Defence Science Journal, Vol. 54, No. 2, April 2004, pp. 249-255

SHORT COMMUNICATION

Thermoplastic Epoxide Resin in the Presence of Polyethylene Glycol as Hot-melt Adhesive in Clean Technology

G.S. Mukherjee, N. Shukla, R.K. Singh, and G.N. Mathur

Defence Materials & Stores Research & Development Establishment, Kanpur–208 013

ABSTRACT

Pollution caused by the process involving handling of solvents is considered as one of the most serious ecological problems. In this perspective, thermoplastic epoxide resins were synthesised from the controlled reaction of bisphenol A, epichlorohydrine, and 3,5-dimethylaniline with a view to prepare ingredients for hot-melt adhesives without involving any solvents. Such thermoplastic epoxide resin (base polymer for hot-melt adhesive) was designated as HMA_{35}. Addition of polyethylene glycol (20 Wt per cent) of molecular weight 6000 (PEG6K) in the blend was found to be optimum towards providing maximum tensile lap shear strength with reference to aluminium/adhesive/ aluminium bonding with a value of 5.05 MPa. The matrix of the blend remains optically transparent till the content of PEG6K remains up to 20 Wt per cent; however beyond 20 Wt per cent of PEG6K, the matrix becomes opaque with the appearance of spherulites due to the presence of excess PEG6K in the blend. Interestingly, blends containing $\leq$ 20 Wt per cent PEG6K showed no endotherm below 100 °C even though the melting point of pristine PEG6K is 55 °C. FTIR data revealed the interactive role of PEG6K with the epoxide resin.

Keywords: Epoxy resin, solvents, adhesive, polyethylene glycol (PEG), HMA, hot-melt adhesive, clean technology , HMA_{35}, PEG6K, thermoplastic epoxide resins

1. INTRODUCTION

Pollution caused by the solvents is now-a-days considered as one of the most serious ecological problems[1]. Handling of toxic solvents during processing of adhesives in the industry is a major threat and is of serious concern to healthcare programmes. Adhesive industry needs to emphasise on consumer safety, and concern for environmental protection, to a greater extent, than many other industries[2]. So, there is a tendency to adopt an alternative approach through hot-melt adhesive (HMA) to replace solvent-based adhesives to help restore normal environment and support healthcare programmes. It is therefore essential to evaluate the properties of newer alternate products and generate knowledge base and enrich databank for HMAs to increase their scope of use and promote their growth[2,3]. For this purpose, information on hot-melt products should be collated to help generate awareness among Defence personnel to make HMAs more acceptable to the Services. In this perspective, some information pertaining to HMA-based technology may be referred here; for example, the hot-melt process reduces space requirements for storage besides easy maintenance with minimal cleaning up costs, etc. These advantages

Received 20 September 2003

are particularly important to the Defence personnel as they often have to work in make-shift conditions within the limited space, and moreover, at the same time by norms and nature they are disciplined and prefer spick and span environment. More importantly, because of the absence of toxic solvents in the HMA systems, the environment is less risky from fire hazard and pollution danger, and therefore, any scheme based on HMA is more attractive towards helping ultimate healthcare management programmes.

It may be recalled that the risk of fire hazard is of utmost concern for the management of Defence stores and defence establishments like central ordinance depot (COD), etc in the backdrop of the fact that in the recent past, there were certain cases of outbreak of fire in some ordinance depots and establishments, eg, establishments at Bharatpur, Bikaner, Rajasthan; CODs at Kanpur, Itarsi, etc. Moreover, attention to healthcare is one of the keys to success of Defence Forces. Therefore, any activity in support of broad-based healthcare management programme through awareness of environment is always important to the Defence Services.

Although thermoplastics like polyolefins, polyesters, polyimides, and polyethylene-co-vinyl acetate are sometimes used as the base resins for HMA systems but the functional role of thermoplastic epoxy resin as HMA in combination with additives is practically unknown[3,4].

In this paper, information on the synthesis of thermoplastic epoxide resins and its adhesive characteristics in the presence of polyethylene glycol (PEG) as additive has been focused upon. It may be noted that PEGs are biodegradable and eco-friendly. Therefore, PEG of molecular weight 6000 (PEG6K) has been selected as a non-volatile additive for epoxide resins to understand the underlying mechanism of improvement of adhesive strength, and the structure of PEG6K is given below:

$$HO\text{–}(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_n\text{–}H, \text{ where } n = 136$$

Structure of PEG6K

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Resin

(i) Diglycidyl ether of bisphenol A (DGEBA), a viscous epoxy resin of epoxy equivalent of 312 g.eq.$^{-1}$ containing one hydroxyl group and two epoxy groups per mole of resin was prepared and reacted with 3,5 dimethyl aniline at 80 °C for 60 h to obtain HMA_{35} as discussed[5] and the synthesised resin was used to prepare blends with PEG6K for subsequent use.

(ii) 3,5 Dimethyl aniline (Lancaster) was distilled under reduced pressure before use.

(iii) Polyethylene glycol (m.p. 55 °C) of molecular weight 6000 (PEG6K) (SD Chemicals, Mumbai) was used without further purification.

2.2 Thermal Analysis of Resins

A Du Pont DSC instrument with 910 module was used for thermal analysis. An oxygen-free nitrogen stream of 40 cm^{3}min^{-1} was maintained through the cell during the measurements. The scan was performed at 10 °C min^{-1}. FTIR (Nicholet) was run at room temperature to study the characteristic features of the pristine resins and their blends.

Table 1. Tensile lap shear strength of aluminium/resin/aluminium joints based on the adhesives prepared from the combination of HMA_{35} and different proportions of PEG6K

HMA_{35} with PEG6K in the formulation (Wt %)	Lap shear strength (MPa)	Standard deviation (σ)
1	0.27	0.79
5	0.53	0.82
10	1.82	0.41
15	4.18	0.70
20	5.05	0.32
25	2.43	0.77

3. MECHANICAL PROPERTIES

Tensile lap shear strength (LSS) was determined as per ASTM-D 1002-53T using Honsfield Tensometer (UK) at 5 mm per min. The value reported is the mean of five specimens tested at 32 °C in the normal atmosphere. The standard deviation (SD) of the test data has been calculated and presented in Table 1.

4. RESULTS & DISCUSSION

The function of thermoplastic HMA is a kind of reversible process in the sense that it melts and spreads over the substrates, and subsequently gets solidified on cooling to bond the desired substrates; however, it gets debonded upon remelting[3]. HMA may be applied as such or used in combination with other ingredients or additives like tackifier, lubricant, or stabilisers. Often, such additives are toxic; therefore, it calls for a non-toxic additive for adhesion. The functional role of the base polymer is to contribute for the general mechanical strength[3,4] and such additives are essential to improve performance characteristics of HMA_{35}. With this background information, the thermoplastic epoxide resin was synthesised by the chain extension reaction of DGEBA epoxy resin through 3,5-dimethyl aniline. The synthesised thermoplastic epoxide resin was designated as HMA_{35} and was used as base polymer for HMAs. The chemical structure of HMA_{35} is shown in Fig. 1.

Thermoplastic epoxide resin, HMA_{35} containing terminal epoxide groups is solid and can be crushed into powder. These solid resins are not sticky unlike usual DGEBA or similar viscous resins[3], and therefore, it is easier to handle these HMAs during processing or applications, thereby providing a cleaner working environment in the industry.

Interestingly, Fig. 1 indicates that there is a particular melting zone in HMA_{35}. The melting zone of HMA_{35} comprises four prominent and distinct premelting transitions $(T_{m,i}S)_{i=1-4}$, because of the quadruplet splitting of melting temperatures. Based on the results of DSC, the glass transition temperature (T_g) and the first premelting transition temperature (T_{m1}) of HMA_{35} were 43.3 °C and 155.4 °C, respectively, such that $T_g / T_{m1} = 0.74$. Bunn[6] and Boyer[7] reported that the ratio of T_g / T_m has about the same value, of the order of 0.67 for many polymers[6,7]. It is also reported that $T_g / T_m \leq 0.5$ for highly symmetrical polymers and > 0.67 for unsymmetrical polymers. In this study, T_g / T_{m1} was 0.74, indicating that HMA_{35} was basically an unsymmetrical polymer[6,7]. The DSC profile for HMA_{35} showing such quadruplet splitting is shown in the Fig. 2. HMA_{35}, so synthesised, melts in steps undergoing a series of relaxations like those reported by Connor[8], *et al.* involving absorption of low amounts of heat in each successive transitions[8]. The total heat of absorption (ΔH_{en}) is 2.3 J/g. The low value of ΔH_{en} is particularly advantageous due to the fact that only small amount of heat is required in the melting process while applying for adhesive with the substrates.

To understand the adhesive properties of epoxide resins in the presence of PEG6K, HMA_{35} was blended with PEG6K by melt process for evaluation. The adhesives were evaluated in terms of LSS with reference to the test samples as $Al/HMA_{35}/Al$ as well as aluminium/HMA_{35}-PEG6K/Al; where Al stands for aluminium panel. When HMA was used as such, very low value of LSS was observed. As PEG6K reduces the value of melt viscosity of HMA_{35}, it is expected to improve wetting with the surfaces, and consequently, leads to better LSS. It should be noted that PEG6K has the characteristic of

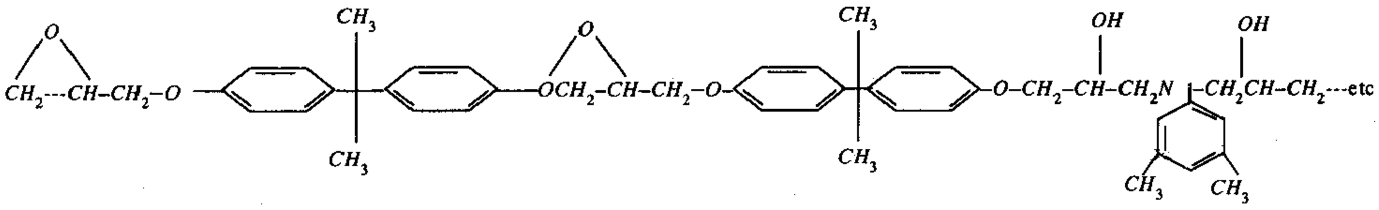

Figure 1. Chemical structure of thermoplastic epoxide resin (HMA_{35})

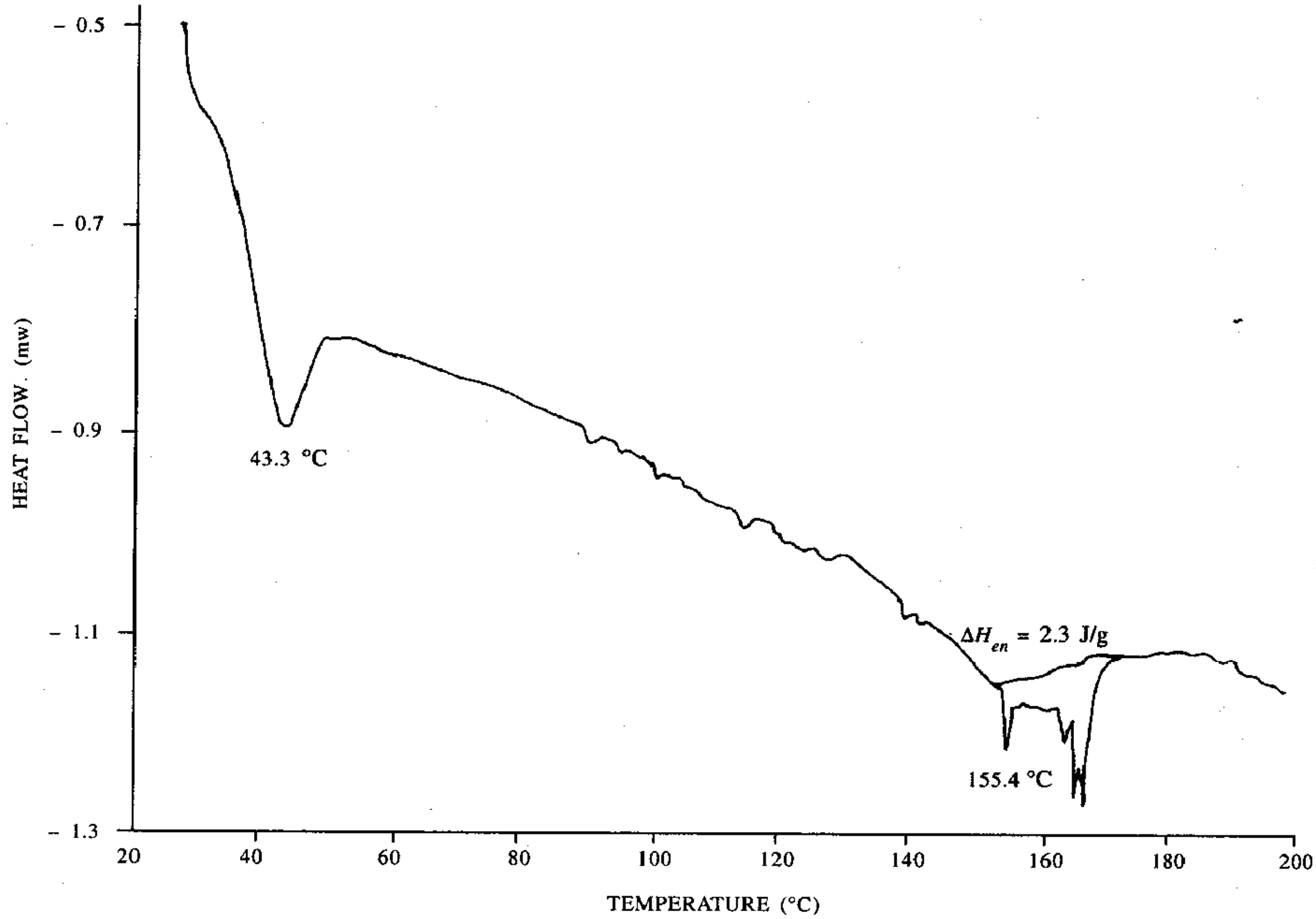

Figure 2. DSC profile of a typical thermoplastic epoxide resin, such as HMA_{35} showing quadruplet splitting of melting temperature

wax-like solid without possessing enough mechanical strength but when it is blended with the thermoplastic epoxide resin (HMA_{35}), it increases the adhesive strength. In fact, judicious combination of thermoplastic epoxide resin with PEG6K can bring about significant improvement in the adhesive strength because of the interaction between PEG6K and HMA_{35}. Interactive role of PEG6K with HMA_{35} can be understood by the comparison of DSC features of pure HMA_{35} vis-à-vis 20:80 wt per cent :: PEG6K:HMA_{35} (Figs 2 and 3) where split-melting is modified to a prominent endothem of ΔH_{en}=195.3 J/g.

The improvement in the adhesive strength suggests the possibility of interactive role of PEG with the thermoplastic epoxide resins. FTIR spectral data, shown in the Fig. 4 in which (a), (b), and (c), representing the spectra of PEG6K, HMA_{35}, and their blend, respectively, were used to understand the characteristic chemical groups and their mutual interactive roles in the blend. Table 1 indicates that with increase in the content of PEG6K in the blend, the LSS values increased up to a certain limit. PEG6K has both terminal hydroxy groups coupled with a spread of polar ether moieties along the chain. The presence of *OH* group in PEG6K is clearly visible at 3459 cm^{-1} of the FTIR spectrum [Fig. 4(a)]. The presence of such polar groups in PEGs makes these highly active lyophilic additives. The aromatic *C-H* stretchings are visible at 3040 cm^{-1} and in the range 1602 cm^{-1}-1465 cm^{-1} for the sample of HMA_{35}; but such peaks are more broadened and slightly blue-shifted in the blends. Figure 4(a) for PEG6K shows minimum transmittance at 3459 cm^{-1} due to the presence of *OH* group[9]. But in the presence of HMA_{35}, such intramolecular hydrogen bonding mostly transformed into forming inter-

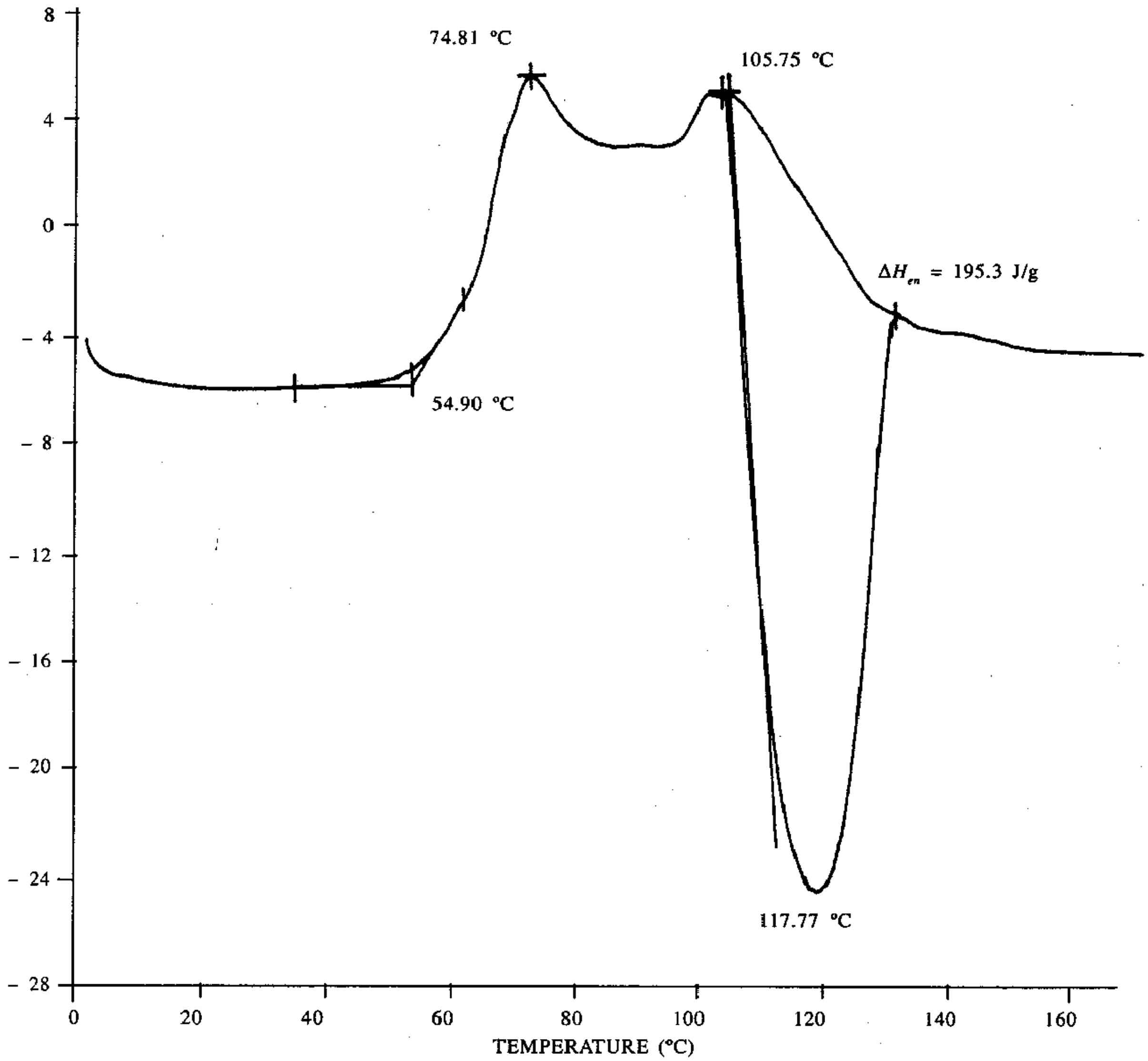

Figure 3. DSC profile of a blend of 20 Wt per cent PEG6K and 80 Wt per cent HMA$_{35}$

material hydrogen bonding. The methyl and methylene groups are responsible for absorption at 2887 cm^{-1}. The absorption due to the presence of *OH* groups in HMA$_{35}$ occurs at a lower frequency (3384 cm^{-1}) than that of PEG6K, presumably because of the influence of *t*-amine group[9] in HMA$_{35}$. Clearly, the absorption of the blend of HMA$_{35}$ and PEG6K occurring at 3408 cm^{-1} is more broadened, indicating the formation of *H*-bonding between PEG6K and HMA$_{35}$.

PEG6K is crystalline and it has spherulitic texture. Because of its spherulitic texture, the bulk mechanical strength of PEG6K is not up to the level as otherwise expected from a crystalline material[10]. Interestingly, when PEG6K was blended with the HMA$_{35}$ up to the level of 20 phr, it's opaque spherulitic texture was completely lost with the appearance of optically transparent matrix system. The boundary regions of the spherulites constitute the sites of potential weakness to cause mechanical properties of the bulk material to go down[10]. Absence of sphelulitic texture in the blends containing < 20 per cent PEG6K, unlike in the virgin PEG6K, implicitly suggests the existence of intermolecular interactions between the resins. HMA$_{35}$ and PEG6K are mutually compatible up to a limit to provide better adhesive properties. It may be noted that the

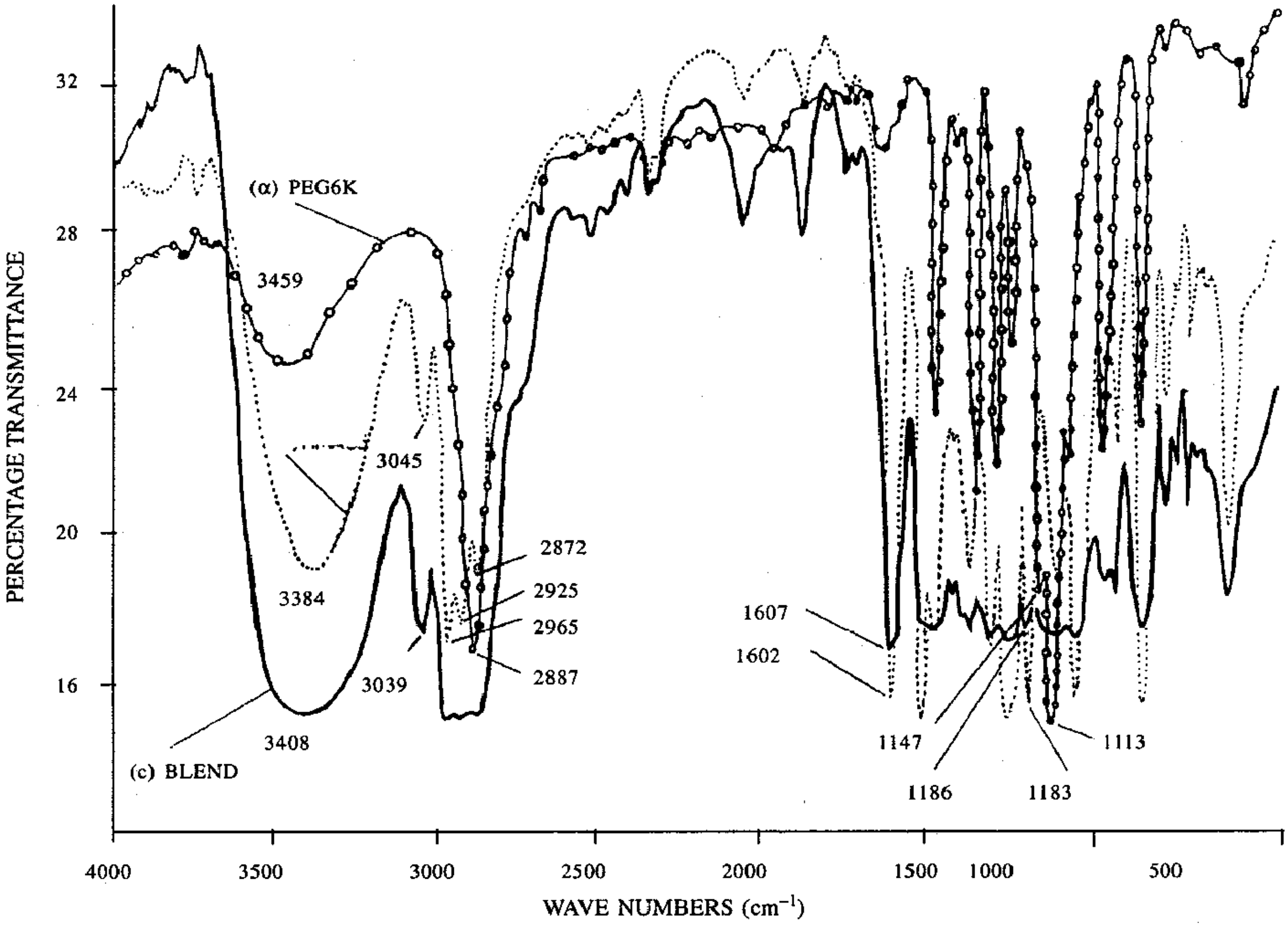

Figure 4. FTIR spectra of: (a) pristine PEG6K, (b) pristine HMA_{35}, and (c) blend of 20 Wt per cent PEG6K and 80 Wt per cent HMA_{35}.

barrier to rotation around the *C–C* bond is ca. 13.0 kJ/mol whereas the barrier to rotation around the *C–O* bond of aliphatic ether[11] is only about 5.0 kJ/mole. Thus, the presence of ether groups in the resin makes the system more flexible in providing better wetting for adhesion. The presence of flexible resin like PEG6K in the adhesive system allows a more uniform distribution of stress over the matrix resin which results in improving the LSS[3].

The content of *OH* in the PEG6K molecule is much less than that of its ether groups. Approximately, there are 68 ether groups (*–O–*) per terminal *OH* group present in the linear chain of PEG6K, whereas the same for HMA_{35} is in the approximate ratio of 2 ether groups per hydroxyl group. Moreover, the spatial disposition of *OH* groups of HMA_{35} is quite different from that existing in PEG6K. The *OH* groups of HMA_{35} exist in the transverse position along the chain, whereas those of PEG6K remain in the longitudinal position along the chain. Therefore, intuitively, the probability of interaction of *OH* group of PEG6K is more likely to be effective through the oxygen of *OH* groups of HMA_{35} rather than with the ethereal oxygen (*–O–*) group of HMA_{35} because the oxygen atom of HMA_{35} rather exists in a comparatively more remote axial position compared to the oxygen atom of *OH* along the transverse position of the chain of HMA_{35}.

On the other hand, the probability of finding the ambience of oxygen atoms of ether groups (*–O–*) of PEG6K is more than from its remote terminal *OH* groups because of the abundance of ether groups in PEG6K. Therefore, intuitively, the *OH* groups of HMA_{35} are likely to be more interactive towards the oxygen atom of ether groups of PEG6K because of the high concentration of (–*O*–) groups and their proximity. Thus, the hydrogen bonding of *OH* of PEG6K is likely to take place through the *OH* groups of HMA_{35} whereas the hydrogen bonding of *OH* of HMA_{35} is likely to be effective through the (–*O*–) of PEG6K.

The lengthening of *OH* stretching in PEG6K arises from the dipole-dipole interaction[9] whereas contraction of *OH* stretching in HMA_{35} is the result of the dominance of London dispersion force[12,13] within the component of the blend. It may also be noted that the stretching due to ether groups of PEG6K is more influenced than the corresponding ether group of HMA_{35}. For example, the absorption at 1147 cm^{-1} or for that matter at 1113 cm^{-1} due to the ether groups (–*O*–) of PEG6K is increased substantially to 1186 cm^{-1} as a result of the interaction between the constituents of the blend. But, interestingly, the absorption at 1183 cm^{-1} due to the oxygen of ether groups (–*O*–) of HMA_{35} (Fig. 4) is only marginally increased to 1186 cm^{-1} (ie, a shift of 3 cm^{-1} only) for similar interaction in the blend system. This implies that the *OH* groups of HMA_{35} more effectively interact with the ether (–*O*–) groups of PEG6K compared to the interaction between the *OH* groups of PEG6K and the ether (–*O*–) groups of HMA_{35} as argued in the foregoing. Moreover, the absorption at 1602 cm^{-1} for HMA_{35} was slightly split and blue-shifted due to its interaction with PEG6K.

The blue shift of *O-H* absorption instead of red shift as a result of mutual interaction between HMA_{35} and PEG6K in the blend implies the formation of inter-material (HMA_{35}-PEG6K) hydrogen bonding of special kind, currently also known as anti-hydrogen bonding, originated essentially from the high degree of London dispersion forces, leading to the contraction of *O-H* bond belonging to HMA_{35}[12,13].

REFERENCES

1. Maeda, Y.; Nakayama, A.; Kawasaki, N.; Rayashi, K.; Aiba, S. & Yamamoto, N. *Polymer,* 1997, **38**, 4719-725.
2. Kirk-Othmer. Encyclopaedia of technolology chemical, Vols 1& 9. John-Wiley Interscience, 1983.
3. Skeist, I. *In* Handbook of adhesives. Ch. 43, Van Nostrand and Reinhold, 1990, pp. 705.
4. Shih, H. H. & Hamed, G.R. *J Appl. Polym. Sci.,* 1997, **63**, 323-31.
5. Mukherjee, G.S.; Shukla, N. & Singh, R.K. *In* Advances in polymers and composites. Allied Publisher, New Delhi, 2000.
6. Bunn, C.W. Melting and second-order phenomena, edited by R. Hill, Ch. 12. Elsevier, Amsterdam, 1953.
7. Boyer, R.F. *Rubber Chem. Technol.,* 1963, **36,** 1303.
8. Conner, T.M. *J Polym. Sci.,* 1970, **A2, 8**, 191.
9. *In* Vogel's textbook of practical organic chemistry, edited by B.S. Furniss, A.J. Rannaford, P.W.G. Smith, & A.R. Tatchell, Ed-5. ELBS, Longman Group UK, Ltd, London, 1991.
10. Tager, A. Physical chemistry of polymers. Mir, Moscow, 1978.
11. *In* Encyclopaedia of polymer science and enggineering, Vol. **6**. Ed. 2, Wiley-Interscience, New York, **1986**.
12. Hobza, P. & Ravlas, *Z. Chem. Revs.*, 2000, **100,** 4.
13. Mukherjee, G.S. & Mathur, G.N. *In* Proceedings of the international conference-Polymer Fibre, 5-7 July 2000, UMIST, Manchester, UK.