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Research Paper

Effect of adhesive application method on lap shear strength of hot-melt adhesive with fracture analysis

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Abstract -Polyamide hot melt adhesive was prepared from dimer acid, sebacic acid, ethylenediamine and piperazine. Piperazine content was varied from 12.5 mol % to 37.5 mol %. Prepared polyamides were tested for adhesion property – lap shear strength. Specimens for lap shear strength were prepared by two methods. In first method, lap joint was formed manually using glue gun while in the second method lap shear joint was formed manually using glue gun while in the second method lap shear joint was formed using compression molding machine. It was found that sample prepared by compression molding gave better values of lap shear strength than that prepared using glue gun. Panels were also fracture analyzed, to find the reason for the properties obtained. Adhesion strength of lap joint formed using second method was found to be 5 to 10 times more than that formed using first method. First method is largely used, commercially, in hot-melt adhesive application. For any of the adhesive application method, as the piperazine content increased lap shear strength decreased.

Keywords: Polyamide; adhesive; hot melt; compression molding; glue gun.

Introduction

Adhesives that harden by cooling from a melt condition are called as hot-melt adhesives. These are generally thermoplastic adhesives that soften and melt when heated and they harden on subsequent cooling. The hot melt system must achieve a relatively low viscosity when in the molten state to achieve wetting and it must not harden too rapidly or it will not have time to completely wet the roughness of the substrate surface. Once the hot melt adhesive is applied in the molten condition, the substrates must be joined immediately. When hardened, the hot melt adhesive can have various degrees of tackiness depending on the formulation^[1].

Polyamide hot melt adhesives are widely used for bonding in packaging and book-binding. Strength of the joint not only depends on the formulation but also on the method of preparation of the joint. We all know this but actually how it is affected, is unknown. Property that is of main importance for an adhesive is lap-shear property of the material ^[2]. Lap shear strength covers the determination of the apparent shear strengths of adhesives for bonding metals when tested on a standard single-lap-joint specimen and under specified conditions of preparation and test. The test method has found applications in controlling surface preparations, primer and adhesive application systems for determining strength properties of tested systems. Chen et al. studied the synthesis of polyamides derived from 97% purity dimer acid, reporting mechanical, adhesion and thermal properties ^[3], but didn't report the effect of adhesive application method on lap shear strength of the adhesive.

In this paper, hot-melt adhesive was prepared from dimer acid, sebacic acid, ethylenediamine and piperazine and was tested for lap shear strength. Samples for lap shear were prepared by two methods. In first method, lap joint was formed manually using glue gun while in the second method lap shear joint was formed using compression molding. Lap shear strength of samples prepared by both the methods is found and they were also analysed for the fracture mechanism they undergo.

Materials and Method

Dimer acid (Pripol 1013), with acid value of 197 mg potassium hydroxide (KOH)/g, was supplied by Croda, Mumbai, India. The contents were as follows: monomer ~1%, dimer ~96%, trimer ~3%. Ethylenediamine was obtained from Ankita Chemicals, Mumbai, India, sebacic acid was procured from Amrut Industrial Products, Mumbai, India and piperazine from Arihant Chemical Corporation, Mumbai, India. All chemical compounds were used as received.

Preparation of polyamides

Table 1 reports the molecular weights of the raw material used to synthesize the polyamides. In order to obtain high molecular weight, the ratio of total acid equivalent present in dimer/trimer and sebacic acids to total amine equivalents present in ethylene diamine and piperazine was always kept at, approximately, 1.

To a four necked 500 ml flask equipped with stirring system, condenser, nitrogen gas inlet and temperature controller, 200 g (0.36 mol dimer acid) of pripol 1017, 124.04 g (0.12 mol) of sebacic acid, 18.40 g (0.21 mol) of piperazine and 15.72 g (0.26 mol) of ethylenediamine were added. The reactants were heated from 220° C to 240° C gradually, with stirring and under nitrogen. This temperature was maintained for 5 h. All polyamides were synthesized according to the above typical synthesis reaction.

Molar ratio of dimer acid and sebacic acid was held constant; dimer acid 37.5 mole %, sebacic acid 12.5%; while mole ratio of piperazine to ethylenediamine was varied from, piperazine 37.5% and ethylenediamine 12.5%, to piperazine 12.5% and ethylenediamine 37.5%. Compositions are shown in Table 2.

End group analysis

Acid Value Determination

50 ml neutralized benzene-alcohol mixture was added to dissolve 2 g sample in 125 ml Erlenmeyer flask, warming in water-bath if necessary. Solution was cooled (if necessary) and added a few drops of phenolphthalein indicator. Solution was titrated against 0.5 N alcoholic potassium hydroxide solution (alc. KOH) to a faint pink colour which remains for 30 seconds or more. The acid value was calculated as:

Acid Value = (56.1 x Volume of alc. KOH x Normality of alc.

Amine Value Determination

50 ml neutralized isopropyl alcohol was added to dissolve 2 g sample in 125 ml Erlenmeyer flask, warming on a heat source if necessary. Solution was cooled (if necessary) and added a few drops of bromocresol green indicator. Solution was titrated against 0.5 N standardized hydrochloric acid (HCl) to a yellowish green colour which remained for 30 seconds or more. The amine value was calculated as:

Amine Value = (56.1 x Volume of HCl x Normality of HCl)/(Weight of sample) (2)

Measurements

The FTIR spectra were recorded on a PerkinElmer, Spectrum GX equipment. 1-2 wt% polyamide was dissolved in chloroform for the characterization and was scanned with a resolution of 2cm^{-1} and the scan range of $450-4000 \text{ cm}^{-1}$. Inherent viscosity was determined by using Ubbelhode viscometer at 32^{0} C in toluene at a concentration of 1.0 g/dl. Lap shear strength was determined according to ASTM D1002-72 with a crosshead speed 1.3 mm/min. Differential scanning calorimetry (Q100 DSC, TA Instruments) characterization was done to investigate the glass transition temperature (T_g) of the prepared polyamides. Heating rate was maintained at 10^0 C/min and nitrogen purge rate at 50 mL/min.

Specimen Preparation

Aluminium panels were used for testing. Panels were surface scrubbed with 150 grit paper. This increases the surface area and also the surface energy of the panels' surface, making it more receptive to the applied adhesive. No chemical treatment was done. Panels used for lap-shear strength determination were prepared in accordance to Figure 1 (ASTM D1002-72). Length of overlap (L) should be approximately 12.7 mm. 5 samples were tested for each formulation and each method.

Method 1: Glue gun was heated up to a temperature of 180° C. Then the prepared hot-melt adhesive was extruded through it. Heat and pressure melts the adhesive. This molten or melted adhesive was then applied on scrubbed portion of the panel meant to be overlapped for formation of lap joint. Second panel was then placed on it. The prepared assembly was compressed with maximum possible manual pressure. Assembly was allowed to condition at room temperature for 24 hrs.

Method 2: Glue gun was not used in this method. Required quantity of hot-melt adhesive was directly cut from the synthesized polyamide using scissors. 4-5 g of sample was kept in between the scrubbed overlapping portion of the aluminium panels. The panel assembly was then pressed in compression molding machine at 200° C for 15 minutes at 30 kPa pressure. The assembly was removed from the machine and was conditioned at room temperature for 24 hrs.

Results and discussion

Characteristics of polyamides

Wheeler and Milun ^[3] expressed the structure of polyamides synthesized from dimer acid, sebacic acid, ethylenediamine and piperazine, as shown in Scheme 1. Acid number, amine number and inherent viscosity of polyamides are listed in Table 3. Since addition of acid number and amine number do not vary significantly, it can be supposed that the difference in molecular weight does not cause any variation in properties. Also in values of inherent viscosity, there is no such appreciable difference suggesting no much difference in molecular weight of the polyamides synthesized.

FTIR spectrum of polyamide S4 sample is shown in Figure 2. A small peak at 3441.9 cm⁻¹ appears due to OH stretching of water. A small band for the amide I ($-NH_2$ in primary amides) groups appears at 3320.8 cm⁻¹. Peaks at 2924.2 cm⁻¹ and 2853.5 cm⁻¹ are due to asymmetric and symmetric stretchings of CH₂, respectively. A small peak at 1739.4 cm⁻¹ is due to C=O stretching. The carbonyl peak ($-CONH_2$) of polyamide is seen around 1651.4 cm⁻¹ (steep peak). Amide II band/CH₂ asymmetric deformation is

indicated by the peak at 1542.2 cm⁻¹. N-H deformation/CH₂ scissoring peak is indicated at 1456.0 cm⁻¹. Peak at 1369.0 cm⁻¹ is due to amide III band/CH₂ wagging. The peaks at 1243.9 cm⁻¹ and 1215 cm⁻¹ correspond to C–N stretching vibration bond. C-C stretching is depicted by a small peak at 1019.6 cm⁻¹. N-H wagging/CH₂ rocking is depicted by a small peak at 773.6 cm⁻¹. A small peak at 671.3 cm⁻¹ is due to C-C deformation in the molecule. Similar method and raw materials were used for preparing other polyamides (S1 to S6), they would also show similar FTIR spectrum. FTIR spectrum thus proves that the compound formed is an amide.

Glass transition temperature graph of the samples is shown in the Figure 3 whereas the values are noted in the Table 4. Glass transition temperature (T_g) decrease as the molar percentage of piperazine increases. This indicates that there is a decrease in crystallinity of the polymer as piperazine content increases. Piperazine consists of one hydrogen atom each on two of its nitrogen atoms, present in the ring structure. When it undergoes reaction with acids to form amide linkage, this hydrogen atom gets consume. Nitrogen atom of the piperazine now has no hydrogen atom present on it. This decreases the hydrogen bond forming capacity of the polyamide, decreasing intermolecular forces of attraction. As the piperazine content increased, decrease in hydrogen bonding becomes intense, decreasing crystallinity, thus the T_g of the polyamides.

Lap shear test values

Table 5 lists the lap shear strength values of sample specimens prepared by method 1 and method 2. This shows that lap shear samples prepared by method 2 are better than that of method 2. Values of lap shear test of samples prepared by method 2 are about 5-10 times higher than that of method 1.

In getting better adhesion (shown by lap shear strength) things that are important are:

- 1. Wetting of the substrates,
- **2.** Adhesive strength and
- **3.** Type of failure.

As the type of adhesive is same for both methods, no issue of it arises while discussing the change in strength values observed. Adhesive strength depends on the formulation prepared. As the piperazine quantity in the formulation decrease, intermolecular forces of attraction increase, increasing adhesion strength. Decrease in piperazine content increases the polar amide linkages, increasing hydrogen bonding. Piperazine, in its molecule, has only one replaceable or reactive hydrogen atom onto its two nitrogen atoms forming part of the ring structure. When it reacts with the acid molecule to from amide linkage, it has no hydrogen atom onto its amide bond. Sebacic acid and dimer acid are kept constant, so has no problem.

Wetting of the substrates is very important, so as to have proper interaction between the substrate and the polyamide. Method of application has a great role to play in it. Sample specimens prepared by method 1, do not wet the substrate properly, especially that on the panel which is to be placed later after the application of the adhesive. The overlapping part of the second panel does not get wet properly. When the second panel was to be placed on the glue gun adhesive applied first panel, adhesive starts cooling/ hardening, decreasing the wetting chances of the second panel. More the time it takes for placing the second panel, lesser are the chances of second panel to get properly wet. This is totally a procedure with ambiguity. In second method, application procedure is more sophisticated, with proper wetting of the two panels, giving better strength.

It is important that the failure of adhesion take place into the adhesive (called cohesive failure), this is so, as adhesive is weakest portion in the joint. As if any stresses are applied on the adhesive joint assembly, weakest portion should get damaged. If failure takes place from the interface of the adhesive and the panel (called interfacial failure or adhesive failure), it is considered to be a bad joint. This shows bad wetting of the substrate/panel. It can be said that failure in the preparation method 1 is in the interface rather in the adhesive, giving lower values while failure in method 2 applied adhesive must be more of cohesive nature. Getting a complete cohesive failure is not possible. Usually it is a mix of cohesive and adhesive failure. This is so, as when adhesive is applied onto the substrate, on some parts the wetting of the substrate could be very good but on some parts it could not be so. This wetting affects the failure mechanism. When piperazine undergoes reaction with acids to form amide linkage, only hydrogen atom present on its two nitrogen atoms, gets consume. Nitrogen atom of the piperazine now has no hydrogen atom present on it. This decreases the hydrogen bond forming capacity of the polyamide, decreasing intermolecular forces of attraction. As the piperazine content increased, decrease in hydrogen bonding becomes intense, decreasing crystallinity, thus the lap shear strength.

Fracture Analysis

Tested lap joint specimens are shown in Figure 4 (prepared by method 1) and Figure 5 (prepared by method 2). It can be properly seen from Figure 4 that the failure in specimen prepared by method 1 is completely interfacial (interfacial failure). The entire adhesive is lying onto the single panel, due to improper wetting of the second panel. Figure 5 supports our view of proper wetting of the two panels. Adhesive applied according to method 2 gives a mix of adhesive and cohesive failure when tested.

Conclusion

From the study it can be concluded that sample preparation has an important role to play in affecting joint strength. Joints prepared by compression molding the adhesive applied panels are better than manually doing the same using glue gun. Wetting is thus an important property for an adhesive, especially an hot melt adhesive. Better the wetting, better the joint strength. Better wetting of the substrates was obtained in method 2 of adhesive application than that of method 1. In method 2 adhesive is not coming in contact with atmosphere, not allowing it to cool faster, increasing wettability. Also piperazine content affects the adhesive strength of the polyamides. As the piperazine content increases, Tg and lap shear strength of the polyamide decreases.

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Table 1: Molecular weights of the compounds used

	▲
Compound	Molecular weight (g/mol)
Dimer acid	560
Sebacic acid	202
Ethylenediamine	60
Piperazine	86

Table 2: Monomer composition of polyamides

Sr. No.	Monomers gm (mole percentage)	S1	S2	S 3	S 4	S 5	S 6
1	Dimer Acid	200 (37.5)	200 (37.5)	200 (37.5)	200 (37.5)	200 (37.5)	200 (37.5)
2	Sebacic Acid	24.04 (12.5)	24.04 (12.5)	24.04 (12.5)	24.04 (12.5)	24.04 (12.5)	24.04 (12.5)
3	Ethylenediamine	7.14 (12.5)	10.02 (17.5)	12.84 (22.5)	15.72 (27.5)	18.54 (32.5)	21.42 (37.5)
4	Piperazine	30.70 (37.5)	26.57 (32.5)	22.53 (27.5)	18.40 (22.5)	14.36 (17.5)	10.23 (12.5)

Table 3: Characteristics of polyamides

Sample	S1	S2	S 3	S4	S 5	S6
Acid number (mg KOH/g)	10.3	11.2	9.6	9.9	10.0	8.2
Amine number (mg KOH/g)	7.7	6.1	7.1	7.3	5.1	6.1
Acid number + Amine number (mg KOH/g)	18.0	17.3	16.7	17.2	15.1	14.3
Inherent Viscosity (dl/g)	0.54	0.56	0.55	0.61	0.58	0.57

Tuble 11 Thermal properties of polyamates.								
Sample	S1	S 2	S 3	S 4	85	S 6		
T _g , ⁰ C	-7.9	-7.8	-7.1	-6.5	-6.2	-5.3		

Table 4: Thermal properties of polyamides:

Table 5: Lap shear test values of specimens prepared by method 1 and method 2

Samples	S1	S2	S 3	S4	S 5	S6
Method 1	0.13	0.59	1.20	1.54	1.74	2.04
Method 2	2.13	2.21	3.45	5.11	5.50	9.34



Figure 1 Panel preparation dimension



Figure 2 FTIR Spectrum of polyamide S4



Figure 3: Glass transition temperature of spolyamides



Figure 4: Fracture appearance in sample prepared by method 1



Figure 5: Fracture appearance in sample prepared by method 2



R1+R2+R3+R4=28 carbons

Scheme 1: Structure of polyamide