Short-Beam Three-Point Bend Test Study in Syntactic Foam. Part III: Effects of Interface Modification on Strength and Fractographic Features

Kishore,[1] Ravi Shankar,[2] S. Sankaran[3]

[1]*Polymer Composites Laboratory, Department of Metallurgy, Centre for Advanced Studies, Indian Institute of Science, Bangalore-560 012, India*
[2]*Department of Material Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7907*
[3]*Aeronautical Development Establishment, C. V. Raman Nagar, Bangalore-560 093, India*

ABSTRACT: Syntactic foam slabs having uncoated microballoons and paraffin oil surface-treated microballoons were fabricated and tested for short-beam three-point bend test. The work points to the role of paraffin oil coating first weakening the interface between the microballoons and the matrix and hence lowering the efficiency of load transfer from matrix to the fillers (i.e., microballoons). This led to an overall decrement of 71% in the experimentally measured strength value compared to the deduced value for uncoated microballoons' specimens. The large strengths for uncoated microballoons specimens can be traced to the presence of the curvilinear marks in the matrix that, incidentally, are absent in the case of paraffin oil coated specimens. These observations are revealed distinctly in the microscopy of test-failed specimens. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 687–693, 2005

Key words: composites; shear; fracture; uncoated microballoons; coated microballoons

INTRODUCTION

Mechanical properties of polymer composites mainly depend upon three major factors, namely, those of matrix, reinforcement, and interfacial region between the matrix and the reinforcement. Reinforcements, depending upon their shape, size, and distribution in the matrix, affect the composite properties. Over the years, it has been established that fracture behavior of a polymer composite system can be varied by attending to the details at the interface.[1–14] Interfaces, constituting the regions about the matrix and the reinforcement, can be modified by resorting to different methods like altering the surface treatments for the reinforcements,[1,2,10–14] by effecting a particular cooling rate,[3–5] and because of use of plasma.[6] Apart from these, an interface also gets modified depending upon the environment to which the polymer composites get exposed.[7] A critical review on the physical and chemical treatment methods that improve the fiber–matrix adhesion and their characterization methods is available in published literature.[8] These interface/interphase modification methods generally are aimed at influencing specific properties that often happen to be a mechanical property. Zafeiropoulos et al.[1] showed the effect of surface treatments of acetylation and stearation on the interface in flax fiber/polypropylene-composites systems and found that both the surface treatments led to improvement in stress transfer efficiency at the interface. In another effort, Zhao et al.[2] studied the effect of inorganic–organic interface adhesion on mechanical properties of Al_2O_3/polymer laminate composites. The work of fracture of the laminate composites, having alumina matrices coated with a layer of epoxy vinyl ester resin (UPR 3201), increased gradually with increasing interface shear strength. The work of fracture, on which alumina matrices were coated with a layer of toughened epoxy vinyl ester resin (T-UPR 3201), decreased greatly as the interface shear strength increased. Cooling rate effects in carbon fiber/poly ether ether ketone (PEEK) composites were studied by Shang-Lin and Jang-Kyo.[3–5] With increasing cooling rate, interface bond strength, tensile strength, and elastic modulus decreased. Ductility, on the other hand, increased with increasing cooling rate. It was also shown that the values of both mode I and II propagation interlaminar fracture toughness increased initially on increasing the cooling rate. Plasma[6] was used to modify interphase/interface in polypropylene and epoxy matrices having chalk and carbon fibers, respectively, in them. Calcium carbon-

ate and carbon fiber surfaces were modified by use of a series of plasma polymers[6] at different selected plasma conditions. Tensile strength and stress to failure values for single carbon fibers were improved by plasma treatment. Adamsa and Singha[7] exposed the samples of several fiber-reinforced epoxies and fiber-reinforced PEEK to steam. Epoxy resin reinforced with glass fiber degraded more than those reinforced with carbon fiber, suggesting that interphase plays a role in the response to moisture conditioning.[8] Hussain et al.[9] investigated effects of different coupling agents on the mechanical properties of TiO_2 particulate-filled epoxy composites. Young's modulus and flexural strength of composite treated with titanate coupling agent were significantly better compared to untreated silane-coupling agent composites. Liang and Li[10] studied glass-bead-filled polypropylene composites and found that the values of Young's modulus and tensile stress of composite filled with untreated glass-bead are somewhat higher than those of the silane-treated glass-bead composites under the same test conditions. However, this is in contrast to the tensile strain at break and tensile fracture energy, especially at higher volume fraction values of the glass beads. The effect of surface treatments on the impact behavior of fly ash filled polymer composites was studied by Kishore et al.[11] Adhesion-increasing treatments (i.e., cleaning with acetone and coating with silane) showed greater absorption of energy and maximum load compared to untreated samples and those subjected to treatment that reduces adhesion. However, ductility index showed reversal in trends.

As regards the interface modification by paraffin oil is concerned, sporadic data are available[12,13] for systems other than polymer composites, where emphasis was on tribological properties,[14] whereas in the case of polymer systems, a few reports are available.[15,16] Iya and Majali[15] showed that use of chlorinated paraffin oil as an additive imparted fire resistance to the wood–polymer composites based on tropical hardwoods and also brought down the gamma dose requirement for total polymerization. In another effort by Thorp,[16] friction of some commercial polymer-based bearing materials against steel is studied where the fact that paraffin oil lubrication significantly reduces friction has been stressed. In another effort by Kulkarni and Kishore,[17] paraffin oil was coated on fly ash particle and compression properties were studied.

As regards the effect of interface on the properties of the advanced composites having hollow microballoons reinforced in epoxy matrix is concerned, references available are sparse.[18,19] Calahorra et al.[18] studied the effect of thin-film parylene coating on the moisture absorption properties of the three-phase syntactic foams. They found only 150–200 mg/cm^2 parylene C coating provides an efficient water vapor barrier.[18] In another effort, Bilow et al.[19] showed that

reticulated polyurethane foam, which was coated with parylene, improved its hydrostatic stability.

As regards the shear strength of syntactic foam with paraffin oil coated microballoons is concerned, no data could be found in the published literature. Therefore, this forms the subject matter of the present study, where the effect of interface modification on the failure features in short-beam three-point bend test (SBT) of syntactic foam has been looked into. Thus, this effort complements the previous articles where the emphasis was on microscopic features in one case[20] and on the effect of the volume percentage of microballoons on the shear strength in the other.[21]

MATERIALS

Syntactic foam slab was prepared by using Araldite LY-556 (bisphenol-A diglycidyl ether) and hardener HT-972 (aromatic diamine hardener) in a ratio of 100 : 27 by weight. Vantico Performance Polymers Pvt. Ltd. (Mumbai, India) supplied the epoxy resin, which had an equivalent epoxy weight value of 190. Paraffin oil was supplied by Vikram Chemical Laboratories (Kanpur, Uttar Pradesh, India). These oils generally display specific gravity 0.92[22] and kinematic viscosity not less than 38.1 mm^2/s at 37.8°C.[22] The HLB (hydrophile–lipophile balance) of mineral oil paraffin generally is about 10,[23] which being in the range of 8–10, indicates a stable milky dispension.[23]

The density of the cured resin system was 1180 kg/m^3. Glass hollow microspheres (called glass microballoons), Ecospheres SI (supplied by Grace Electronic Materials, Westerlo, Belgium), constitute the filler material. Density of the glass microballoons was 250 kg/m^3, while the diameter was in the size range of 44–175 μm. This size range is similar to the ones employed for the microscopy studies of the syntactic foam presented in Part I[20] and differing from the ones employed for strength correlation studies presented in Part II[21] (size range 75–90 μm).

Coating of microballoons

Paraffin oil was used to coat the hollow glass microballoons by evaporation condensation method. The process involves the heating of the paraffin oil that leads to its evaporation. The vapors were then allowed to condense onto the surface of the hollow microspheres by enclosing the whole assembly in a chamber. This process is repeated four to five times so that the oil layer envelops the surface of the microspheres.

Material processing

Syntactic foam slab was processed by taking the required quantities of resin and hardener in a beaker and then mixing them thoroughly. The mixture was

TABLE I
Details of the Fabricated Syntactic Foam Slabs

Foam designation	Volume % of microballoons[a]	Volume % of resin	Density (kg/m^3)
Slab 1	36	64	853.04
Slab 2	32.19	67.81	803.0
Slab A	45.99	54.01	757.5
Slab B	52.36	47.64	717.0

[a] Determined from the burn-out test performed on post-compression-failed test coupons.

heated to 95°C. For the fabrication of two sets of slabs, one having uncoated microballoons and the other with coated microballoons, an identical quantity of the resin was taken in two containers. A fixed quantity of microballoons was taken and divided into two equal parts. One part was taken for the fabrication of syntactic foam slab with uncoated microballoon by adopting the procedure mentioned in Parts I[20] and II.[21] The second part was initially used for the paraffin oil coating on the microballoons by the aforementioned procedure and then the introduction of such microballoons in several lots to the resin system to yield the second slab. Stirring was done gently to avoid the breakage of microballoons. Addition and mixing of microballoons was easier with paraffin-coated microballoons compared to the uncoated materials because no agglomeration of microballoons was observed in the former. Also, the flowability of the slurry was better compared to the slurry system seen with the cases of uncoated microballoons. The slurry was filled into a metallic mold with dimensions of 150 × 150 × 25 mm. Curing cycle as mentioned in previous parts (Part I[20] and Part II[21]) was followed. Briefly stated, it is cured at room temperature for 24 h and at 100°C for 4 h followed by postcuring at 160°C for 3 h. The above-mentioned procedure was repeated in making two additional slabs that had different volume percentage of microballoons' bearing samples and which did not have microballoons in the coated condition. Instead, both these additional ones had the same size range, namely, 44–175 mm used for this part of the investigation. In making these, care was taken to see that they were in the neighborhood of 50% by volume for the filler (slabs A and B), all of which are included in Table I.

Short-beam three-point bend tests

Short-beam three-point loading tests were carried on MTS 810. The machine was programmed to apply the load at a rate of 1.3 mm/min. Tests were performed on samples having dimensions of 3 × 15 × 21 mm conforming to the ratio 1 : 5 : 7 for thickness : span length : total length. Five samples were tested for the two different slabs, namely, slab 1 and slab 2.

Microscopy

The failed samples from SBT were examined in a JEOL make JSM 840A scanning electron microscope (SEM) to observe the fracture surface. Gold coating was done in a sputtering unit at a current of 10 mA on the test samples before putting them into the vacuum chamber of the SEM.

Infrared spectrum (IR)

IR spectra of the coated and uncoated hollow glass microballoons in potassium bromide (KBR) pallets were obtained from Shimadzu FTIR 4002 series spectrometer.

RESULTS AND DISCUSSION

Infrared spectrum

IR spectra obtained on both coated and uncoated microballoons are presented in Figure 1. From the data, it is seen that the spectrum of coated microballoons has C—H stretching centered around 2920 cm^{-1}, which is absent in the uncoated microballoons case. A peak that is present in uncoated spectrum at 1695 cm^{-1} possibly corresponds to a carbonyl group present in the silane-coupling agent, which is comparatively insignificant in absorption spectrum for the coated microballoons case. Such an occurrence may be traced to the possibility that the silane coating present on the surface of the microballoons may have been depleted during repeated vapor condensations, adopted a few times to ensure a good envelop of this oil on the surface of the microballoons. The strong peak at 460 cm^{-1} and the peaks in the region of 1092–1230 cm^{-1} are characteristics of Si—O—C vibrations. Further, to corroborate this, randomly selected coated microballoons were examined under SEM. Figures 2 and 3 show the features of uncoated and coated microballoons, respectively. The envelope of oil is very distinct from an examination of the latter.

Mechanical data

It is evident from Figure 3 that coating varies to some degree on the surface of the microballoons. Therefore, to calculate the correct amount of matrix and microballoon constituents, the failed SBT samples were themselves subjected to burn-out tests, which yielded a value of 32.19 and 36 vol % of microballoons content for the coated and uncoated cases, respectively. These are recorded in Table I. Further, it is seen from Table I that interface modification has resulted in lowering the density of the slab. Accordingly, the volume fraction of microballoons is comparatively lower in the interface-modified foam slab. Consequently, the primary objective of this work to compare the strength
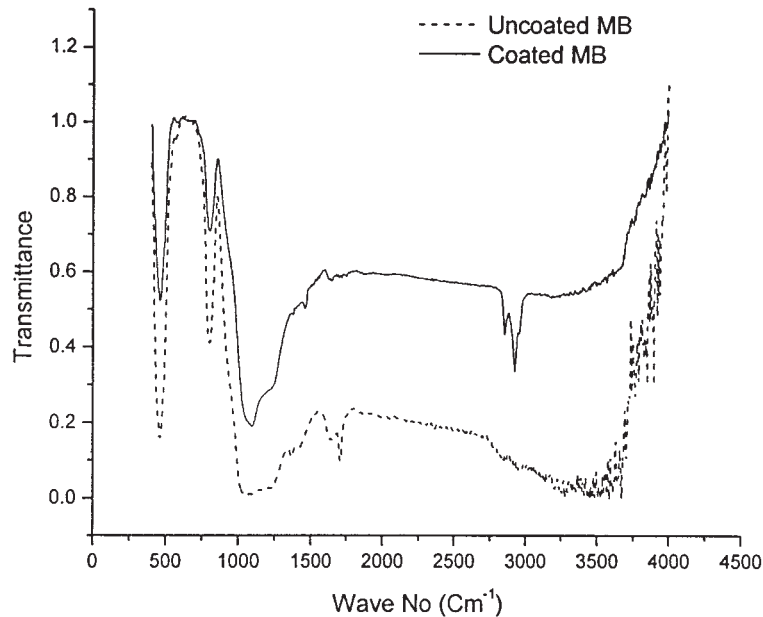
Figure 1   IR spectra of the uncoated and coated microballoons' specimens.

values having the same vol % of microballoons is not fulfilled. Though two slabs were made by taking the same vol % of epoxy resin, the result showed differences in vol % of microballoons and matrix for the two cases. This is due to the fact that paraffin oil forms a varying level coating on microballoons surface and therefore adds to the matrix content. Therefore, it was difficult to fabricate the uncoated slabs containing the same microballoons content as that of the oil surface-bearing ones. To overcome this technical problem, a procedure of using rule-of-mixture data was adopted. In this rule, the matrix strength and its volume percentage as well as the fillers' volume and strength form one side of the equation, while the strength of the composite forms the other side. This right-hand side was determined for the two volume percentage bearing cases (i.e., slab A and slab B) precisely by performing the three-point bend test. For the left-hand side, the proportions of the matrix and resin were deter-

mined earlier on by burn-out test. This exercise yielded a value of 23.5 MPa for the strength of the resin. To check how close this value is from an actual experiment, a plain (i.e., without any filler bearing) epoxy was also cast and its strength under short-beam three-point bending was determined. The value so obtained was about 17 MPa, which was lower than the rule of mixture value owing to the differing levels of defect population present in the two cases. Whenever an epoxy with hardener was stirred thoroughly to make a good mixture, invariably air entrapment in the system results, which appear as voids in the cured cast slab. The voids are known to bring down the strength of the system. The situation prevailing under similar circumstances in the microballoon-bearing system may be different.

Thus, having proved the utility of such an exercise, the rule of mixture-derived value of 23 MPa for the cured resin was used to calculate the strength of the
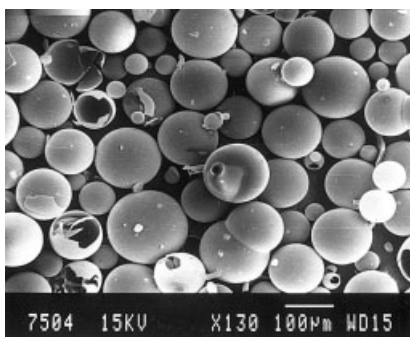

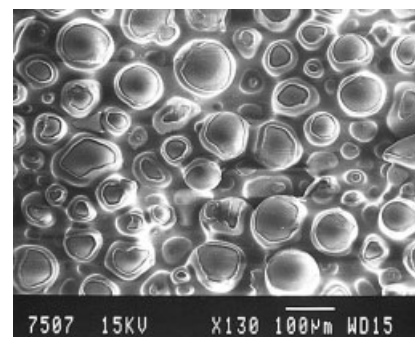**Figure 2**   The microballoons seen in uncoated condition.

Figure 3   The coated microballoons.

TABLE II
Comparison of Experimentally Determined Strength of the Fabricated Coated Syntactic Foam Slab (slab 2) with the Value Deduced for an Uncoated Syntactic Foam Slab (coded slab D)

Foam designation	Volume % of microballoons	Short beam test strength (MPa)
Slab D[a]	32.19	12.69
Slab 2	32.19	3.71

[a] Deduced data employing the rule of mixtures and using the experimentally determined values for the two compositions coded Slab A and Slab B in Table I.

composite, which had the 32.19% of microballoons in the system. Again, the void content was neglected in such a calculation. This yielded a value of 12.7 MPa, which is recorded in Table II (for a slab coded D) and also in Figure 4, as a histogram where additionally the derived value for plain epoxy is included.

This comparison leads to the fact that there is 71% decrease in strength for the oil-bearing case compared to the oil-free case. This substantial drop in strength values requires an explanation. To achieve this, microscopy was used in the same way as was employed in the previous parts of this reporting.[20,21] As microscopy of the two cases can only be compared when they are having the same level of epoxy resin content, this examination under the SEM was done for the test-failed samples of the two fabricated slabs bearing similar levels of epoxy resin content. In what follows, therefore, is the microscopy of the failed sample, whereby an explanation for the drop in strength values to the tune of 71% for the oil-bearing case is attempted.
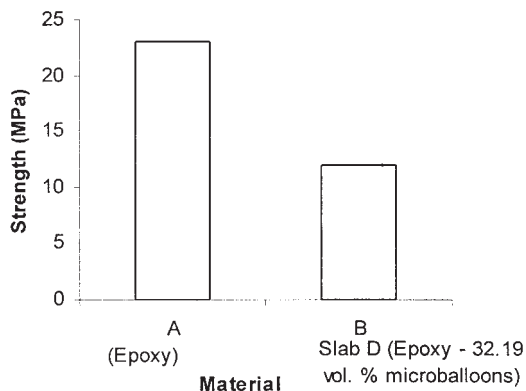

Figure 4 The value of strength of plain epoxy (material A), deduced from the two additional compositions (i.e., slabs A and B) cast for the purpose (Table I) and utilizing the rule of mixtures. Material B is the calculated strength of an epoxy—32.19 vol % microballoons system (coded slab D), using the deduced epoxy strength and again the rule of mixtures.
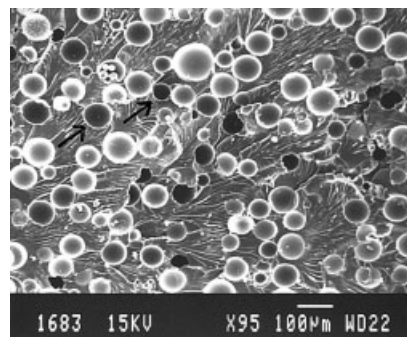

Figure 5 Low-magnification micrograph of the uncoated microballoons sample showing shear deformation marks and the cavity formation.

Microscopy

To explain the mechanical data, microscopy was done at different magnifications, which can be grouped into three categories, namely, low (Figs. 5 and 6), medium (Figs. 7-10), and high (Figs. 11 and 12). The low magnification is meant to show the overall features of the failed samples in the short-beam test. Micrographs taken at medium magnifications are designed to show clearly the fracture features of the matrix and the microballoons under load in the slabs. The high-magnification micrographs are included to show the characteristic features of the matrix sandwiched between the microballoons in samples displaying differing strength levels due to surface coating of the microballoons.

The effect of paraffin oil on the fracture features of the SBT specimens can be clearly seen in Figures 6, 8, 10, and 12 as against the micrograph of the uncoated microballoons specimens recorded in Figures 5, 7, 9, and 11. Figure 5 shows the uniform distribution of microballoons in the matrix and well-marked deformation bands in the matrix-rich regions of the micrograph. In addition, partial pull-out of the microballoons can clearly be seen here and there in the micrograph. Generally stated, the pull-out regions have
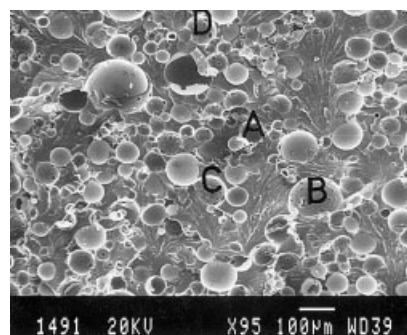

Figure 6 Low-magnification micrograph of the coated microballoons case showing boundaries, due to pull out of microballoons, being not sharp.
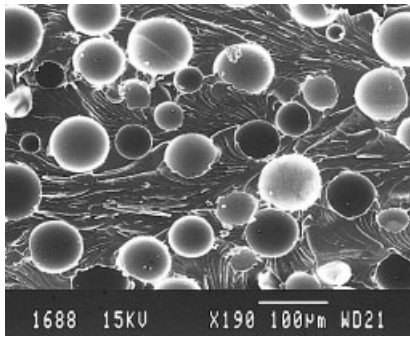
Figure 7 A higher magnification micrograph of the uncoated microballoons case showing prominent deformation marks and darker-appearing cavity having a clearly defined boundary.

Figure 9 A higher magnification micrograph of uncoated microballoons showing deformation marks of the matrix surrounded by the five (marked 1 to 5) microballoons.

sharp boundaries (a few marked by arrows). Figure 6 is the low-magnification micrograph for the coated system. This micrograph shows the matrix-rich regions that are not as conspicuous with shear deformation bands as was in the uncoated samples case shown in Figure 5. Also noticeable is the fact that pull-out of the microballoons is less in Figure 6 compared to Figure 5. Further, these do not have well-focused boundary for the pulled-out regions with respect to the matrix. One such region is marked A in Figure 6. Also, a close perusal of Figure 5 shows that the surface of the microballoons is bright and smooth, while those in Figure 6 (marked B, C, and D) have what could be correlated as droplet-like features coming from paraffin oil. At somewhat higher magnifications, the effect of matrix shear deformation in the case of uncoated microballoons specimens can be clearly seen (Fig. 7). The coated microballoons specimens, as shown in Figure 8, on the other hand, have sparsely distributed deformation marks in the matrix. This can be invoked to suggest that the specimen in Figure 7 had sustained higher load before failure, resulting in its higher strength. Figure 7 also shows microballoons
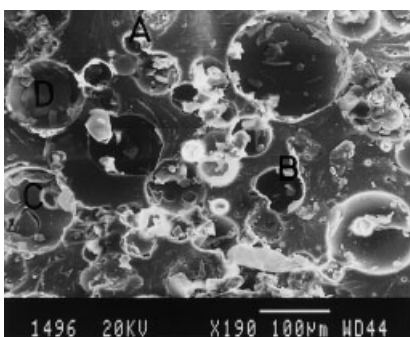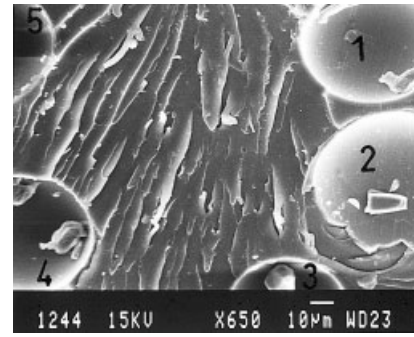
pull-outs having sharper boundaries, whereas Figure 8 shows features of collapsed microballoons (marked A and B). Intermittent fracture of microballoons occurring here and there, as shown at C and D, also can be seen in Figure 8. This validates the fact that paraffin coating has weakened the interface between the microballoons and the matrix and, therefore, the load transfer from matrix to the fillers (i.e., microballoons) is not quite effective. This results in a lower strength for the paraffin-coated system.

Microscopy is done at still higher magnification and these are shown in Figures 9 and 10 for uncoated and coated microballoons' specimens, respectively. Figure 9 shows prominent matrix deformation features in the matrix-rich regions formed among the five (numbered 1 to 5) microballoons. Shear cracking of the matrix leading to partial fracture of the microballoons can be seen in microballoons marked 2. These features can be taken to mean that effective load transfer from matrix to microballoons has taken place in Figure 9. The shear deformation marks seen in Figure 10 are less frequent compared to those in Figure 9. These features can be
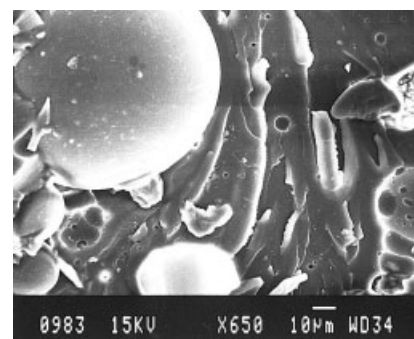

Figure 8 Paraffin-coated microballoons, some of which are showing fissures on their surface and others indicating tendency for collapsing-in trends.

Figure 10 Mid-range magnification micrograph for the coated microballoons case showing deformation marks which occur less frequently and the appearance of a fissure in the matrix region at right of center.

interpreted to convey that the load sustained by the specimen photographed in Figure 10 is less than that for the specimen detailed in Figure 9. The microscopy was done at still higher magnification to see the response of the matrix that is sandwiched in between the microballoons under load. In Figure 11, matrix sandwiched among three microballoons shows the resistance offered by the uncoated microballoons specimen in the form of prominent curvilinear marks in the matrix. At the same magnification for the paraffin-coated specimens, the absence of curvilinear marks is conspicuous (Fig. 12). A collapsed microballoon in the top portion of Figure 12 can be seen, while a partial cavity is seen in another microballoon adjacent to the top microballoon. All these features can together account for the lower failure strengths, exhibited by this coated specimens, owing to a weak interface present between the microballoons and the matrix.

CONCLUSIONS

It is clear from the work that paraffin oil alters the interface characteristics between microballoon and the matrix. This leads to a lowering of the load transfer from the fillers (i.e., microballoons) to matrix. The strength recorded for coated ones are roughly 29% of those foams without surface treatment for microballoons. Also, syntactic foams with coated microballoons have less population of the curvilinear-appear-
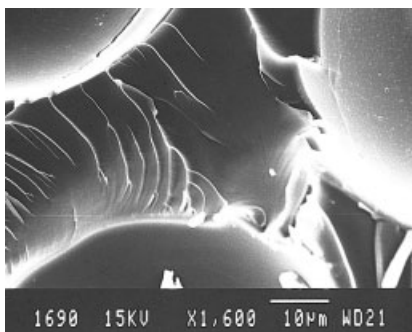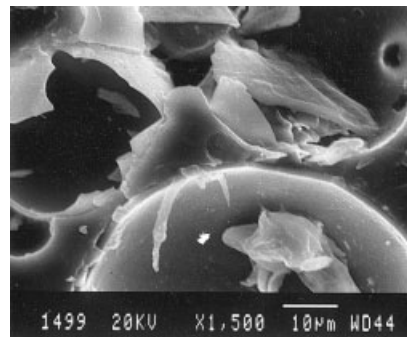

Figure 12 Partial cavity formation in the matrix phase of the coated microballoons sample.

ing deformation patterns in the matrix compared to the uncoated microballoon case.

References

1. Zafeiropoulos, N. E.; Williams, D. R.; Baillie, C. A.; Matthews, F. L. Compos Part A 2002, 33, 1083.
2. Zhao, S.; Zhang, J.; Zhao, S.; Li, W.; Li, H. Compos Sci Technol 2003, 63, 1009.
3. Shang-Lin, G.; Jang-Kyo, K. Compos Part A 2000, 31, 517.
4. Shang-Lin, G.; Jang-Kyo, K. Compos Part A 2001, 32, 763.
5. Shang-Lin, G.; Jang-Kyo, K. Compos Part A 2001, 32, 775.
6. Akovali, G.; Dilsiz, N. Polym Eng Sci 1996, 36, 1081.
7. Adamsa, R. D.; Singha, M. M. Compos Sci Technol 1996, 56, 977.
8. George, J.; Sreekala, M. S.; Thomas, S. Polym Eng Sci 2001, 41, 1471.
9. Hussain, M.; Nishijima, A.; Nakahira, A.; Niihara, K. Mater Lett 1996, 26, 299.
10. Liang, J. Z.; Li, R. K. Y. Polym Intl 2000, 49, 170.
11. Kishore; Kulkarni, S. M.; Sunil, D.; Sharathchandra, S. Polym Intl 2002, 51, 1378.
12. Qunji, X.; Weimin, L.; Zhijun, Z. Wear 1997, 213, 29.
13. Jingfang, Z.; Zhishen, W.; Zhijun, Z.; Weimin, L.; Hongxin, D. Wear 2001, 249, 333.
14. Huang, W.; Tan, Y.; Dong, J.; Chen, B. Tribol Intl 2002, 35, 787.
15. Iya, V. K.; Majali, A. B. Rad Phys Chem 1978, 12, 107.
16. Thorp, J. M. Tribol Intl 1982, 15, 69.
17. Kulkarni, S. M.; Kishore, J Mater Sci 2002, 37, 4321.
18. Calahorra, A.; Gara, O.; Kenig, S. J Cell Plast 1987, 23, 383.
19. Bilow, N.; Sawko, M. P. J Cell Plast 1975, 11, 207.
20. Kishore; Shankar, R.; Sankaran, S. J Appl Polym Sci, to appear.
21. Kishore; Shankar, R.; Sankaran, S. J Appl Polym Sci, to appear.
22. Myers, P. in Encyclopedia of Chemical Technology; Howe-Grant, M., Ed.; Wiley: New York, 1997; p 23.
23. Griffin, W. C. in Encyclopedia of Chemical Technology; Mark, H. F., Ed.; Wiley: New York, 1979; p 8.

Figure 11 Matrix sandwiched among the three microballoons and prominent marks on the matrix.