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Investigations on performance and failure mechanisms of high temperature thermoplastic polymers as adhesives

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ABSTRACT

Ability of high temperature thermoplastic polymers (TPs) to create strong bonds with metals provides an attractive solution to develop adhesives for harsh operating conditions. However, exploration of such TP based adhesives needs evaluation in desired operating temperature conditions along with understanding of failure mechanism which will serve as a platform for developing successive batches of composite adhesives or blends. In this work poly (ether sulphone) (PES), poly (ether ketone) PEK and poly (ether-ether ketone) PEEK were explored as adhesives for joining cold rolled steel lap joints. The lap joints were evaluated for bond performance at various temperatures. The adhesive-bond performance order differed at different temperatures. At ambient temperature (AT) it was as; PES > PEK > PEEK, while at higher temperatures PEK proved the best followed by PEEK. Micro-Raman spectroscopy (MRS) analysis of failed films was carried out to understand the failure mechanism as a function of thermal and mechanical stresses. Differential scanning calorimetry and scanning electron microscopy (SEM) of fractured films was carried out to understand the changes in crystallinity, thermal characteristics and failure mechanisms.

1. Introduction

Thermoset polymers such as epoxies, polyimides etc. are used as structural adhesives. Structural adhesives are defined as load bearing materials with high modulus and strength that can transmit stresses without loss of structural integrity. However, these materials mainly suffer from poor impact resistance, slow cure times etc. To overcome these issues thermoplastic (TP) based hot melt adhesives are being widely employed nowadays. During melting they are compressed between the joints so as to lead to a good quality bond with the substrates after cooling. The melting temperatures of the substrates need to be higher than that of the TP used for bonding. These solvent-free hot melt adhesives produce a low viscosity molten liquid/melt when heated that wets the substrate surface and rapidly solidifies upon cooling. The service temperature of the joint is definitely lower than the melting point of the TPs [1–5].

Every structural joint has different performance requirements. With advances in technology, the performance pressure on the materials is increasing continuously and hence, newer TP based adhesives along with composite adhesives which can sustain higher operating temperatures are being developed and evaluated [6–13].

Most of the engineering TPs are incapable of retaining their strength properties at high temperatures and hence specialty polymers are more favoured for such applications. The benzene group containing specialty TPs such as poly (aryl ether ketones) (PAEKs), poly (ether imide) (PEI), poly (sulphones) or poly (ether sulphone) (PES), poly (phenylene sulphide) (PPS) etc. are being exploited as adhesives. Sugama et al. [14–16] studied the interfacial chemistry of failed adhesive bonds based on PAEKs, PPS and PES under varying process conditions and various substrates. The interfacial chemistry of surfaces of lap shear strength (LSS) samples was studied with X-ray photoelectron spectroscopy (XPS).

Ramani et al. [8,17,18] explored poly (ether ketone ether ketone ketone) (PEKEKK) and PEI adhesives in tensile butt mode. The influence of process conditions, substrate type and adhesive melt viscosity was studied. Shimizu et al. [19] more recently studied the durability of PEEK adhesive on modified stainless steel substrates. In spite of the intentions and claims of final applications of such adhesives at high temperatures, no reports are available on their performance evaluation at higher temperatures, which is essential.

Raman spectroscopy is among the most powerful means to examine changes that occur to polymer structures due to interactions with stress or strain and to understand molecular deformation mechanisms of polymer chains. The vibrational modes of

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some oriented polymers experience considerable shift in frequency when the polymers are subjected to mechanical or thermal stresses. The sensitivity to an external tensile stress is expressed in terms of frequency shift per unit tensile strain [20–27]. This technique has been extensively explored for investigating the molecular deformation of highly oriented polymers and fibres in general; but not, so far, for studies relating to deformation in failed adhesives.

In this paper, three high performance polymers viz. PES, PEK, PEEK differing in flexibility of backbone and crystallinity were selected for evaluating their potential as high temperature adhesives at different temperatures which to date has not been reported. Failure mechanisms were studied in detail using micro Raman spectroscopy (MRS) for the first time. Moreover, efforts were also focussed on critically examining the changes in melting, crystallization temperature, glass transition temperature (T_g) etc. with differential scanning calorimetry (DSC) which again has not been reported.

2. Experimental

2.1. Materials

Poly (ether ketone) (Grade G-PAEK 1100 P) and poly (ether sulphone) (GAFONE 2500 B) were supplied by Gharda Chemicals Ltd., Mumbai. Poly (ether ether ketone) (Grade Victrex 150UF) was procured from Victrex, India and properties are shown in Table 1 and chemical structures are shown in Fig. 1. Coupons of dimensions shown in Fig. 2 of cold rolled steel (CRS) (ASTM A 240-09a, Grade 316) with 0.1 μm roughness (R_o) were used as substrate.

2.2. Sample preparation

The CRS substrates (LSS specimens) were degreased with acetone and dried before bonding. The LSS specimens were prepared using a specially prepared mould (Fig. 2) to be used on a compression moulding machine. The moulding temperatures of PES, PEK and PEEK were 365, 420, 400 °C respectively with moulding pressure of 30 bars.

2.3. Contact angle and surface energy studies

Contact angles were measured using a Krüss GmbH DSA25S. Stainless steel substrates were coated with polymer using an electrostatic spray gun and then kept in oven at 380 °C for 30 min and slowly cooled to ambient temperature. Contact angles were measured with a drop (2 μl) of distilled water and cyclohexane on a previously ultra-sonicated surface. The surface energy was calculated using the Owens, Wendt, Rabel and Kaelble (OWRK) geometric method.

2.4. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed on a DMA+150, MetraviB, France in tension mode. The test was carried out at a frequency of 1 Hz with 5% strain and data was obtained from ambient temperature to 300 °C for PEK and PEEK and 275 °C for PES.

2.5. Lap Shear Strength (LSS) test

LSS tests were carried out on an INSTRON 5582, 100 kN UTM machine (with an integrated furnace capable of attaining 300 °C; ±5 °C) according to ASTM D1002. Tests were performed at ambient temperature, 150 °C, 225 °C and 300 °C by keeping the sample under test temperature for 20 min before application of

Table 1
Physical and thermal properties of polymers selected for adhesives*.

Property	PES	PEK	PEEK	Trends in performance property
Designation	A	B	C	
Density	1.37	1.34	1.32	–
Crystallinity (%)	–	31	34	PEEK > PEK
Tensile strength (MPa) ASTM D638	86	105	100	PEK > PEEK > PES
Tensile elongation (%)	6.5	15	15	PEK=PEEK > PES
Tensile modulus (GPa)	3.22	4.00	3.7	Flexibility- PES > PEEK > PEK
Flexural strength (MPa) ASTM D790	123	185	170	PEK > PEEK > PES
Flexural modulus (GPa)	2.9	4.1	4.1	PEK=PEEK > PES
Glass transition temperature (T_g,°C)	220	155	145	PES > PEEK > PEK
Melting point (T_m, °C)	340–377	372	343	PEK > PEEK
Melt flow rate (g/10 min)	33	5.00	5.5	PES > PEK > PEEK
Thermal stability (degradation temp., °C)	440	450	440	PEK > PEEK=PES

*Supplier's data

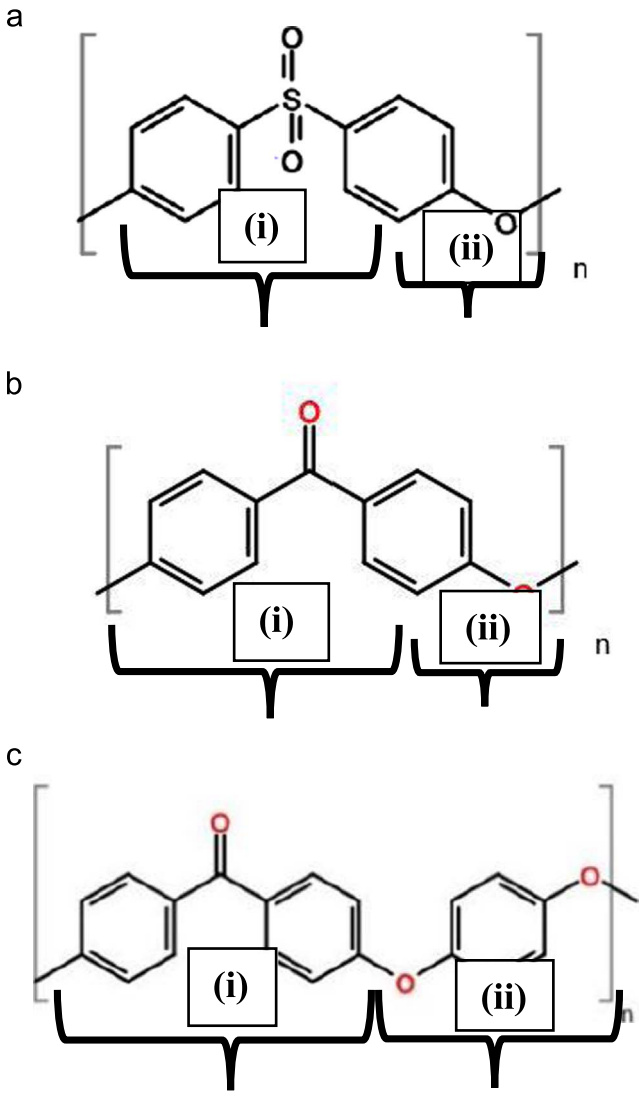

Fig. 1. Chemical Structures of; (a) PES – Poly (ether sulphone); (b) PEK – Poly (ether ketone) and (c) PEEK – Poly (ether ether ketone). (i) *(arylene sulphone; Rigid and polar in case of PES and arylene carbonyl; in case of PEEK and PEK)* (ii) *arylene ether segment; flexible, non-polar ether linkage.*