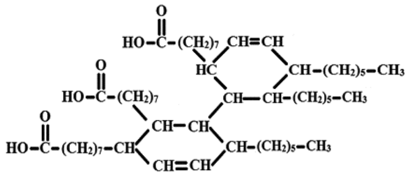


$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_7-CH{=}CH-CH{=}CH-(CH_2)_5-CH_3$

(a) Linoleic Acid



(b) Dimer Acid



(c) Trimer Acid

$H_2N-CH_2-CH_2-NH_2$

(d) Ethylenediamine

Figure 1: Molecular structure of the reactants used in the preparation of the polyamide HMA.

Obtained PFA consists of 98% dimer acid, 1% trimer acid and 1% linoleic acid. Linoloeic acid and trimer acid were present in negligible amount, so their quantities were not considered in calculating the required quantity of ethylenediamine.

Table 1. Molecular weights of the reactants used in the synthesis of polyamide HMA.

Sr. No.	Compound		Molecular weight (g/mol)
1.	Polymeric Fatty Acid (PFA) components	Trimer acid	840
		Dimer acid	560
		Linoleic acid	280
2.	Ethylenediamine		60

Thus, the PFA was supposed to consist of 100% dimer acid. 200 gm of PFA thus had 200 gm of dimer acid and no trimer acid or linoleic acid; i.e. it had 0.36 moles of dimer acid and no moles of trimer acid or linoleic acid. The acid equivalent of PFA is 0.36. Thus, ethylenediamine required was 0.36 moles, which is 21.6 g.

2.3. Experimental Procedure

To a four necked 500 ml reactor equipped with stirring system, condenser, nitrogen gas inlet and temperature controller, 200 g (0.36 mol dimer acid) PFA and 21.6 g (0.36 mol) ethylenediamine were added. The reactants were heated gradually to 240°C with stirring at 1500 rpm, under nitrogen. Acid and amine value of the reacting mixture was measured after every 30 min in order to determine the progress of the reaction. This temperature was maintained till the acid and amine value for the system decreased below or about 10, requiring about 5 h, thus preparing polyamide HMA. Thus the polyamide HMA was prepared by melt polycondensation method without the use of solvent or catalyst. None of the reactants were expected to remain unreacted in the mixture. So, no purification step was thought to be necessary for the final products. Prepared formulation is listed in Table 2.

Table 2. Prepared HMA formulation with nomenclature.

Reactants	PAHMA	
	gm	**mole**
Trimer Acid	-	-
Dimer Acid	200.0	0.36
Linoleic Acid	-	-
Ethylenediamine	21.60	0.36

2.4. Acid and Amine Value

Acid and amine values were determined as per the procedure mentioned by Kadam and Mhaske [10, 14].

2.5. Differential Scanning Calorimetry

Differential scanning calorimetry (Q100 DSC, TA Instruments) was used to investigate the crystallization and melting behavior of the HMA. Two consecutive scans were obtained to minimize the influence of possible residual stresses in the material due to any specific thermal history. A scanning rate of the 10°C / minute was used for both the exo- and endo- thermal cycle with the nitrogen purge at 50 ml/min. The melting temperature (T_m) and enthalpy of melting (H_m) was determined from the second heating scan, while the crystallization temperature (T_c) and enthalpy of crystallization (H_c) was determined from first cooling scan.

2.6. FTIR Analysis

The FTIR spectra were recorded with a PerkinElmer, Spectrum GX equipment. 1-2 wt% solution of HMA was dissolved in chloroform and was scanned with a resolution of 2 cm^{-1} in the scan range of 450–4000 cm^{-1}. FTIR of pure solvent was run prior to running the FTIR of the samples, to use its peaks as baseline, so as to automatically subtract it from the samples peak.

2.7. Mechanical Properties

Tensile strength of compression molded sheet was measured in accordance with ASTM D638 with the crosshead speed of 50 mm/min. Shore D hardness was determined in accordance with ASTM D2240.

2.8. Adhesion Properties

Polyamide adhesive films were also obtained by compression molding. The adhesive joint was then obtained by pressing the film between two pieces of surface treated aluminum adherent at temperatures of 140, 155, 170, 185 and 200°C, and at a pressure of 30 KPa for 20 min, followed by cooling at room temperature for 24 h. Adhesion properties obtained for the joints prepared were correlated with the rheological properties obtained. Lap shear strength was determined according to ASTM D1002-72 at a crosshead speed of 1.3 mm/min. T-peel strength was measured in accordance with ASTM D1876 with a crosshead speed d of 254 mm/min. Average thickness of adhesive layer in the lap and T-peel joints was kept within 0.035 ± 10 % mm (0.001 inch). Tensile test, Lap shear strength and T-Peel strength were all measured using a Universal Testing Machine (LR 50K, Lloyds Instruments, UK).

2.9. Rheological Analysis

A rheometer (MCR 101, Anton Paar, Austria) with a parallel plat assembly was used to investigate the rheological behavior of the prepared HMA. Parallel plates (diameter: 25 mm, D-PP25-SN0) were separated by a distance of 1.0 mm during the rheological analysis. The rheological data analysis was performed using Rheoplus/32V3.40 software supplied by the manufacturer. HMA samples were set on the rheological peltier for 2 min of relaxation before each measurement.

2.9.1. Effect of shear rate at various temperatures

The viscosity (Pa.s) vs shear rate (s^{-1}) was determined at various temperatures – 140, 155, 170, 185 and 200 °C. 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 500 s^{-1} shear rate within the experimental time of 200 s. This study was undertaken to understand the effect of shear rate on the viscosity of the HMA at different temperatures. These temperatures are some of the actual HMA application temperatures. However, the selection of particular temperature and shear rate will depend on the substrates to be joined, thickness of adhesive layer required, HMA application set up etc. This study will however provide knowledge of how the viscosity of the HMA is affected by temperature and shear rate.

2.9.2. Effect of time at various temperatures

The viscosity (Pa.s) vs time (s) was determined at various temperatures – 140, 155, 170, 185 and 200 °C. Twenty five viscosity/time data points were obtained, measured at interval of 10 s, during the shearing of the samples at a constant shear rate of 1s^{-1} within the experimental time of 250 s. This study was undertaken to understand the effect of time on the viscosity (thixotropicity) of the HMA at different temperatures. Selection of particular time will depend on the stability of the HMA and additives added in it (if any), thixotropic nature of HMA etc. This study will however provide knowledge of how the viscosity of the HMA is affected by temperature and time.

2.9.3. Viscoelastic study at various temperatures

2.9.3.1. Stress amplitude sweep: The linear viscoelastic (LVE) region of the sample was determined using a stress amplitude sweep, whereby a range of incremental shear strain from 0.1 to 100 % at constant frequency of 10 rad/s was applied to the sample. This test was also performed at different temperatures – 140, 155, 170, 185 and 200 °C, in order to understand the effect of temperature on the LVE range of the HMA.

2.9.3.2. Frequency sweep:

The sample was oscillated over a range of angular frequencies (0.5-500 s^{-1}), at constant amplitude of 5% within the LVE range at different temperatures -140, 155, 170, 185 and 200 °C, in order to understand the effect of temperature on the frequency sweep test.

3. RESULTS AND DISCUSSION

3.1. Acid and Amine Values

Acid and amine values of the polyamides are listed in Table 3. These values are below or about 10, as targeted. Similar acid and amine values have been reported by many researchers for both academic and commercial polyamide HMAs.

Table 3. Acid and Amine Values obtained for the HMA synthesized.

Characterization	**PAHMA** (mg KOH/g)
Acid Value	10.1
Amine Value	9.7

3.2. FTIR Analysis

FTIR spectra of polyamide HMA is shown in Figure 2. A small band of the amide I (–NH_2 in primary amides) group appeared at 3293.4 cm^{-1}. Peak at 2924.5 cm^{-1} was due to the asymmetric and symmetric stretching of CH_2. The carbonyl peak (-$CONH_2$) of polyamide was at around 1639.9 cm^{-1} (steep peak). Amide II band/CH_2 asymmetric deformation were indicated by the peak of wave-number 1559.9 cm^{-1}. N-H deformation/CH_2 scissoring peak was indicated at wave number 1461.9 cm^{-1}. Peak at 1377.6 cm^{-1} was due to CH_2 wagging. The peak at 1243.9 cm^{-1} was corresponded to C-N stretching vibration bond. Small peak at 719.4 cm^{-1} showed C-C deformation. FTIR analysis thus proves that compound formed was an amide.

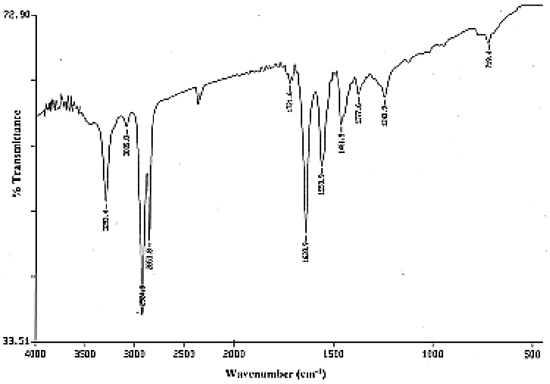


Figure 2: FTIR spectra obtained for the prepared polyamide HMA.

Table 4. Thermal properties of the HMA synthesized.

Characterization	**PAHMA**
Melting Temperature (T_m, °C)	98.99
Enthalpy of melting (H_m, J/g)	16.93
Enthalpy of Crystallization (H_c, J/g)	20.54
Crystallization Temperature (T_c, °C)	87.47

3.3. Differential Scanning Calorimetry

DSC thermograms for the enthalpy of melting (H_m) and enthalpy of crystallization (H_c) of the synthesized HMA is shown in Figures 3 and 4 respectively. Values of T_m, T_c, H_m and H_c of the HMA are listed in the Table 4. It was found that T_c was lower than T_m, however H_c was higher than H_m. Thus, the prepared HMAs would require lesser amount of energy for melting, but will release higher amount of energy during the cooling process. Thus, this HMA can be applied using a glue gun at any temperature above 100 °C, as it will be in a completely molten form. However, practically HMAs are applied at temperatures T_m+40 °C, as the HMA will be in a state of continuous movement when it will be applied using a glue gun. This continuous movement may not give it sufficient time to absorb heat and get converted into molten form. So, it's always safe to apply HMA at a temperature higher than T_m.

3.4. Mechanical Properties

Table 5 lists the tensile strength, % elongation at break and shore D hardness values obtained for the prepared polyamide HMA.

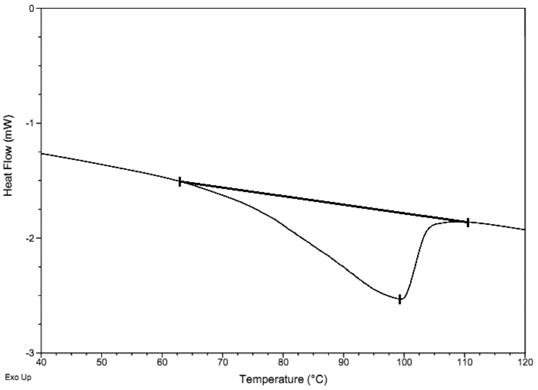


Figure 3: Heating curve obtained for the polyamide HMA using differential scanning calorimetry.

These values are in very much correlation with the published literature. It can be seen that this polyamide HMA is not a very elongating material. This is attributed to the molecular structure of this HMA (scheme 1). The amine used in our study is ethylenediamine, which is the smallest diamine available. It makes the dimer acid molecules come closer, decreasing the level of flexibility. Flexibility is also low due to the knotting effect caused but this smallest ethylenediamine molecule.

3.5. Rheological Properties

4.5.1. Effect of shear rate at various temperatures

Figure 5 is a plot of viscosity (Pa.s) vs shear rate (s^{-1}) obtained for the prepared polyamide HMA. This study provides insights into the effect of shear rate on the flow behavior of the HMA prepared. As, this test was also performed at varied temperatures, it enhances the knowledge regarding the effect of temperature on its flow behavior.

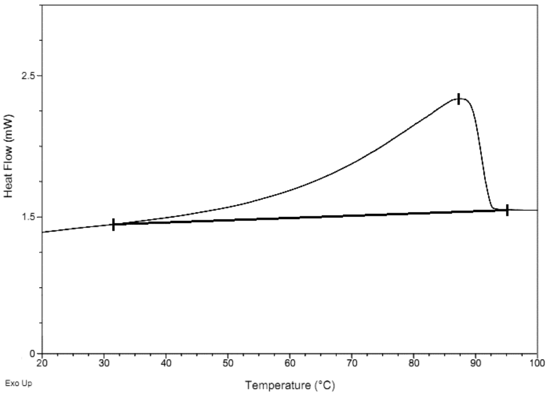


Figure 4: Cooling curve obtained for the polyamide HMA using differential scanning calorimetry.

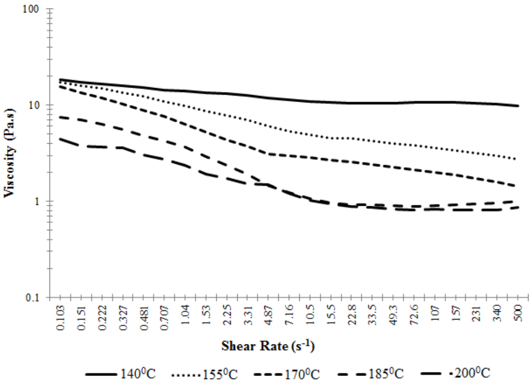


Figure 5: Plot of viscosity (Pa.s) vs shear rate (s^{-1}) obtained for the polyamide HMA at different temperatures.

Table 5. Mechanical properties of the HMA synthesized.

Characterization	PAHMA
Tensile Strength (MPa)	8.35
Elongation at break (%)	4.75
Shore D hardness	72.00

It was determined that the viscosity of the HMA samples, tested at varied analysis temperatures, decreased with increase in shear rate. Thus, all the samples exhibited non-Newtonian shear thinning behavior. Secondly, it can be seen that at lower test temperature, the viscosity didn't decrease much, however, the rate of decrease of viscosity with shear rate increased with increase in the analysis temperature. Plot obtained for the test performed at 200 °C, viscosity is decreasing drastically with the curve falling unevenly. This type of behavior was not observed in the curves obtained for the test performed at lower temperatures; they all had smooth curves.

At lower temperature (140 °C), energy provided to the polyamide HMA was not sufficient to make them undergo flow to the extent possible at higher temperatures. Intermolecular forces of attraction were sufficiently strong to resist the forces exerted by the rotating spindle of the rheometer. However, higher temperature increases the vibrational motion in the polymer molecules making them loose their intermolecular forces of attraction and undergo easy movement. Thus, the resistance exerted by the polyamide molecules to the rotating spindle of the rheometer, decreases with increase in temperature. However, at 200 °C, temperature must be more than required, which might have caused some degradation or cross-linking into the polymer structure, as evident from the uneven flow curve shape.

From the flow curves obtained, it can be said that 185 and 170 °C are the best temperatures to apply this HMA so as to get the best possible flow properties in the HMA, in the temperature ranges we selected. At low temperature (140 °C) the decrease in the viscosity of the HMA is not sufficient, to bring about proper wetting of the substrates to be joined. Whereas, too high temperature (200 °C) brings about molecular changes in the material, making the wetting of the substrates uneven. This can be confirmed by the adhesion test, explained later.

3.5.2. Effect of time at various temperatures

This study was undertaken to understand the effect of time on the rheological flow behavior (thixotropicity) of the prepared polyamide HMA. Again, this analysis was performed at varied temperature – 140, 155, 170, 185 and 200 °C, so as to investigate the effect of temperature on the thixotropicity of the polyamide HMA. Obtained graph for thixtropy study of the prepared polyamide HMA at various is shown in Figure 6.
It was determined that the viscosity of all the test samples, tested at varied temperatures, decreased with increase in time. This test was performed at a constant shear rate – $1s^{-1}$. Thus, all the samples demonstrated thixotropic nature. However, HMA sample tested at lower temperature (140°C) showed faint decrease in viscosity with time; whereas as the temperature of analysis increased, the thixotropic nature of the HMA increased i.e. viscosity decreased more drastically with increase in time at a particular shear rate. But, at the analysis temperature of 200°C, the curve obtained for the viscosity vs time was wavy and uneven, demonstrating some degradation or cross-linking into the polymer structure, due to the sufficiently high temperature.

Thus, it can be said that at lower temperature (140 °C) the polyamide HMA is very stable with respect to time. The material can sustain any time lapse during the application of the material using a glue gun and can be hold in the glue gun for some time without expecting any changes in its rheological behavior. However, as temperature increases, the vibrational motion of the polymer molecules increases, and they become more flow-able, bringing about changes in the rheological flow behavior and the stability of the HMA decreases with respect to time. Thus, one needs to be precautious as to how much time one can be safe for keeping the HMA in the glue gun without expecting appreciable change in the viscosity. But the very high temperature of 200 °C is not recommended, due to the wavy nature of the flow curve, making the flow behavior of the HMA unpredictable.

3.5.3. Viscoelastic study at various temperatures

3.5.3.1. Stress amplitude sweep:

Amplitude sweep test is used to obtain the linear visco-elastic (LVE) range of the polyamide HMA. The position and length of the straight portion of the curve indicates the ability of the sample to resist flow and its stability over a range of stresses. In the LVE region, the shear stress (s) is proportional to the shear strain (g) and the rheological parameters (G' and G") are expected to be independent of the magnitude of the applied stress. In order to establish the LVE region, the rheological parameters are measured as a function of strain amplitude at a fixed frequency. Once the linear viscoelastic region is established, measurements are then made at fixed stress amplitude (within the LVE region) as a function of frequency.

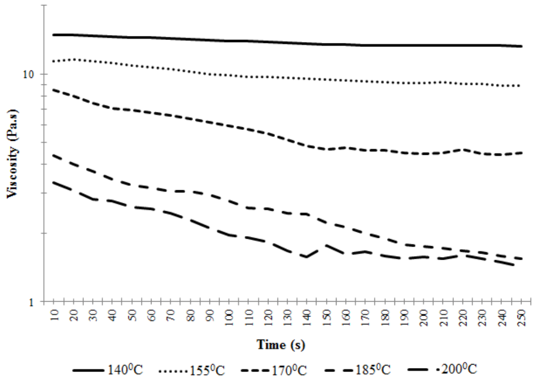


Figure 6: Plot of viscosity (Pa.s) vs time (s) obtained for the polyamide HMA at different temperatures.

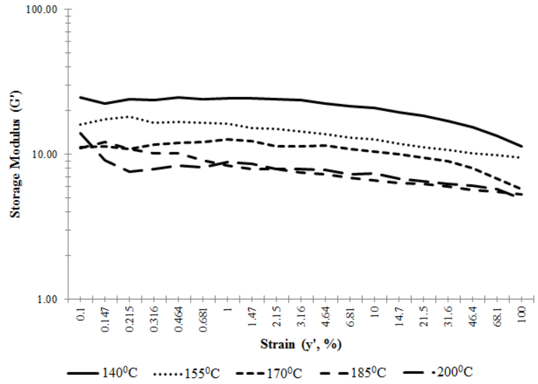


Figure 7: Plot of storage modulus (G') vs strain (%) obtained for the polyamide HMA at different temperatures.

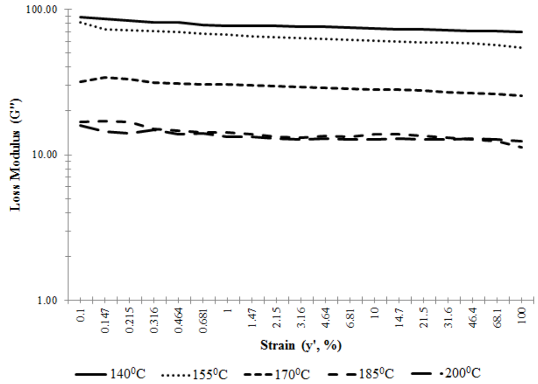


Figure 8: Plot of loss modulus (G") vs strain (%) obtained for the polyamide HMA at different temperatures.

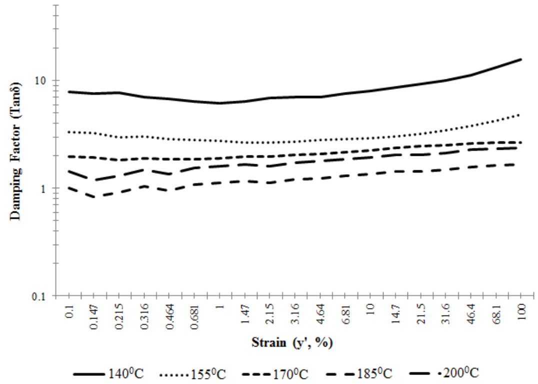


Figure 9: Plot of damping factor (Tanδ) vs strain (%) obtained for the polyamide HMA at different temperatures.

Figures 7 and 8 plot the storage modulus (G') vs strain (y', %) and loss modulus (G") vs strain (y', %) obtained for the prepared polyamide HMA. It was determined that plots of storage modulus remained near about linear upto a certain strain % and then started decreasing with increase in strain %. However, the point from which this decrease started shifted towards left (lower strain %) with increase in the analysis temperature. This approximate point of strain % from where the values of storage modulus started decreasing for various temperatures is listed in Table 6. It can be seen that the values of starin % listed in Table 7 are decreasing drastically as compared to the increase of temperature. Thus it can be said that the polymer molecules of polyamide HMA gest easily sheared at lower stain % with increase in temperature. Thus, the adhesive can be easily applied on the substrates with lower back force coming on the glue gun during application. Secondly, it can be seen that the curves of storage modulus are shifting down as a whole with increase in temperature. This indicates decrease in the elastic nature of the polymer molecules with increase in temperature. Higher analysis temperature enables the HMA polymer molecules to move past each other easily instead of remaining entangled, thus, decreasing the resistance to movement exerted on the rotating spindle of the rheometer. However, from the plot one can choose 5% strain to determined the effect of varying frequency on the damping factor and comples viscosity, as upto that particular value all the plots show near about linear trend in their values both in loss modulus and storage modulus graphs.

Table 6. Values of strain % from where the values of storage modulus started decreasing for various temperatures.

Analysis temperature (°C)	Strain (y', %)
140	45.8
155	31.5
170	29.4
185	10.5
200	6.8

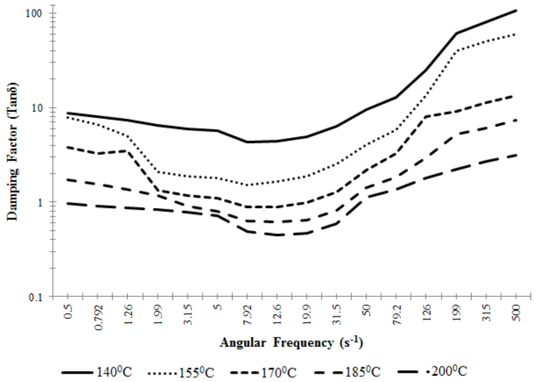


Figure 10: Plot of damping factor (Tanδ) vs angular frequency (s^{-1}) obtained for the polyamide HMA at different temperatures.

Plot of loss modulus (G") vs strain (y', %) also shows similar trend. However, the overall values of loss modulus for any particular temperature are higher than storage modulus. Thus, indicating the easy flow behavior of the material. This HMA is more viscous than elastic, making this material better able to wet the substrates to be joined. Damping factor (Tan δ) is a ratio of loss modulus (G") to storage modulus (G'). It gives clear idea of the viscoelastic nature of the material. However, in this study we can know the effect of % strain on the viscoelastic nature of the material and not that of angular frequency. Damping factor (Tan δ) vs strain %) in plotted in Figure 9. It was found that Tan δ increased with increase in % strain, but the increase was negligible upto a certain value and after that increased more intensely. This point of increase can be seen to have shifted towards left (lower % strain) with increase in temperature. Tan δ values were higher than 1, indicating higher loss modulus values as compared to storage modulus values, which indicates the HMA being more viscous than elastic. But, the plots of Tan δ shifted downwards with increase in temperature, which was due to the higher vibrational motion induced into the HMA polymer chains because of increased temperature, making them unable to resist the spindle motion as that possible at lower temperature. Initial values of Tan δ for the sample analyzed at 200 °C were below 1. This indicates that at lower strain % samples were more elastic than viscous, which might have happened due to the cross-linking effect caused at such high temperature. Thus it is preferred to apply this polyamide HMA at lower temperatures than 200 °C. However, frequency sweep test will provide better insight into this investigation.

3.5.3.2. Frequency sweep:

Plot of damping factor (Tanδ) vs angular frequency (s^{-1}) is illustrated in Figure 10. All the samples showed similar trend in their curve shape. It was found that initially all the samples had nearly a constant Tanδ, upto a certain angular frequency, however, decreased later giving a bell shaped curve and eventually again increased at the last. The increase in the values of Tanδ at the last (or higher frequency) was higher than the constant Tanδ obtained at lower angular frequency. All the curves shifted down with increase in the analysis temperature. Also, it was determined that the point of angular frequency from where Tanδ started decreasing, shifted towards left with increase in analysis temperature upto 170 °C and then shifted towards right for 185 and 200 °C. Lastly, it can be seen that the area of the bell shaped part of the curve is decreasing with increase in the analysis temperature.

As the HMA, at any analysis temperature, had Tanδ value higher than 1 (except for the HMA analyzed at 200°C), it can be said that all had higher viscous nature than elastic nature. The curves shifted down due to the increase in the analysis temperature, which led to increased vibrational motions in the polyamide HMA polymer molecules making them resist less to the rotating spindle of the rheometer. Tanδ values of HMA sample analyzed at 200 °C, even certain Tanδ values of sample analyzed at 185 °C, were lower than 1. Thus they had higher elastic nature than viscous at those particular frequencies and are unacceptable for adhesive application, as they will not be able to wet the substrates to be joined. This could be due to the possibility of cross-linking happening in the polyamide HMA at those higher temperatures. So, from the frequency sweep test 170 °C can be chosen as the best temperature for application of this adhesive to give better wetting of the substrates at lowest possible temperature. Tanδ values were higher at higher angular frequency than that at lower angular frequency due to the shearing action caused due to the rotating motion of the spindle, which made the polyamide HMA polymer chains move past each other easily making them behave more as viscous than elastic.

3.6. Adhesion Properties

Adhesion properties like T-peel strength and lap shear strength obtained for the adhesion joints prepared at varied temperature – 140, 155, 170, 185 and 200 °C are listed in Table 8.

Table 7. Adhesion properties of the HMA synthesized.

Analysis Temperature (°C)	T-Peel strength (N/mm)	Lap Shear strength (MPa)
140	7.5 ± 0.2	4.4 ± 0.1
155	8.8 ± 0.3	5.3 ± 0.2
170	10.9 ± 0.3	6.8 ± 0.2
185	9.8 ± 0.4	6.2 ± 0.3
200	7.1 ± 0.3	4.1 ± 0.1

It can be seen that the T-peel strength and lap shear strength increased with increase in the joint formation temperature, but started decreasing from 185 °C. Highest values were obtained for the joints formed at 170 °C, whereas the lowest were determined at 200 °C. Difference in adhesion values for joints formed at 170 and 185 °C are minimum, but correlated with rheological properties (especially the frequency sweep test), joint formed at 170 °C illustrated higher performance as compared to 185 °C.

Temperatures of 140 and 155°C were not sufficient to convert the polyamide HMA into the highest possible molten state so as to get best possible wetting of the substrates. However, at higher temperatures of 185 and 200 °C, due to the formation of cross-linked structure the HMA would not have had enough wetting of the substrates, as crosslinking decreases adhesion property of the material by increasing its cohesive property, leading to decrease in the joint strength. So, 170 °C is the best temperature to apply this particular polyamide HMA.

I would like to bring it to notice that, this particular study was carried out for polyamide HMA based on high purity dimer acid and ethylenediamine polymerized to get an acid and amine values of about 10. Rheological properties and adhesion values will vary depending on the molecular weight of the polyamide, its molecular weight distribution, adhesive application method, test conditions etc. But, this study aims to provide an insight in the utilization of rheological analysis to predict the adhesion properties of the HMA.

4. CONCLUSION

Polyamide hot melt adhesive with acid value of about 10 had been successfully prepared and characterized for FTIR, mechanical, thermal, rheological and adhesion properties. It was found that the prepared HMA had mechanical and thermal properties in correlation with the values reported in literature. Prepared HMA was made to form adhesive joint at varied temperature – 140, 155, 170, 185 and 200°C using a compression molding machine and the same was analyzed for rheological properties at same temperature to correlate the two properties. It was found that at lower temperatures -140 and 155°C, HMA had very high viscosity because of which it was not able to wet the substrates properly demonstrating lower adhesion values; whereas, at very high temperatures due to the effect of cross-linking it demonstrated uneven rheological behavior and higher damping factor. From the correlative study it was found that 170°C is the best temperature to apply this adhesive. Thus, rheological analysis can be very well utilized to predict the adhesion properties.

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