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Characterization of Mechanical and Electrical Properties of Epoxy-Glass Microballoon Syntactic Composites

Nikhil Gupta[1], Shashank Priya[2], Rashed Islam[2], William Ricci[1]

[1]Composite Materials and Mechanics Laboratory
Mechanical, Aerospace and Manufacturing Engineering
Polytechnic University, Brooklyn, NY 11201
Phone: 718-260 3080, Fax: 718-260 3532, Email: ngupta@poly.edu
[2]Materials Science and Engineering
Automation Robotics Research Institute, University of Texas at Arlington
Arlington, TX 76019

Abstract

The density of hollow particle (microballoon) filled composites called syntactic foams can be varied by two methods. The first method is the variation in microballoon volume fraction and the second method is the variation in the microballoon wall thickness, while keeping their volume fraction the same. A comparison of compressive properties of syntactic foams having microballoons of four different wall thicknesses in five volume fraction each is presented here. It is found that the compressive strength and modulus vary linearly with respect to the foam density. Dielectric constant, dielectric loss and electrical impedance are measured for four syntactic foam compositions with respect to temperature and frequency. Dielectric constant and loss are found to decrease with increase in frequency and with decrease in temperature in the range of 40 – 140°C.

Keywords: Particle-reinforced composites (A), Polymer-matrix composites (A), Electrical properties (B), Porosity (B), Syntactic foam.

Introduction

Hollow glass particles (microballoons) are filled in polymers or metals to create low density composite materials called syntactic foams. Large numbers of published studies have characterized epoxy resin matrix syntactic foams for a variety of properties. Compressive properties have been studied in great detail because most of the applications of these materials are in the marine structures where hydrostatic compression is the most common force applied on the material. For the same reason, moisture absorption is also found studied. It is found that these materials have a capacity to absorb large compressive strains because of the hollow space within their structure. However, under tensile loading condition the epoxy based foams were found to fracture in brittle manner, at the end of their linear elastic region. Tensile properties of syntactic foams are highly dependent on the characteristics of matrix material. Matrix modification can be carried out to enhance the elastic and plastic strain in syntactic foams.

It is known that the strength of syntactic foams increases with an increase in their density. Two approaches have been found studied in the published literature to modify the density of syntactic foams. The first approach is based on increasing the microballoon volume fraction (V_{mb}) in the syntactic foam structure to decrease their density. Typically, microballoons are lighter than the polymer used as the matrix material, hence, increase in V_{mb} leads to decreased density of the composite. However, a newer approach uses microballoon wall thickness to vary the density of syntactic foams. Microballoons with higher wall thickness have higher strength and lead to stronger syntactic foams. In these studies a parameter named Radius Ratio (η), defined as the ratio of inner to the outer radius of microballoons is used to relate the microballoon size and wall thickness. Although, considerable amount of data on compressive strength and modulus can be found published in the literature, there is absence of comprehensive studies that utilize the same type of microballoons and matrix material to compare the effectiveness of both approaches. Existence of such comprehensive data will also make it possible to validate theoretical models developed for these materials. The present study is an attempt to fill his gap by comprehensive experimental characterization of twenty types of syntactic foams having four different types of microballoons in five volume fractions, over the range of 0.3-0.65, each.

New applications of syntactic foams are being continuously developed making it necessary to characterize other types of properties also. Epoxies are widely used in electrical and electronic insulation and packaging applications. Epoxy based syntactic foams are also used as low density materials in electronic applications. However, only a few studies are available that characterize syntactic foams for their electrical properties. It is found that impedance and phase angle increase with increase in volume fraction of microballoons in the foam. The impedance increased and dielectric constant decreased with increasing filler content at the frequency of 10 kHz. Park et al have tested some syntactic foams with only 1 and 2 wt% microballoons. They found that the dielectric constant decreases with increasing frequency and filler content within this range. A study on hollow glass fiber filled composites was also found published where addition of glass fibers was found to decrease the dielectric constant of the material.

Syntactic foams can vary in the type and volume fraction of microballoons. A comprehensive investigation of their electrical properties with respect to various material and electric parameter must be carried out. The present paper investigates impedance, dielectric constant and dielectric loss of four types of syntactic foams selected from various foams synthesized in this study. The temperature dependence of dielectric constant is also investigated in the temperature range of 40-140°C.

Experimental

Constituent Materials

Epoxy resin DER 332 with hardener DEH 24, manufactured by DOW Chemical Company, is used as the matrix resin. A diluent C_{12}-C_{14} aliphaticglycidylether (ERISYS 8) is used in 5 vol% quantity to reduce the viscosity of the resin and to facilitate mixing and wetting of microballoons.

Scotchlite™ glass microballoons, manufactured and supplied by 3M, are used in synthesizing syntactic foams. The size, density and calculated η for microballoons used in synthesis of these foams are given in Table 1. The average outer diameter of all types of microballoons is nearly the same. Hence, a difference in their densities is caused by their η values. The microballoon type in Table 1 is the manufacturer's code for these microballoons. Syntactic foams containing 30, 40, 50, 60 and 65% microballoons by volume are fabricated.

Table 1. Properties of microballoons used in synthesized syntactic foams.

Microballoon Type	Microballoon Diameter (μm)	True Particle Density (kg/m^3)	Radius Ratio η
S22	35	220	0.970
S32	40	320	0.956
S38	40	380	0.947
K46	40	460	0.936

Syntactic Foam Synthesis

Stir mixing of microballoons in the epoxy resin system is the processing method adopted for synthesizing syntactic foams in the present study. The synthesis process consists of mixing 5 vol% of diluent in the resin and heating them to 50°C. Addition of diluent and heating them to higher temperature help in reducing the resin viscosity and facilitate the mixing of microballoons in the resin system. Hardener is added to this mixture and then microballoons are mixed. The mixing of microballoons is carried out using a wooden dowel until a slurry of uniform viscosity is obtained. The slurry is cast in molds, cured at room temperature for 24 hr and then post cured at 100°C for 3 hr.

Compression Testing

The compression testing is carried out using a computerized Instron 4467 mechanical test system. The system is capable of obtaining load-displacement data, which is later converted to stress-strain information. The specimens of 10×10 mm^2 cross section and 17 mm height were used for the testing. The compression rate was maintained at 1 mm/min for the testing. The tests were stopped at the collapse of the specimen due to failure or when the densification was completed.

Electrical Testing

The foam slabs were sectioned to obtain pieces of 10×10 mm^2 cross section and 6 mm thickness for the measurement of their electrical properties. In order to perform the dielectric measurements, an Ag electrode was applied on the samples and fired at 40°C for 1 hr. Impedance characteristics were determined by HP 4194A impedance analyzer (Hewlett Packard Co., USA). Dielectric constant as a function of temperature was measured via HP 4274A LCR meter (Hewlett Packard Co. USA). Since the magnitude of the dielectric constant is quite low in the range of 4 – 7, careful attention was paid in designing the sample holder. However, it should be pointed out that there may be some effect of the capacitance due to wiring and holder on the measured value.

Results and Discussion

The microstructure of SF460-60 type syntactic foam is shown in Figure 1, which is representative for all types of syntactic foams fabricated in this study. Glass microballoons can be observed dispersed in epoxy resin matrix in this micrograph.

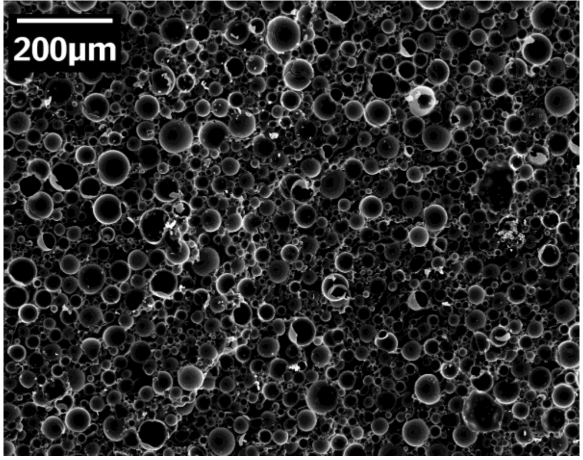
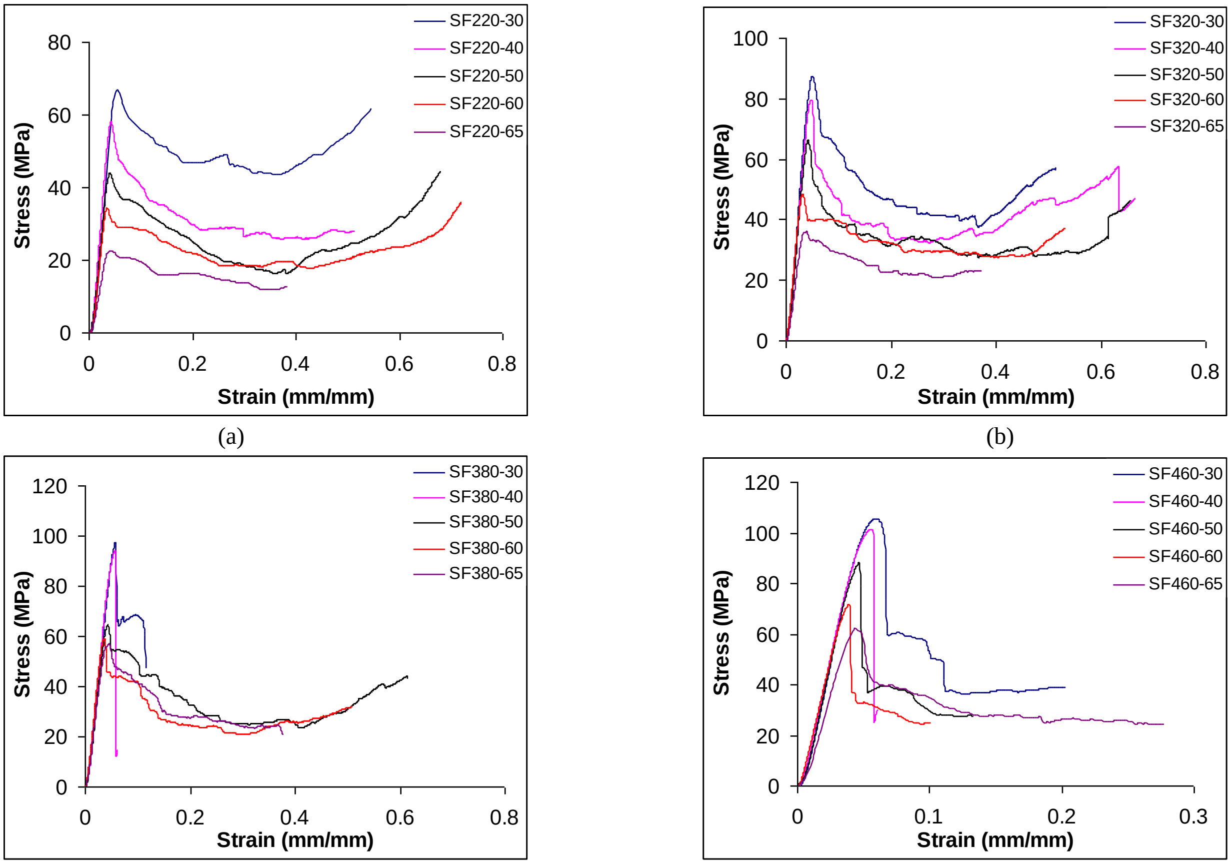


Figure 1. Microstructure of syntactic foams showing glass microballoons embedded in epoxy resin matrix.

The theoretical density, calculated using rule of mixture, and the measured density of all kinds of syntactic foams synthesized in this study are presented in Table 2. During the mechanical mixing of microballoons in the matrix resin system some air gets entrapped into the material structure, which remains in the cast foam slab. This entrapped air is termed as matrix porosity. An estimate of matrix porosity (V_v) is derived from the theoretical and measured densities of syntactic foams using Equation 1.

$$V_v = \frac{\rho_{th} - \rho_m}{\rho_{th}} \qquad (1)$$

where ρ_{th} and ρ_m are the theoretical and the measured densities, respectively. Most of the foams in the present study contain 3-12 vol% of matrix porosity. Presence of matrix porosity is undesirable in the structure as it weakens the material and may lead to increased moisture absorption.



(a) (b)

(c) (d)

Figure 2. Compressive stress-strain curves for syntactic foams having four types of microballoons having (a) $\eta = 0.970$ (b) $\eta = 0.956$ (c) $\eta = 0.947$ and (d) $\eta = 0.936$ in 0.3-0.65 volume fractions.

Table 2. Nomenclature, theoretical density and measured density of various syntactic foam compositions.

Micro-balloon Density (kg/m^3)	Volume Fraction of Micro-balloons	Syntactic Foam Nomen-clature	Syntactic Foam Density (kg/m^3)		Matrix Porosity (%)
			Theoretical	Measured	
220	30	SF220-30	878	850	3.2
	40	SF220-40	784	735	6.3
	50	SF220-50	690	611	11.4
	60	SF220-60	596	550	7.7
	65	SF220-65	549	490	10.7
320	30	SF320-30	908	875	3.6
	40	SF320-40	824	780	5.3
	50	SF320-50	740	670	9.5
	60	SF320-60	656	611	6.9
	65	SF320-65	614	545	11.2
380	30	SF380-30	926	887	4.2
	40	SF380-40	848	800	5.7
	50	SF380-50	770	694	9.9
	60	SF380-60	692	625	9.7
	65	SF380-65	653	575	11.9
460	30	SF460-30	950	931	2.0
	40	SF460-40	880	846	3.9
	50	SF460-50	810	732	9.6
	60	SF460-60	740	645	12.8
	65	SF460-65	705	650	7.8

A detailed discussion on the porosity effects on the mechanical properties of syntactic foams has been published previously. The electrical properties of syntactic foams can be affected by the level of porosity present in these samples. Hence, these figures are presented in Table 2. However, porosity is not considered as a study parameter in the present work.

Compressive Properties

The compressive stress-strain curves for syntactic foams containing microballoons of different η in volume fractions of 0.3-0.65 can be compared in Figure 2. As the general trend, like most other types of foams, syntactic foams show a linear elastic region, followed by a stress plateau region. At the end of the plateau region the stress starts increasing again. Several previous studies have observed and reported this kind of stress-strain curves in polymer and metal matrix syntactic foams. It is noted that the stress reaches a peak value at the end of the linear region, followed by a decrease before the stress-plateau is attained. Cracks initiate at the peak stress value and specimen tends to generate fragments as a result of these cracks. The stress-plateau is the region where the densification of the material takes place. Microballoons fracture and their enclosed porosity opens up for the compressing material to occupy. The stress starts increasing when the densification ends. These observations can be found extensively documented in the previous studies focusing on interpreting the stress-strain curves.

From the compressive stress-strain curves it is observed that the difference between the peak stress and the plateau stress increases as the V_{mb} decreases and also as the microballoon η decreases.

The initial cracks that generate in the specimens are either due to the shear stresses or the secondary tensile stresses. Such cracks normally initiate and propagate in the matrix material with fracture of only a small number of microballoons. Hence, increase in the matrix volume fraction and specimen rigidity cause enhancement in the specimen cracking, which leads to a sharp drop in stress after the peak stress is attained. It can be observed in Figure 2 that the decrease in strength becomes greater when V_{mb} increases for foams containing the same type of microballoons. For SF220-65 foams the decrease in strength is only about 10%, whereas for SF220-30 foams it is on the order of 20%. A similar trend is found to exist for other types of foams also. It can also be observed that decrease in η has a significant effect on the strength drop. The drop is in the range of 10-20% for various compositions of SF220 type foams, however, it is on the order of 40-60% for SF460 type foams. In most applications such steep decrease in strength is enough to consider complete failure of the material. Consistent with the previous studies, the strain at which the densification completes decreases with decreasing η and V_{mb}. The densification strain depends on the total porosity in the specimens, which is found to be maximum in SF220-65 foams and minimum in SF460-30 foams.

The results for compressive strength and modulus are presented in Table 3. The compressive strength and modulus are found to increase with decrease in V_{mb} and η. Decrease in V_{mb} and η cause increase in matrix volume fraction and stronger microballoons, respectively. Since, matrix has higher compressive strength and modulus than microballoons, decrease in V_{mb} leads to increased strength of the composite. Hence, a combination of V_{mb} and η can provide close control over the strength and modulus of syntactic foams. The composite with the least density can be designed for the given mechanical properties by considering both these parameters simultaneously.

Graphical representation of strength and modulus is found to be very illustrative in observing the trends between the density and mechanical properties of syntactic foams as shown in Figure 3. Microballoon η and V_{mb} both are found to be important parameters in determining the compressive strength and modulus of syntactic foams. It can be observed in these figures that the strength and modulus increase linearly with the foam density. For SF320, SF380 and SF460 type syntactic foams the strength values are found to on the same trendline, whereas the values are found to be lower for SF220 type foams. This observation can be related to the strength of microballoons. The strength of microballoons used in SF220 foams is lower because of their lower wall thickness. Hence, their fracture starts in early stages of compression leading to overall lower strength and modulus of these foams. For foams containing higher density microballoons, which are stronger, the trend fits on one trendline a shown in Figure 3. Depending upon the relative and absolute strengths of microballoons and matrix material the strength of syntactic foams may vary but it linearly varies with respect to their density. In some previous studies also it is observed that very low strength microballoons lead to weakening of syntactic foams as V_{mb} increases. The compressive properties of metal matrix foams are also found to follow the linearly increasing trend with density.

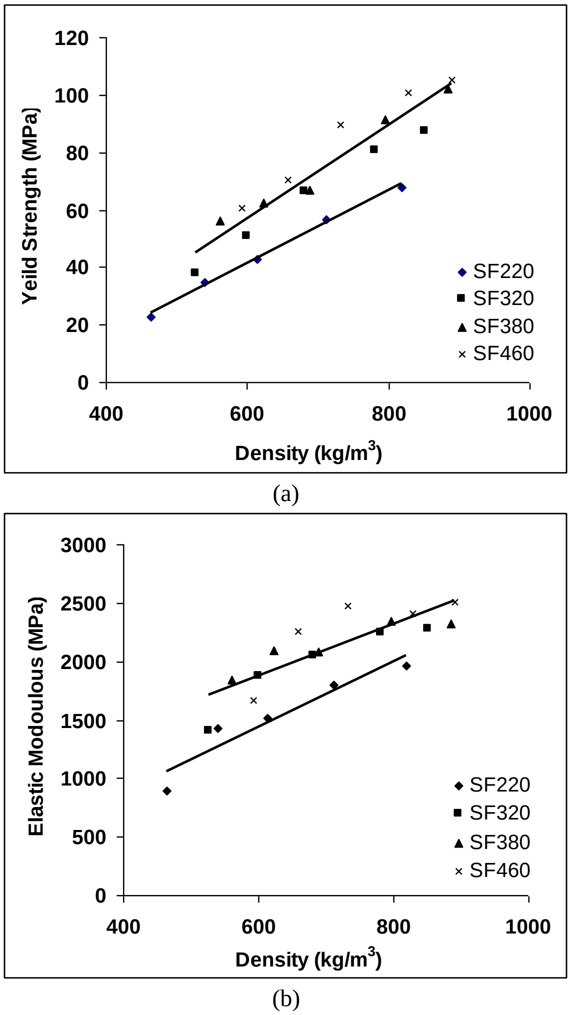


Figure 3. Relation between the density and (a) compressive strength and (b) modulus of syntactic foams.

Electrical Properties

In the first step the electrical properties of neat epoxy resin and four types of syntactic foams are measured. Properties of the neat resin will serve as a base for interpretation of electrical properties of syntactic foams, which contain glass microballoons in the resin matrix. The four types of syntactic foams selected for the measurement of dielectric properties represent four extremes of the compositions among the synthesized syntactic foams in the present study. Foams having the lowest and highest η values in lowest and highest V_{mb} are selected, which are SF220-30, SF220-65, SF460-30 and SF460-65. Comparison of properties of these foams will help in developing an understanding of the relationship between material parameters such as η and V_{mb} and electrical properties such as dielectric constant, dielectric loss, and impedance. The electrical properties are measured with respect to temperature and the applied frequency. In this study, the dielectric constant was measured in the low frequency region for two reasons: (i) material used for the sensor (capacitive sensors) work in the low frequency region and (ii) stresses and vibrations occurring in the material during its lifetime are low frequency signals.

Figure 4 shows the dielectric constant and loss data for the neat epoxy resin as a function of temperature and frequency.

The dielectric constant and loss at room temperature were found to be of the order of 6.8 and 4% at 10 kHz. Since all the samples were exposed to the temperature of 40°C during electroding the dielectric data was measured from this temperature onwards. As can be seen in Figure 4 that dielectric constant increases slightly with increase in temperature but the trend saturates quickly and it remains almost constant in the frequency interval of 10 – 100 kHz. It can be observed that the dielectric losses increase with the frequency and temperature after a steep initial decrease within a narrow range of 0 – 10 kHz.

Figure 5 shows the dielectric constant variation as a function of temperature and frequency for the four types of syntactic foams selected for the study. Clearly, the dielectric constant drops with the increasing V_{mb} for the same type of microballoons. For the case of SF220, the dielectric constant was of the order of 4.8 with 30 vol% microballoons and it dropped to 3.8 with 65 vol% microballoons. For the case of SF460, the dielectric constant was of the order of 5.1 with 30 vol% microballoons and it dropped to 3.7 with 65 vol% microballoons. The dielectric constant in both cases was found to increase to 5 – 10 % with increase in temperature. The variation in the dielectric loss as a function of temperature and frequency is shown in Figure 6 for the four types of syntactic foams. With increasing frequency a drop in the dielectric loss was observed at higher temperatures but this effect may be due to the poor contact of the electrode and material. This problem can be resolved by using electrodes which can adhere and form strong bonds at low curing temperature with the foam surface.

Figure 7 shows the impedance characteristic for the neat epoxy and SF220 type syntactic foams. The impedance characteristics for the SF460 foams were found to be similar to that of the SF220. The impedance drops with frequency, which is a common characteristic for the dielectric materials. The change in the impedance was found to be similar for both cases. The phase difference remains close to -90°, which reflects the capacitive nature of the material. The data of Figures 5 and 7 shows that these materials have the possibility to function as sensors. The sensing is achieved by the variation in the magnitude of the capacitance due to external stress or other factors. The health monitoring is conducted by recording the variation in the magnitude of the electrical impedance and comparing it with the reference signal from virgin material.

Conclusions

The detailed experimental study related to the compressive properties of syntactic foams concludes that for syntactic foams the compressive strength and modulus

1. increase with increase in microballoon wall thickness and decrease in microballoon volume fraction.
2. increase linearly with the foam density.
3. depend on the relative strength of microballoons and the matrix resin. Foams with very low strength microballoons tend to show greater dependence of mechanical properties on the microballoon properties.

The investigation of electrical properties concludes that

1. dielectric constant increases with increase in microballoon wall thickness and decreases with increasing microballoon volume fraction. It is found to decrease with test frequency and increase with temperature.
2. dielectric loss also follows the trend observed for dielectric constant with respect to the material and electrical test parameters.

The results show that the syntactic foams have a possibility to be developed as sensors with appropriate microstructural modification and their electrical properties can be effectively controlled by means of microballoon wall thickness and volume fraction.

Acknowledgments

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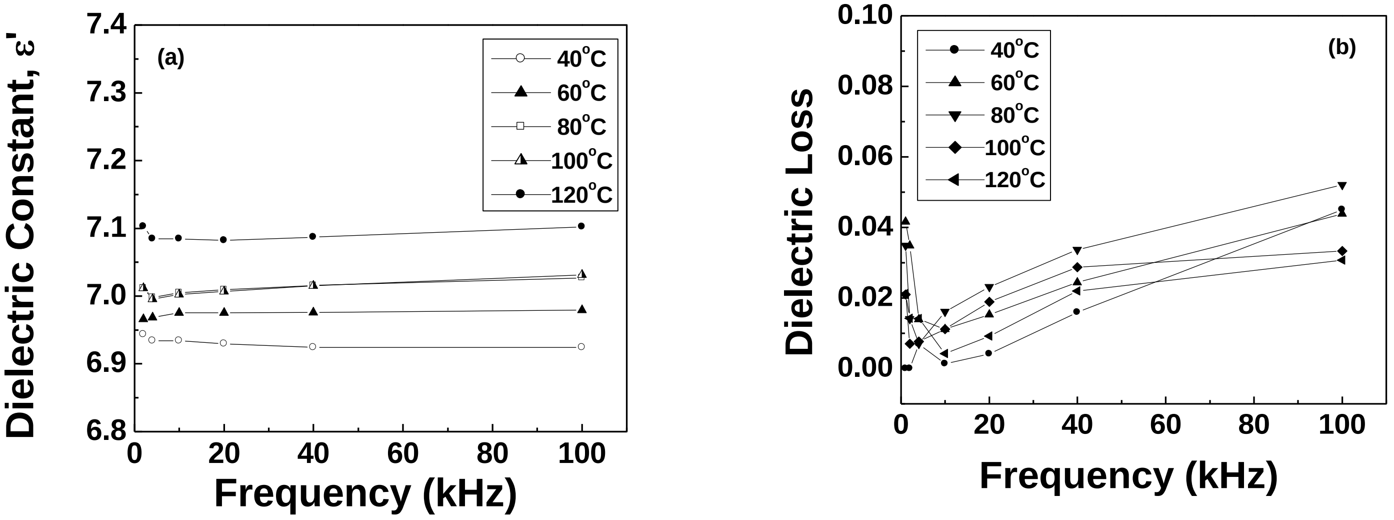
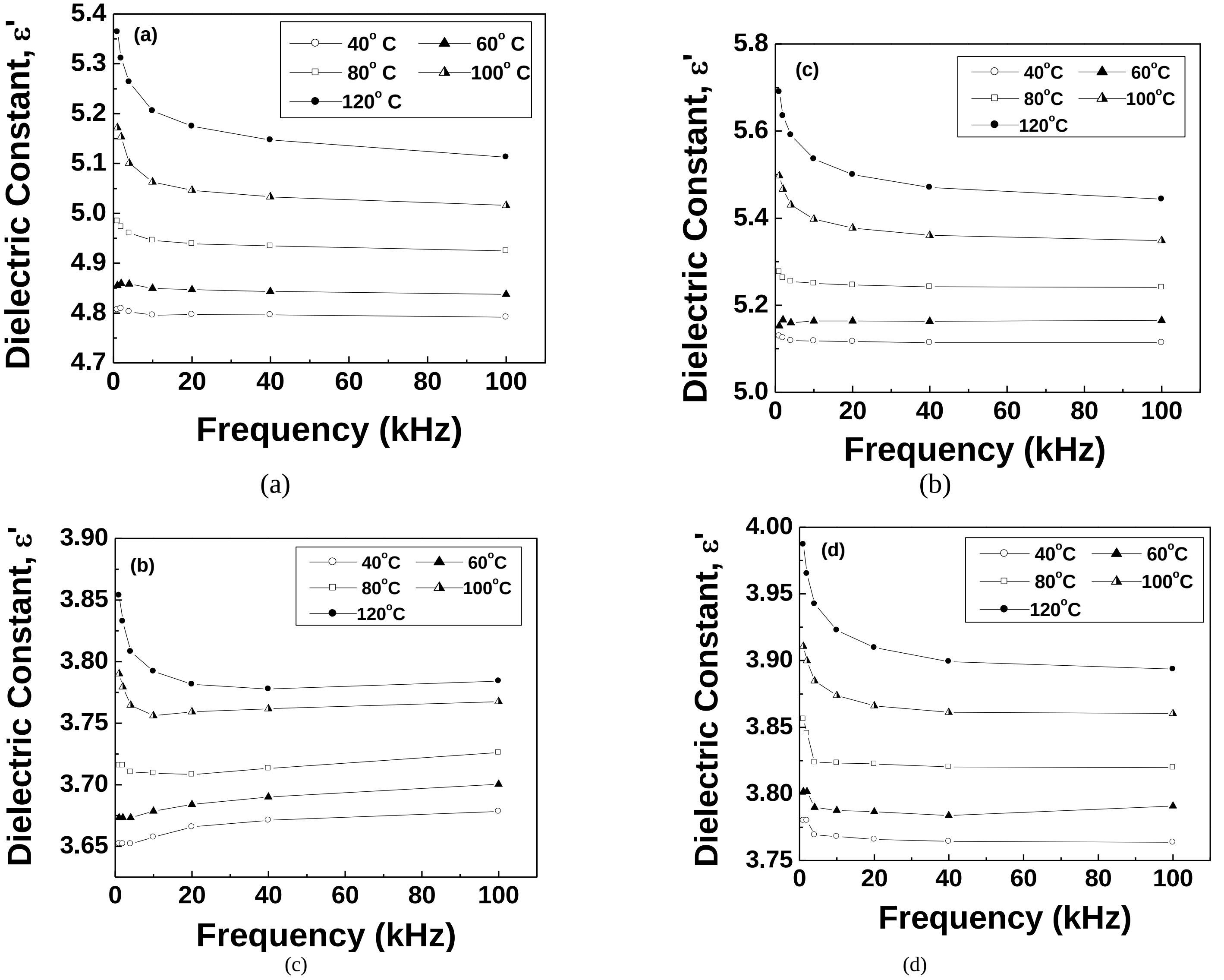


(a) (b)

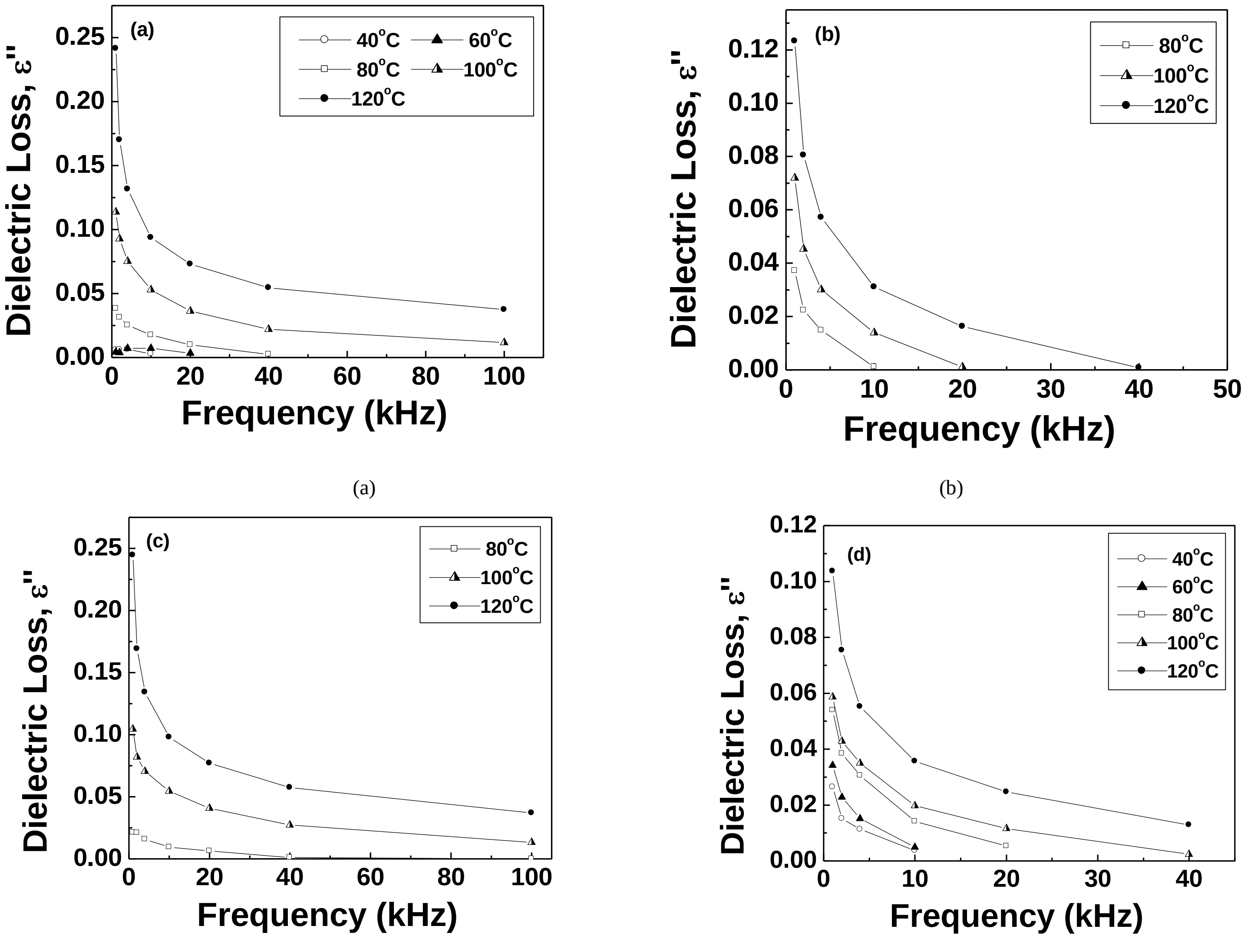
Figure 4. Measurements of (a) dielectric constant and (b) dielectric loss with respect to Frequency for the neat epoxy resin at different temperatures.



(a) (b)

(c) (d)

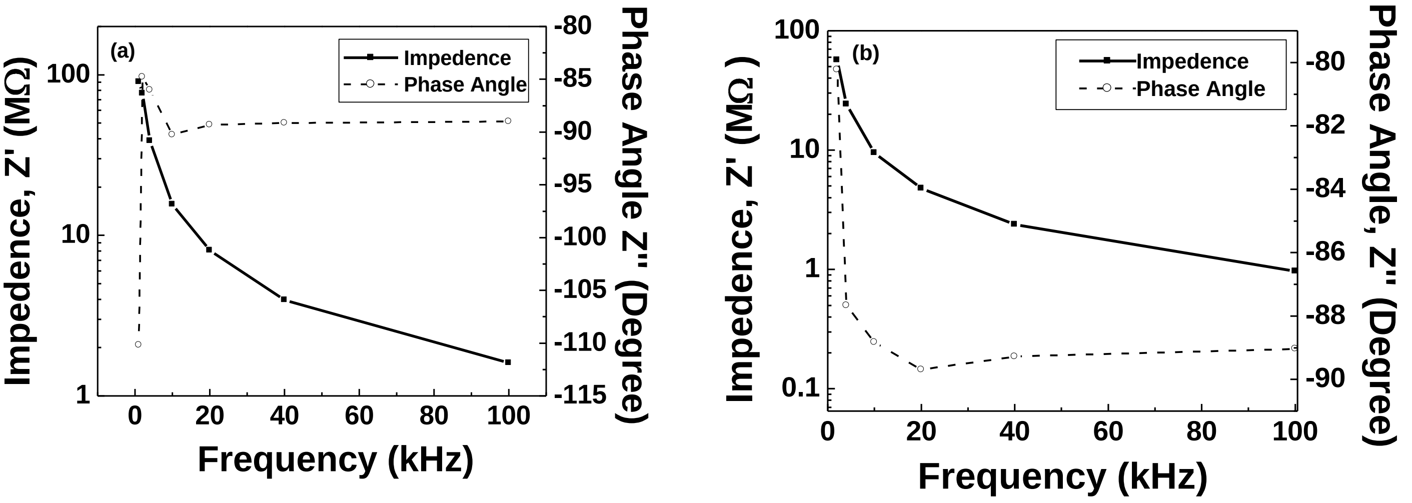
Figure 5. Variation in dielectric constant with respect to frequency at different temperatures for (a) SF220-30, (b) SF220-65, (c) SF460-30 and (d) SF460-65 syntactic foams.



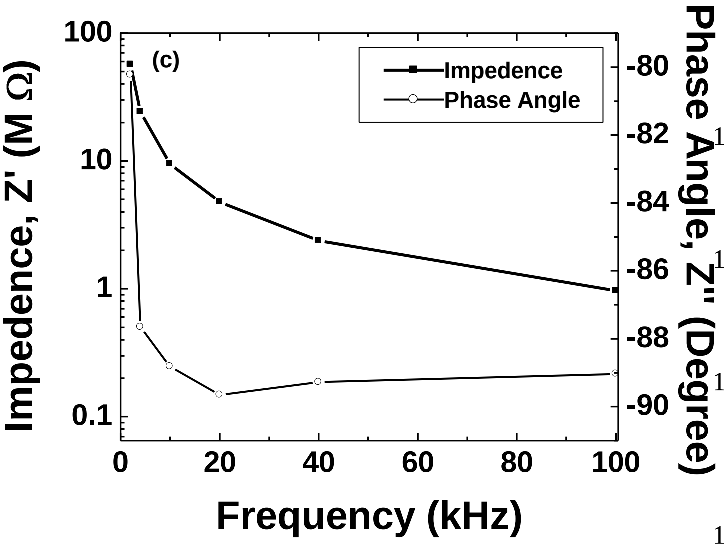
(a) (b)

(c) (d)

Figure 6. Dielectric loss as a function of frequency at different temperatures for (a) SF220-30 (b) F220-65, (c) SF460-30 and (d) SF460-65 syntactic foams.



(a) (b)



(c)

Figure 7. Impedance and phase angle Vs Frequency at room temperature for (a) neat resin, (b) SF220-30 foam and (c) SF220-65 foam.

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