AFM Investigation of Microscopic Flow of Matrix Leading to Interphase Formation in Short Melamine Fiber Reinforced Rubber Composites

R.S. Rajeev[1], S. Bandyopadhyay[2], S.K. De[3] and A.K. Bhowmick[4*]
[1]*Dep of Chemical Eng, U South Carolina, Columbia, SC-29208, USA: RAJEEV@engr.sc.edu*
[2]*School of Materials Sci & Eng, UNSW, Sydney 2052, Australia: S.Bandyopadhyay@unsw.edu.au*
[3]*College of Leather Technology, Salt Lake City, Kolkata, India: sadhan41de@yahoo.co.in*
[4]*Rubber Technology Center, IIT Kharagpur-721302, India : anilkb@rtc.iitkgp.ernet.in*
*Corresponding author: *anilkb@rtc.iitkgp.ernet.in*

SUMMARY: Melamine fiber reinforced elastomer composites are potential candidates as insulators for launch vehicles by virtue of their low density and excellent ablative properties. In this paper atomic force microscopy (AFM) study of the interphase formation in short melamine fiber reinforced rubber composites with ethylene propylene diene (EPDM), maleated EPDM and acrylonitrile co-butadiene rubbers (NBR) as matrices is reported. A dry bonding system comprising of resorcinol, hexamine and hydrated silica was used for enhancing wetting and aiding microscopic matrix flow onto the fiber. Mechanical testing of the composites proved the reinforcing capability of the melamine fiber; particularly containing the bonding agent. Further, thermal aging of the fibers increased the tensile strength and modulus. A probe using AFM revealed the presence of a thick, well-defined fiber-matrix interphase in the composites with the bonding system. For the thermally aged fibers, AFM studies revealed an increase in the surface roughness providing a greater interfacial surface area enabling the matrix to flow into the crevices of the roughened fiber. The improved tensile strength and modulus of the aged composites can thus be attributed to the excellent mechanical interlock, as was evident from the AFM images. All the three matrices portrayed similar behavior. The studies reveal that melamine fiber is a suitable reinforcing fiber for EPDM, mEPDM or NBR matrices, and that AFM is a powerful novel technique to investigate the microscopic flow of the matrix onto the fibers and obtain wetting and interface formation..

KEY WORDS: atomic force microscopy; interphase; melamine fiber; rubber matrix, microscopic flow, wetting.

INTRODUCTION

Though short fiber-rubber composites (SFRCs) find application in hose, belt, tires, and automotives [1], one of the most important recent applications of these composites is as thermal insulators [2] where the material will protect the metallic casing by undergoing a process called ablation i.e. sacrificial removal of material to protect structures subjected to high rates of heat transfer [3]. FRP composites and SFRCs are potential ablative materials because of high specific heat, low thermal conductivity and the ability of the fiber to retain the char formed during ablation [4]. Originally, asbestos-filled phenolic resins and elastomers were used for this purpose

[2]. Because of the health hazards, replacement of asbestos fibers in high temperature applications is a must. Melamine fiber, a recent generation high performance fiber offering i) high operating temperature, ii) high limiting oxygen index, iii) combined fire protection & heat stability properties along with iv) good chemical, hydrolysis and UV resistance and v) superior thermal and ablative properties is an extremely good candidate for replacing asbestos [5]. Like aramid fiber, melamine fiber has no specific melting point - an important prerequisite as an ablative material.

Although the lifetime of rubber compound as insulator is short, its mechanical as well as aging properties are important [6]. The density of the rubber should be as low as possible. The choice of rubber matrix for insulator development is based on these criteria. Nitirle rubber based compositions are widely used in solid rocket motor insulators because of the better rubber-metal adhesion. Since EPDM rubber combines low density with high specific heat, good thermal stability, good resistance to chemicals, low thermal conductivity compared to all other general-purpose synthetic elastomers, it has potential application in the area of thermal insulators such as solid rocket motor insulators [7]. Achieving proper fiber – matrix adhesion is one of the most important challenges in the development of SFRCs for high performance applications. The use of external bonding agent is important, especially in the case of a non-polar matrix like EPDM rubber. A dry bonding system consisting of resorcinol (or a resorcinol derivative), hexamethylene tetramine (hexamine) and hydrated silica [RHH], is useful in such cases [8]. The objective of the present study is to analyze, using AFM and SEM, the effect of incorporation of melamine fiber and dry bonding system on the microscopic flow of matrices of EPDM, maleated EPDM and nitrile rubber based vulcanizates. Special attention has been made to analyze the role of the dry bonding system in improving the wetting of the fiber surface by the matrix and providing smooth extrudate, as are important in the development of high performance SFRCs.

EXPERIMENTAL

Matrices used: EPDM rubber (Royalene 535, supplied by M/s Uniroyal Chemical Co. USA), maleated EPDM rubber (Royaltuf 490, supplied by M/s Uniroyal Chemical Co. USA) and nitrile rubber (supplied by Japan Synthetic Rubber, Japan). The respective masterbatches were prepared by mixing the rubber, melamine fiber (supplied by M/s BASF Corporation, Singapore) and other compounding ingredients in a Brabender Plasticorder at 80°C at a rotor speed of 30 rpm. The curatives were added in a two roll rubber mixing mill. The RHH system is used as the dry bonding system. Typical formulation (in phr) contains rubber, 100; ZnO, 5; strearic acid, 1; antioxidant TQ, 1; melamine fiber, 30; MBT, 1.5; TMTD, 1 and sulfur 1.5 apart from resorcinol, hexamine and silica, whose concentration varied in the order 0/0/0, 5/3/15 and 10/6/15, to optimize the level of the bonding system. Vulcanization of the compositions was carried out in a hydraulic press. EPDM and nitrile rubber based compositions are cured by using sulfur-accelerator system only. Since maleated EPDM rubber contains maleic anhydride groups as well as double bonds, it can be cured by conventional covalent crosslinking system based on sulfur/accelerator or ionic crosslinking system using metal oxides or mixed crosslinking system consisting of both covalent anA@ linking system contained no sulfur/accelerator but 10 phr ZnO and 20 phr zinc stearate. In order to study the suitability of the composites as solid rocket motor insulators, the ablative properties were determined by subjecting the cylindrically shaped composites to plasma arc jet facility to simulate the high temperature environment of the insulators. The specimen was exposed to plasma arc jet of know heat flux for 20 seconds. The length of the specimen before and after exposure is used to calculate the thermal erosion rate.

Stress-strain properties of the cured samples were measured according to ASTM D 412-98a specification. Aging studies were performed by determining the mechanical properties after aging of the composite test specimens at 150°C for 48 hours in a circulating air oven. The tensile fractured samples and the extrudate surfaces, obtained after extruding through the Monsanto processibility tester were studied by using a JEOL scanning electron microscope (model, JSM 5800). Extrudate surfaces were obtained by extruding the compounds through a capillary rheometer at 120°C and at a shear rate of $64.1 s^{-1}$. For AFM investigations, a relatively flat surface structure is necessary to avoid damaging of the tip. AFM specimens were prepared by cryomicrotoming in a Reichert-Jung Ultracut Ultramicrotome, using glass knives after freezing the specimens to below the T_g of the matrix using liquid nitrogen. Average sample thickness was 20 microns. AFM study was carried out in air at ambient conditions (25°C) using a Dimension 3000 Atomic Force Microscope made by Digital Instruments, Santa Barbara, CA, USA. Topographic images were scanned and recorded in the tapping mode. Images were subsequently analyzed using Nanoscope IIIa software. Details of AFM technique/application/analysis for fiber composites [5, 8, 9-11], filler-composites [12, 13], polymer recycling [14-16] and polymer blends [17, 18] by the authors and the co-researchers are available in the literature.

RESULTS AND DISCUSSION

Mechanical Properties of the Composites: As is evident from Table 1**,** the interfacial adhesion between melamine fiber and the rubber matrix is significantly improved in presence of the dry bonding system. Without bonding system, the composite $EB_0Si_0F_{30}$ is weak; having tensile strength only 1.6 MPa and the value is comparable to that of the gum compound $EB_0Si_0F_0$. Addition of resorcinol, hexamine and silica in the ratio 5:3:15 increases the tensile strength and modulus more than 3 times (composite $EB_1Si_{15}F_{30}$). When the concentration of the constituents of the dry bonding system is optimized (resorcinol, hexamine and silica concentration 10/6/15, composite $EB_2Si_{15}F_{30}$), there is further improvement in the mechanical properties (17% increase in tensile strength and 25% increase in tensile modulus). Similar results were obtained in the case of composites based on both maleated EPDM rubber and nitrile rubber, as shown in Table 1. Apparently, a multilayer adhesion, involving fiber, bonding system and the elastomeric matrix takes place here [19]. The methylol group in the melamine fiber forms hydrogen bonding with the hydroxyl groups in the dry bonding system. The binding force between the adhesive and the elastomer comes from the vulcanization of the elastomer. The dry bonding system, upon heating, produces resorcinol-formaldehyde resin through crosslinking between the unsaturated bonds in the elastomer and the bonding system, assisted by the heat of vulcanization in the presence of sulfur/accelerator. This hypothesis is confirmed by the improvement in properties of the aged composites containing the dry bonding system.

Aging at 150°C for 48 hours causes a distinct change in the mechanical behavior of the composites. Again Table 1 shows that the composites display an increase in tensile strength and modulus after aging, particularly in the presence of the bonding system. At the same time in the absence of fiber, aging causes a drop in tensile strength ($EB_2Si_{15}F_0$). Even in the absence of bonding system, there is an increase in tensile strength and modulus of the composite $EB_0Si_0F_{30}$ due to aging, however, when bonding system is present, the strength and modulus are further increased (composite $EB_2Si_{15}F_{30}$). This illustrates the contribution of dry bonding system in improving the fiber-matrix adhesion.

Table 1. Mechanical properties of the composites based on EPDM rubber.
(Values in the brackets indicate properties obtained after aging the vulcanizates at 150°C for 48 hours)

Compositions[a]	$EB_0Si_0F_0$	$EB_0Si_0F_{30}$	$EB_1Si_{15}F_{30}$	$EB_2Si_{15}F_0$	$EB_2Si_{15}F_{30}$	$SB_0Si_0F_{30}$	$SB_2Si_{15}F_{30}$	$NB_0Si_0F_{10}$	$NB_2Si_5F_{10}$
Rubber	EPDM	EPDM	EPDM	EPDM	EPDM	Maleated EPDM	Maleated EPDM	Nitrile	Nitrile
Resorcinol/hexa/ silica (phr)	0/0/0	0/0/0	5/3/15	10/6/15	10/6/15	0/0/0	10/6/15	0/0/0	10/6/5
Fiber (phr)	0	30	30	0	30	30	30	10	10
Stress at 100% elongation (MPa)	1.2 (1.5)	1.5 (--)	4.8 (--)	1.7 (2.8)	6.0 (--)	2.5 (--)	6.8 (--)	1.2 (1.4)	3.6 (3.3)
Tensile strength (MPa)	1.5 (1.5)	1.6 (2.2)	5.9 (8.5)	5.5 (5.2)	6.9 (9.8)	3.7 (4.3)	9.3 (11.0)	2.4 (2.5)	10.6 (10.7)
Elongation at break (%)	141 (109)	124 (60)	197 (79)	362 (183)	154 (81)	137 (66)	214 (72)	388 (222)	416 (300)
Hardness (Shore A)	47 (50)	61 (68)	66 (74)	53 (61)	67 (73)	67	76 (79)	51(52)	62 (64)

a, all compositions contain common ingredients, EPDM-100, ZnO-5, stearic acid-1, antioxidant-1, MBT-1.5, TMTD-1, sulfur-1.5

In the case of maleated EPDM rubber based composites, though fiber in presence of the dry bonding system improves the mechanical properties of those cured by using sulfur/accelerator crosslinking system (Table 1), presence of fiber and/or dry bonding system significantly reduces the tensile strength of the composites cured by using ionic crosslinking system (Table 2). This is possibly due to the fact that the presence of fibers and other compounding ingredients partially hinder the aggregation of ionic groups to form multifunctional crosslinking sites. The higher elongation at break of the gum compound ($IB_0Si_0F_0$) is due to the occurrence of the stress induced ion exchange, lowering stress concentration resulting in high elongation. The lowering of strength of the fiber filled composites even in the presence of the bonding system (composite $IB_2Si_{15}F_{30}$) confirms that the RHH dry bonding system is more effective if sulfur and accelerator are also present in the matrix.

Table 2. Mechanical properties of the maleated EPDM rubber-melamine fiber composites (ionic crosslinking system)

Compositions	$IB_0Si_0F_0$	$IB_0Si_0F_{30}$	$IB_2Si_{15}F_0$	$IB_2Si_{15}F_{30}$
Resorcinol/hexamine/silica (phr)	0/0/0	0/0/0	10/6/15	10/6/15
Fiber (phr)	0	30	0	30
Stress at 100% strain (MPa)	1.2	1.3	2.1	3.4
Tensile strength (MPa)	12.3	7.1	7.5	6.4
Elongation at break (%)	1001	850	637	466

Ablative Properties of the Composites: The thermal erosion rate of the unfilled and fiber filled composites based on the EPDM rubber matrix are given in Table 3.

Table 3. Thermal erosion rate of the composites

Composite	Thermal erosion rate (mm/sec)
$EB_0Si_0F_0$	0.40 ± 0.01
$EB_0Si_0F_{30}$	0.22 ± 0.03
$EB_2Si_{15}F_0$	0.38 ± 0.02
$EB_2Si_{15}F_{30}$	0.20 ± 0.01

Incorporation of 30 phr melamine fiber even in the absence of the bonding system causes around 45% reduction in the erosion rate ($EB_0Si_0F_{30}$). However, when the fiber-rubber adhesion is improved through the dry bonding system, there is a significant reduction in thermal erosion rate (composite $EB_2Si_{15}F_{30}$ vis-à-vis $EB_0Si_0F_{30}$). The presence of silica alone does not help in improving the ablative properties, as is evident from the high erosion rate of the compound $EB_2Si_{15}F_0$. The fiber, when properly bonded to the matrix, adds strength to the char until they reach their own decomposition temperature.

AFM and SEM Analysis of the Composites: The AFM images shown in Figs. 1(a) to 1(c) are the section analyses of the EPDM-melamine fiber composites with resorcinol/hexamine concentration of 0/0, 5/3 and 10/6 phr respectively. The improved wetting of the matrix on the fiber due to the presence of the bonding system is evident here. It is seen that in the absence of the dry bonding system, the width of the interphase is only 0.59 μm (Fig. 1(a)). The fiber matrix interphase is very smooth, indicating insignificant interaction [poor wetting] between the fiber and the matrix. When resorcinol and hexamine are added in the ratio 5:3, the width of the interphase is increased to 1.79 μm (Fig. 1(b)). When the concentration of resorcinol and hexamine is increased to 10 and 6 phr respectively, the width of the interphase is further increased to 5.39 μm (Fig. 1(c)). So, as the ratio of the constituents of the dry bonding system is raised, the interphase thickness is increased. The mechanical properties described earlier are in line with the increase in interphase thickness. SEM photomicrographs of the tensile fracture surfaces also show that in the absence of the bonding system, the fibers are loosely held to the matrix and the fracture mode is fiber pullout (Fig 1(d)) However, better fiber-matrix adhesion is observed in presence of the bonding system, as shown in Fig. 1(e).

Table 1 shows that aging improves the tensile strength and modulus of the composites. AFM images in Fig. 1(b) also reveal that though an interphase is formed with the addition of the dry bonding system, the bonding between the fiber and the matrix is not achieved to the maximum in the case of the unaged composites. There is debonding between the fiber and the matrix before aging. In some areas, the gap between the fiber and the matrix is in the range of 0.74 to 0.93 μm. This distance is proportional to the extent of debonding. The fiber surface is also smooth, which shows inadequate mechanical interlocking.

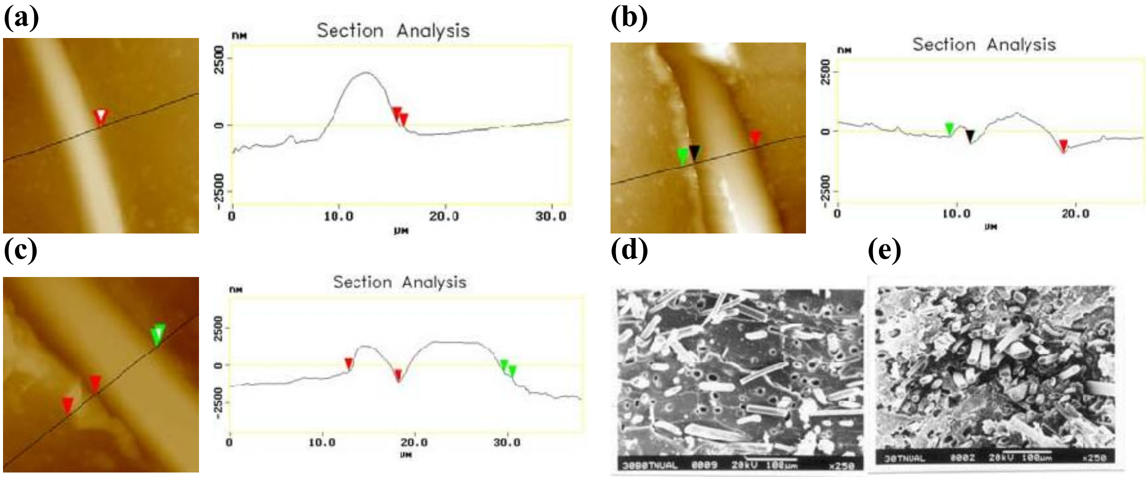

Fig.1. (a)-(c) AFM section analysis of the unaged EPDM-melamine fiber composites with resorcinol/hexa/silica concentration 0/0/0, 5/3/15 and 10/6/15 respectively; (d) and (e), SEM photomicrographs of the tensile fracture surfaces of the unaged EPDM-melamine fiber composite- (d) without and (e) with dry bonding system

The improved wetting of the matrix on the fiber surface, in the presence of the bonding system is evident in the SEM and AFM images of the aged EPDM-melamine fiber composites, given in Fig.2. In the SEM image of the tensile fracture surface of the aged composite (Fig. 2 (a)), the failure mode is mainly fiber breakage because of the improved fiber-matrix adhesion. AFM section analysis also shows that before aging the fiber surface is smooth (Figs. 1(b) and 1(c)); however, after aging, due to the greater mechanical interlocking between the fiber and the matrix, the undulations are more (Fig. 2 (b)). Comparison of the surface profile generated by the AFM tip over the fiber surface of the composite $EB_2Si_{15}F_{30}$ before and after aging, given in Fig. 2 (c), reveals the changes induced on the fiber surface by aging. The surface roughness of the fiber itself is changed upon aging. The AFM phase images of a single melamine fiber filament before and after aging are given in Fig. 3 along with corresponding AFM section analysis of the height images. The changes in the surface morphology of the filament due to aging are visible here.

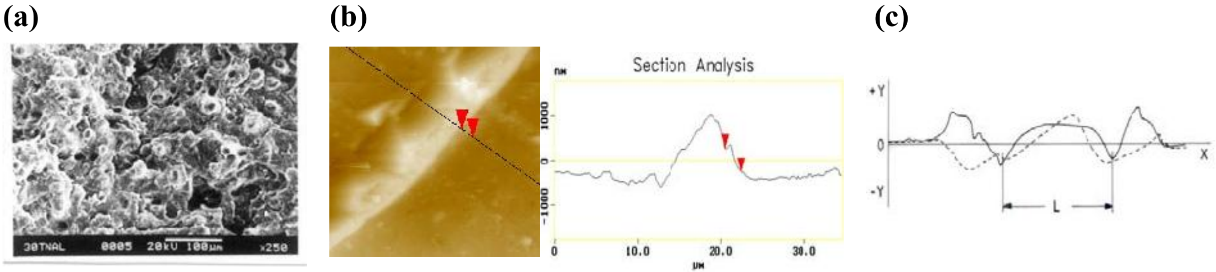

Fig. 2. (a) SEM fractograph and (b) AFM section analysis of the aged composite $EB_2Si_{15}F_{30}$ containing the dry bonding system; (c) surface profile generated by the AFM tip over the fiber surface on the composite before aging (_______) and after aging (---------)

AFM roughness analysis of the melamine fiber filaments show that the average filament surface roughness is increased from 5.66 nm to 12.61 nm due to aging at 150°C for 48 hours. This presents a greater interfacial surface area [typically 4 times] enabling the matrix to flow into the crevices of the roughened fiber, causing improved wetting. Dry bonding system assists the matrix flow. The better tensile strength and modulus of the aged composites are considered as the consequence of this excellent mechanical interlock, as evident from the AFM images. The enhanced roughness of filament surface upon aging are probably due to surface oxidation as well as removal of adsorbed water layer [5].

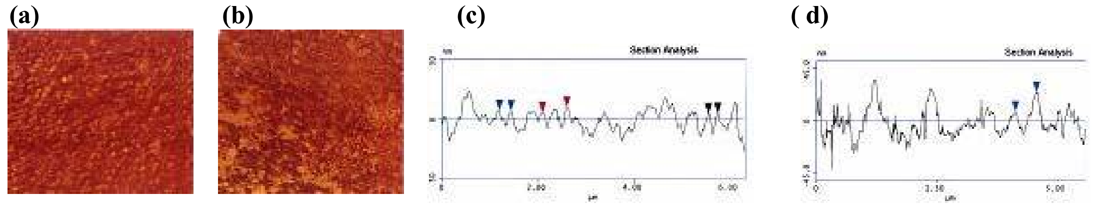

Fig. 3. (a) and (b) AFM phase image of the unaged and aged single melamine fiber filament; (c) and (d), section analysis of the AFM height image of the unaged and aged single melamine fiber filament.

The improved wetting due to aging is only observed in the presence of the dry bonding system, by comparing SEM and AFM images of the aged composites containing no bonding agent (Fig. 4 (a) and (b)) with those containing the bonding system (Figs. 2(a) and 2(b)). This observation is further confirmed in the three dimensional AFM topographic image of the aged matrix of the composite $EB_0Si_0F_{30}$ (Fig. 4 (c)), which contains no bonding system. The figure shows a bed in the matrix, which is actually the position where the fiber was laid on. In the absence of the bonding system, the fiber is easily removed leaving the matrix unreinforced.

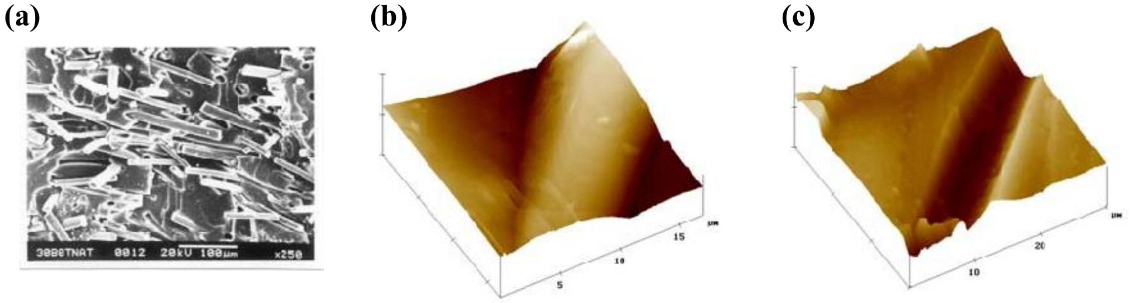

Fig. 4. (a) SEM fractograph and (b) AFM surface plot image of the aged composite $EB_0Si_0F_{30}$, containing no bonding system; (c) AFM surface plot image of the matrix showing the bed where fiber was laid on, for the composite $EB_0Si_0F_{30}$, aged at 150°C for 48 hours.

AFM images of composites based on maleated EPDM rubber and nitrile rubber also display similar trend – shown in Figs. 5(a) and 5(b) for maleated EPDM rubber based composite without and with bonding agent; similarly in Figs. 5(c) and 5(d) for nitrile rubber composites.

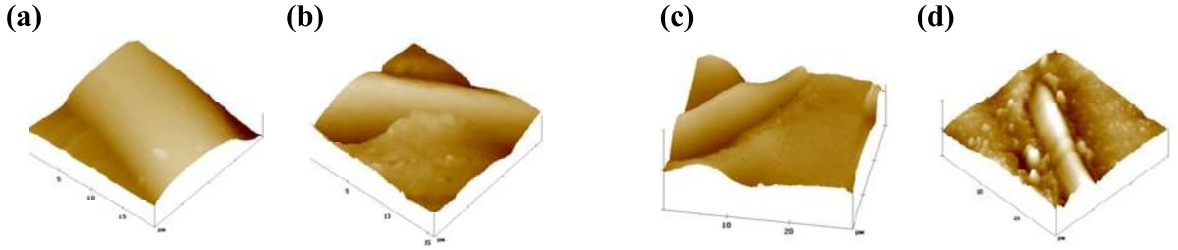

Fig.5. AFM surface plot images of the composites: (a) and (b), maleated EPDM rubber –melamine fiber composites without and with dry bonding system; (c) and (d), nitrile rubber-melamine fiber composites without and with dry bonding system.

Dry bonding system helps to achieving a smooth extrudate surface, which is important in the development of high performance composites. Figs. 6 (a) and 6 (b) present SEM micrographs of the extrudate surfaces of EPDM-melamine fiber compounds without and with dry bonding system. Melting of resorcinol at the extrusion temperature and the presence of silica helps in obtaining a smooth extrudate. Also, the fiber prevents melt fracture and reduce die swell.

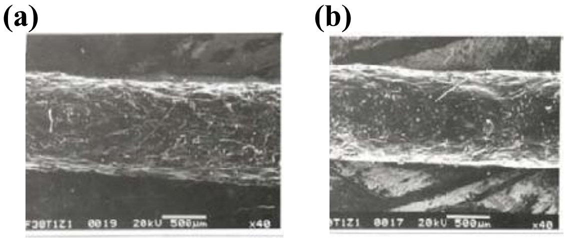

Fig. 6. SEM photomicrograph of the extrudate surface of the compounds based on EPDM and melamine fiber; (a) without dry bonding system and (b) with dry bonding system

CONCLUSIONS

The present study shows that high performance fiber-rubber composites can be prepared using melamine fiber. It is found that reinforcement of EPDM, maleated EPDM and nitrile rubbers using melamine fiber takes place through RHH dry bonding system. Tensile strength and stress at 100% strain of the composites increase when both fiber and bonding system are simultaneously present. Fiber-rubber composites in presence of the bonding system show higher retention of strength and modulus even after prolonged aging at 150°C due to better matrix flow and wetting. Without fiber, the mixes show lowering of properties due to aging, which explains the role of melamine fiber in retaining the properties on aging. Using AFM and SEM, the role of the bonding system in improving the fiber-matrix interaction and the reasons for the improved strength and modulus of the composite after aging are quantitatively analyzed. As the ratio of the bonding system is increased from 5:3:15 to 10:6:15, the width of the interphase is increased from 1.79 μm to 5.39 μm. SEM fractographs of the aged composites show that after aging there is no debonding of the fiber from the matrix and failure occurs mainly due to the breakage of fibers, which are well bonded to the matrix due to better wetting. AFM studies also confirm, quantitatively, change in surface morphology of the fiber as well as the composites due to thermal aging. Comparison of mechanical properties and analysis of SEM and AFM images of unaged and aged composites suggest that presence of both fiber and bonding system are necessary for improvement in strength and modulus of the composites by thermal aging. There is a significant improvement in the ablative properties of the composites in the presence of melamine fiber especially if there is proper adhesion between the fiber and the matrix through the dry bonding system. Determination of the interphase modulus using an ultramicro/nano-indentor [20] should be a useful future work.

ACKNOWLEDGEMENT

The authors thank Indian Space Research Organization, Bangalore for sponsoring the project and providing some of the experimental facilities. They also thank M/s BASF South East Asia Pte Ltd., Singapore for the free supply of melamine fiber. One of the authors, R.S. Rajeev, acknowledge the financial support provided by the Australia-India Council, Canberra, Australia for carrying out the AFM studies at the University of New South Wales, Sydney, Australia. Special thanks are due to Mr. Sergei Magonov, Digital Instruments, Santa Barbara, CA, USA, for performing some of the AFM analyses.

REFERENCES

1. V.M. Murty and S.K. De, “Short Fiber Rubber Composites”, *Polymer Engineering Review*, Vol. 4(4), 1984, pp.313.
2. A.P. Foldi in *Short Fiber-Polymer Composites*, Eds. S.K De and J.R White, Woodhead Publishing Limited, Cambridge, England, 1996, pp.242.
3. N.S. Vojvodich in *Ablative Plastics*, G.F. D’Alelio and J.A. Partker, Eds., Marcel Dekker Inc., New York, 1971, pp.41.
4. V. Fitch and N. Eddy, *33rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference,* Seattle, June 6-9, 1997 (in AIAA-97, No. 2992).
5. R.S. Rajeev, Anil K Bhowmick, S.K De, Bill Gong and S. Bandyopadhyay, “Atomic Force Microscopy, X-ray Diffraction, Electron Spectroscopy and Thermal Studies of New melamine Fiber”, *Journal of Adhesion Science and Technology,* Vol. 16(14), 2002, pp.1957.
6. A Saha Deuri and Anil K Bhowmick, “Aging of rocket insulator compound based on EPDM”, *Polymer Degradation and Stability*, Vol. 16(3), 1986, pp.221.
7. R.S. Rajeev, S.K. De, Anil K. Bhowmick and Baby John, ““Studies on thermal degradation of short melamine fiber reinforced EPDM, maleated EPDM and nitrile rubber composites”, *Polymer Degradation and Stability,* Vol. 79(3), 2003, pp. 449.
8. R.S. Rajeev, Anil K Bhowmick, S.K De, G.J.P. Kao and S. Bandyopadhyay, “New composites based on short melamine fiber reinforced EPDM rubber”, *Polymer Composites* Vol. 23(4), 2002, pp.574.
9. Rajeev, R S, S K De, A K Bhowmick, GJP Kao and S Bandyopadhyay, “Atomic force microscopic studies of short melamine rubber reinforced EPDM rubber”, *Journal of Materials Science*, Vol. 36(11), 2001, pp.2621.
10. Rajeev R.S, Anil K. Bhowmick and S.K De, S. Bandyopadhyay, “Effect of crosslinking system on the properties of short melamine fiber filled maleated EPDM rubber composites with special reference to atomic force microscopic and scanning electron microscopic studies”, *Journal of Applied Polymer Science*, Vol. 89(5), 2003, pp. 1211.

11. Rajeev R.S, Anil K. Bhowmick, S.K De and S. Bandyopadhyay, “Short melamine fiber filled nitrile rubber composites”, *Journal of Applied Polymer Science*, Vol. 90(2), 2003, pp. 544.
12. A. M. Shanmugharaj, Sudip Ray, S. Bandyopadhyay and A. K. Bhowmick, “Surface morphology of styrene-butadiene rubber vulcanizate filled with novel electron beam modified dual phase filler by atomic force microscopy”, *Journal of Adhesion Science & Technology,* Vol. 17(9), 2003. pp.1167.
13. Sudip Ray, Anil K. Bhowmick and S. Bandyopadhyay, “Atomic force microscopy studies on morphology and distribution of surface modified silica and clay fillers in an ethylene-octene copolymer rubber", *Rubber Chemistry and Technology,* Vol. 76(5), 2003, pp. 1091.
14. S. Anandhan, P. P. De, S. K. De, S. Bandyopadhyay and Anil K. Bhowmick, “Mapping of thermoplastic elastomeric nitrile rubber/poly(styrene-co-acrylonitrile) blends using tapping mode atomic force microscopy and transmission electron microscopy”, *Journal of Materials Science*, Vol. 38(13), 2003, pp.2793.
15. S. Anandhan, P. P. De, A. K. Bhowmick, S. K. De and S. Bandyopadhyay, “Thermoplastic elastomeric blends of nitrile rubber and poly [styrene-co-acrylonitrile]. II. Replacement of nitrile rubber by its vulcinizate powder”, *Journal of Applied Polymer Science*, Vol. 90(9), 2003, pp. 2348.
16. S.Anandhan, S. K. De, P. P. De, S. Bandyopadhyay and Anil K. Bhowmick, “Novel thermoplastic elastomers based on acrylonitrile-butadiene-styrene (ABS) terpolymer and nitrile rubber”, *Rubber Chemistry and Technology,* Vol. 76(5), 2003, pp. 1146.
17. S. Ghosh, D. Khastagir, A. K. Bhowmick, S..Bandyopadhyay, G.J.P. Kao and L. Kok, “Atomic force microscopy studies of molded thin films of segmented polyamides”, *Journal of Materials Science Letters*, Vol. 19(23), 2000, pp. 2161.
18. A. Ghosh, Rajeev R. S, A.K. Bhattacharya, A.K. Bhowmick, S K De, B.Wolpensinger and S. Bandyopadhyay, “Atomic force microscopy studies on microheterogeneity of blends of silicone rubber and tetrafluoroethylene/propylene/vinylidene fluoride terpolymer”, *Rubber Chemistry and Technology,* Vol. 76(1), 2003, pp. 220.
19. Y. Kubo in *Elastomer Technology Handbook*, Ed. Nicholas P. Cheremisinoff, CRC Press, Boca Raton, USA, 1993, pp. 857.
20. T. Das, P.R. Munroe, S.Bandyopadhyay, T. Bell and M.V. Swain, “Interfacial behavior of 6061/Al_2O_3 metal matrix composites”, *Materials Science and Technology,* Vol. 13(9), 1997, pp. 778.