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Characterization of epoxy syntactic foams by dynamic mechanical analysis

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Epoxy syntactic foams that are capable of withstanding use-temperatures in the range of 106 to 175°C were fabricated with DGEBA or novolac based epoxy resins and appropriate amine hardener materials. These foams were characterized for dynamic mechanical properties in single cantilever mode. The storage modulus, loss modulus and tan δ values were recorded over a wide temperature range. A typical density value of around 0.45 g/cm^3 of the syntactic foams made respectively from a cycloaliphatic amine hardener, aromatic amine hardener-I, aromatic amine hardener-II recorded storage modulus (E′) values of 1354 MPa, 1500 MPa and 1530 MPa respectively and tan δ values of 0.0139, 0.0090, 0.01039 respectively at 30°C. The storage modulus values gradually decreased with increasing temperature while the loss modulus values showed corresponding gradual increase in the same temperature range. There is a steep variation in these values when the material softens in the vicinity of the glass transition temperature (T_g) indicating the upper temperature limits to which they can be put in use. The reduction in the storage modulus values with increasing temperature and the glass transition temperature values are characteristic of the resin/hardener systems as well as the curing/post curing cycles employed. © *2006 Springer Science+Business Media, Inc.*

1. Introduction

Syntactic foams are composite materials in which hollow microspheres or other small hollow particles are dispersed in a polymer binder. The hollow spheres may be made up of metals, polymers or ceramics [1, 2]. The cellular structure of a syntactic foam is entirely different from the conventional foams like polyurethanes, PVC etc. In syntactic foams majority of the voids are enclosed within rigid walls and therefore isolated from each other and hence are called 'closed-cell foams'. Syntactic foams are essentially isotropic materials due to the randomness of the microstructure. They are used extensively for construction of boats and deep-water submarines [3, 4]. They have also been successfully used in electrical and electronic industries [5]. Syntactic foams are used as core material for structural sandwich composites in military aviation applications. High-density syntactic foams are employed in composite tooling to give rigidity at comparatively low weights [6].

This paper presents the material characterization details of three different epoxy syntactic foams, all fabricated with glass microspheres as reinforcement but differing in their epoxy binder formulation, using dynamic mechanical analysis (DMA). The epoxy formulations vary from room temperature to elevated temperature curing systems and the foams studied were of similar density values (0.45 g/cc). The wealth of viscoelastic information obtained from such DMA studies is extremely useful for material development and quality control of syntactic foam composite structures.

1.1. Structure of syntactic foams

Syntactic foams can be classified either as two phase or three phase depending on whether additional voids are dispersed between the matrix binder and the microballoon reinforcements, see Fig. 1. The microballoon aggregate

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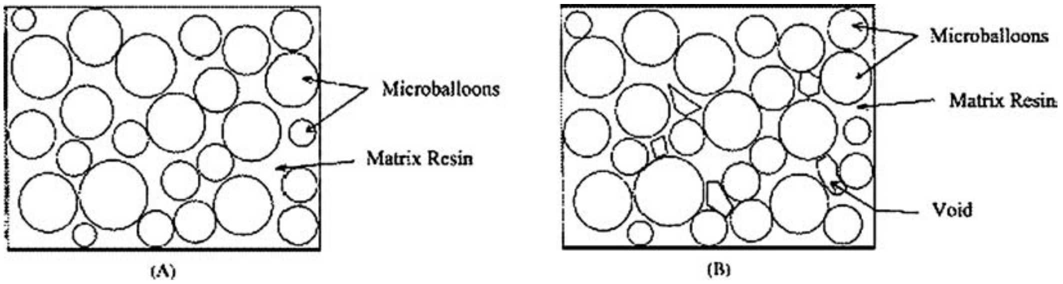

Figure 1 A representative sketch depicting (A) the two phase structure involving microballoons and the matrix material and (B) three phase structure due to the presence of voids.

with its enclosed void/gas is considered as a single phase in this classification [7].

Though due to hollowness glass microballoons lower the density of foam structure, the rigid wall material (silica glass) increase the stiffness resulting in high specific properties of the foam material. The nature of the polymer matrix binder, depending upon its chemical class, governs the fabrication process and also temperature/environment performance of the foam.

1.2. Dynamic mechanical analysis

Dynamic mechanical analysis methods are widely used to investigate the structures and the viscoelastic behaviour of polymeric and composite materials for determining relative stiffnesses and damping characteristics [8]. Elastic modulus (or storage modulus, E′), viscous modulus (or loss modulus, E″) and damping coefficient (tan δ, the ratio of loss modulus to storage modulus) are recorded as a function of temperature, frequency or time. Results are typically provided as a graphical plot of E′, E″, and tan δ versus temperature. DMA identifies transition regions in polymers and composites, such as the glass transition temperature (T_g) that may be used for quality control or product development. DMA can recognize small transition regions that are beyond the resolution of other thermal analysis techniques such as differential scanning calorimetry (DSC).

The test specimen is fixed between a movable and a stationary clamp fixture, the design of which is decided by the mode of the oscillatory loading condition to be applied (flexural, tension, compression etc.) and then enclosed in a thermal chamber. Frequency, amplitude, and a temperature range appropriate for the material being tested are given as input. The analyzer applies sinusoidal oscillatory load to the test sample, in the specified temperature range with the programmed temperature ramp. The viscous force lost in each oscillation is compensated every time externally and this is a measured output in the entire temperature range.

TABLE I. Properties of hollow silica microballoons eccospheres – SI

1. Bulk density	0.180 g/cm^3
2. True Particle density	0.254 g/cm^3
3. Composition: Particle Size Range (μm)	% by Weight
a) 100–175	36
b) 44–100	55
c) <44	9
4. Average Wall Thickness (μm)	1.5
5. Average Particle Diameter (μm)	80
6. Softening Temperature (°C)	980

2. Experimental

2.1. Materials and methods

The raw materials used to fabricate syntactic foams were glass microspheres (microballoons) Eccospheres-SI supplied by M/s Grace Electronic Materials, Belgium. The specification details as supplied by the manufacturer are given in Table I.

Room temperature curing, Novolac based as well as DGEBA based high temperature curing epoxy systems supplied by M/s Hindustan Ciba-Geigy Ltd. with appropriate amine hardeners were used for the fabrication of syntactic foams. Some details on the materials and fabrication of the three foams SF–01, SF–02 and SF–03 are given in Table II.

The syntactic foams were prepared by mixing initially stoichiometric quantities of resin and hardener and later adding glass microballoons in apportioned quantities, with gentle and thorough mixing intermittently. The mix develops a dough form, which was uniformly filled

TABLE II. Materials and process details of syntactic foams

Sl. No.	Id. No.	Density (g/cm^3)	Materials	Cure details
1	SF-01	0.45 ± 0.015	Novolac—epoxy resin, Cycloaliphatic Amine hardener	RT Curing, Post Cure at 120°C
2	SF-02	0.45 ± 0.010	DGEBA epoxy, Aromatic Amine I hardener	Elevated temperature cure, Post cure at 160°C
3	SF-03	0.45 ± 0.015	DGEBA epoxy, Aromatic Amine II hardener	Elevated temperature cure, Post cure at 190°C

TABLE III. Density* and composition** of syntactic foams

Sl. No.	Id. No.	Density (g/cc)	% Vol. of Matrix, V_M	% Vol. of Microballoons, V_μ	% Vol. of Voids, V_V
1	SF-01	0.45 ± 0.015	25.15	62.12	12.73
2	SF-02	0.45 ± 0.010	22.41	68.33	9.26
3	SF-03	0.45 ± 0.015	20.06	71.70	8.24

*The density values are the average of 5 specimens (Standard deviation for SF-01, SF-02 and SF-03 are 0.012, 0.009 and 0.011 respectively).

**The composition i.e. V_M, V_μ, V_V were calculated on the basis of the average foam density of 0.45 g/cc.

in a rectangular metal mould and cured. In the case of the aromatic amine hardeners, which are solid at room temperature, the resin was heated to temperatures around 100°C before mixing the hardeners in powdered form. The microballoon also was added at a higher temperature in these cases. In the case of cycloaliphatic amine hardener, which is liquid at room temperature, the entire process of mixing was carried out at room temperature as gelling of matrix critically depends on the mixing time and temperature. Samples for density measurements and for the DMA, were cut from cast slab to required dimensions.

The measured densities of the fabricated foam samples and the corresponding volume fractions of the constituents, as calculated from densities of cured resin and microballoons are presented in Table III.

2.2. DMA test parameters

The dynamic mechanical analyses of syntactic foams described in this paper were carried out in a DMA 2980 of the TA Instruments Inc. USA. The specimens were tested in single cantilever mode at 1 Hz frequency, 40 μm amplitude. The specimen sizes were 35 mm × 12.5 mm and thicknesses in the range of 2.5 to 2.9 mm. A temperature ramp of 5°C per minute was maintained during the analysis. The viscoelastic parameters such as the storage modulus, loss modulus and the damping factor were plotted with temperature, at the end of each experiment.

3. Results and discussions

3.1. Density and composition of syntactic foams

From Table III it is evident that for similar density value of the foams fabricated from the same raw material microballoon but with different binder matrix, the percentage volume of the constituents varies over a small range. It may be noted that within this range, the foams made from aromatic amine hardeners, due to processing at higher temperature result in a comparatively higher volume of microballoons. The void volume fractions in the foams fall in the range of approximately 8 to 13 percent thereby resulting in three-phase syntactic foams. Such voids in fact lower the density values of the foams from a corresponding two-phase construction.

3.2. Interpretation of DMA thermograms

Figs 2–4 are the DMA thermograms respectively of foams SF-01, SF-02 and SF-03, presented along with thermograms of their respective neat resin—casts, fabricated by adopting same cure/post cure cycle as that of the syntactic foams. In each of the figures, the variation of storage modulus as well as loss modulus of both the foam and the corresponding neat resin-cast are shown.

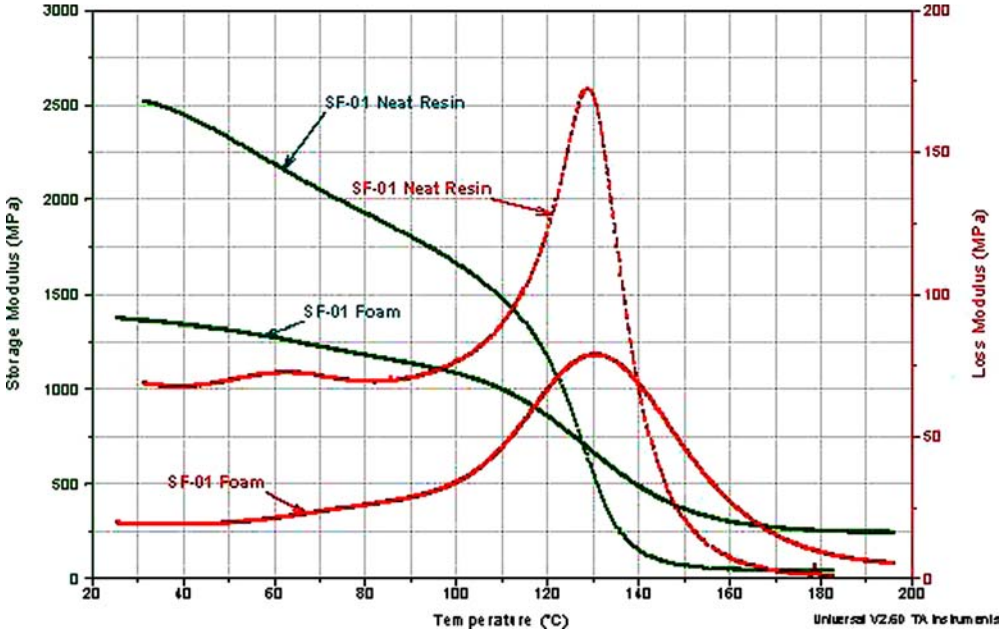

Figure 2 DMA Thermogram of SF-01 Neat Resin and Foam Sample.

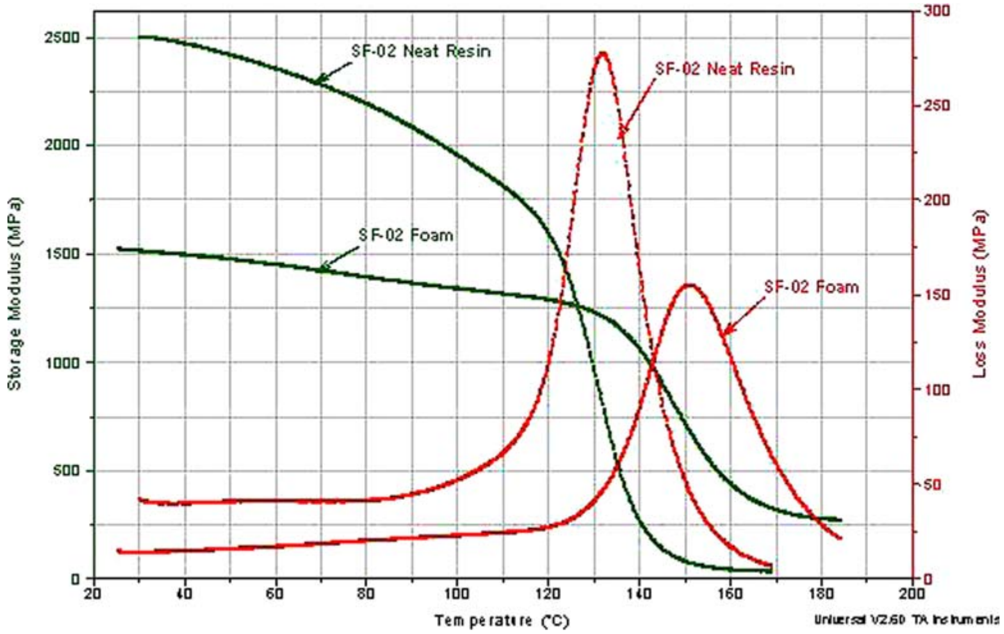

Figure 3 DMA Thermogram of SF-02 Neat Resin and Foam Sample.

3.2.1. Storage, loss modulus values and glass transition temperature (T_g)

Tables IV and V partly summarize the results obtained in the DMA thermograms of Figs 2–4, by selectively reading the storage and loss modulus values at two different temperatures 30°C and 60°C for the sake of comparison. It is observed from Figs 2–4, that the storage modulus values decrease with increasing temperature in both the foam and the neat resin cast, but the decrease is gradual till attaining the region of T_g, where a steep reduction in the value occurs. This reduction with the increasing temperature is associated with the softening of matrix. Table VI summarizes the maximum use-temperatures (T_{max}) for the syntactic foams and the percentage reduction in storage modulus values at T_{max}. The T_{max} temperatures are taken as the temperature at which the storage modulus values start decreasing steeply in the thermograms.

The loss modulus values show either retention or a marginal increase till reaching the maximum use-temperature (T_{max}) after which they increase sharply with

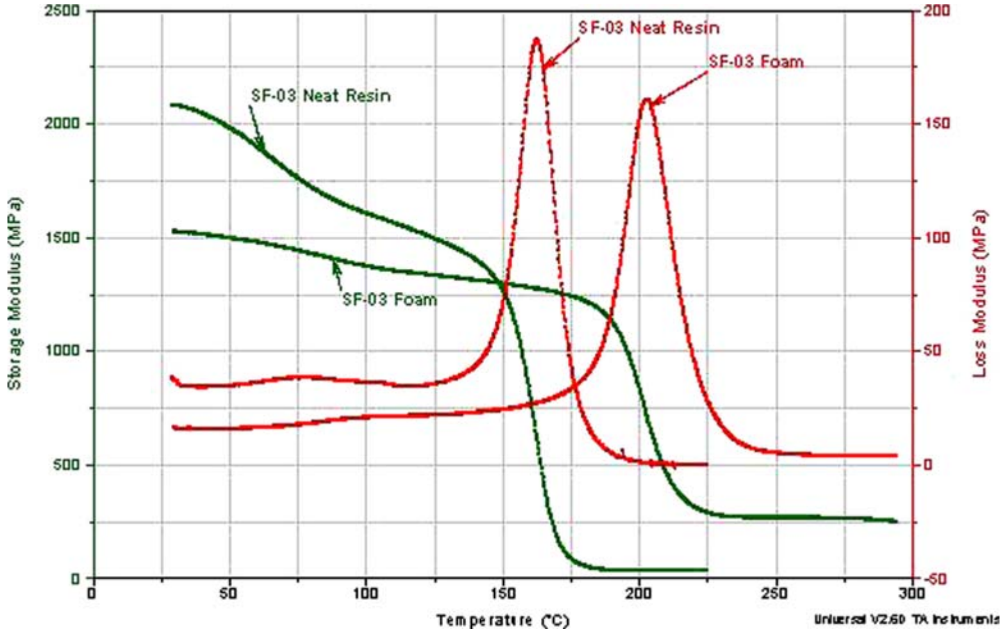

Figure 4 DMA Thermogram of SF-03 Neat Resin and Foam Sample.

TABLE IV. Comparison of storage modulus (SM) and loss modulus (LM) values of neat resins and syntactic foams (as read from their respective DMA thermograms)

Sl. No.	Temp. (°C)	Id. No.	Neat Resin SM (MPa)	Neat Resin LM (MPa)	Syntactic Foam SM (MPa)	Syntactic Foam LM (MPa)
1.	30	SF-01	2515*	68.45*	1354	18.86
		SF-02	2499*	40.54*	1500	13.58
		SF-03	2079	36.90	1530	15.84
2.	60	SF–01	2185	72.21	1269	21.01
		SF–02	2364	40.69	1440	16.59
		SF–03	1897	35.98	1477	16.09

*Values obtained by "measure mode" option of the DMA instrument.

TABLE V. Glass transition temperature values of neat resin and syntactic foams

Id. No.	Tg (°C) Neat Resin	Tg (°C) Syntactic Foam	% increase
SF-01	128.5	130.7	1.71
SF-02	132.1	151.0	14.31
SF-03	162.1	202.4	24.86

temperature. The temperature at which the loss modulus values peak is generally interpreted as the T_g of the material. The T_g values of foams are found to be 130.7°C, 151.0°C and 202.4°C for SF-01, SF-02 and SF-03, respectively. It is also observed that the T_g is higher for the syntactic foam compared to the corresponding resin cast though the same cure/post cure cycles were followed. This is due to the reinforcing effect of the microballoons, that affect the mobility of the polymeric chains in the interphase region between the matrix and the microballoons.

The enhancement in T_g of the syntactic foams in comparison to the neat resins is predominant in the aromatic hardener systems SF-02 and SF-03 but not significant in the cycloaliphatic amine system SF-01(Refer Table V). Partially this may be due to the increased volume fraction of the binder and reduced microballoon content in SF-01 in comparison to SF-02 and SF-03. The reduction in the storage modulus values with increasing temperature (below $T_{g)}$ is steeper in the case of SF-01 than SF-02 and SF-03 (Table IV). It can be concluded that the binder matrices of aromatic amine hardener systems have better temperature performance as syntactic foam materials.

3.2.2. Maximum use temperatures of syntactic foams

It is evident from Table IV that the reduction in modulus values with increasing temperature is much higher in neat resins than the corresponding foams. It is understandable that the stiffness values of the composite foams are dominated by the rigid glass microballoons, which do not undergo any transition in this temperature range. From Table VI it can be seen that at the maximum use-temperature, the reduction in storage modulus values are within 25% of the foams at room temperature. This is a useful input for structural design involving these foams. Considering percentage reduction in the storage modulus values, reinforcing efficiency is less in SF-01 system as far as thermal performance is concerned.

3.2.3. Damping coefficients

Fig. 5 shows the variation in the tan δ values for the neat resins as well as the foams with temperature. Table VII

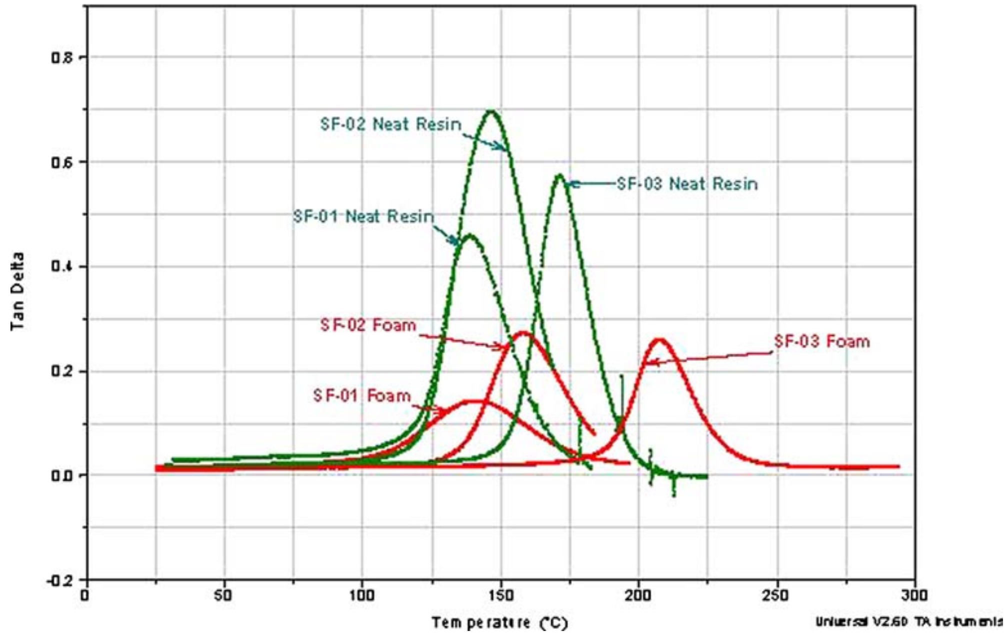

Figure 5 DMA Thermogram of Damping Coefficients (tanδ).

TABLE VI. Maximum use temperatures and percentage reduction in storage modulus of syntactic foams

Sl. No.	Id. No.	Max. Use Temperature	Percentage Reduction of Storage Modulus at max. use temperature
1.	SF–01	106.0°C	24.0%
2.	SF–02	125.0°C	16.1%
3.	SF–03	175.0°C	19.1%

TABLE VII. Comparison of tan δ values (30°C) and tan $\delta_{\max}$ of neat resins and syntactic foams

		tan δ			
		Neat Resin		Syntactic Foam	
Sl. No.	Id. No.	30°C	Max	30°C	Max
1	SF–01	0.02722*	0.4561	0.01393	0.1414
2	SF–02	0.01623*	0.6945	0.00903	0.2711
3	SF–03	0.01775	0.5718	0.01039	0.2583

*Values obtained by "measure mode" option of the DMA instrument.

tabulates tan δ values at room temperature of the foams and neat resins as well as the tan $\delta_{\max}$ values, which are attained after the material crosses the T_g.

Tan δ values reflect the damping behaviour of the composite. The composition of polymer composites is the key factor in determining damping behaviour though other factors such as interaction between reinforcement and matrix also affect damping characteristics. A relatively large decrease in room temperature tan δ values of the syntactic foams in comparison to their neat resin counterpart, is due to the presence of rigid glass microballoons that too at such a high volume percentage levels. Apart from being a low damping material, rigid glass microballoons hinder the chain flexibility and segmental motion especially in the vicinity of the interface. This lowers the energy dissipation in the foam material as evidenced in the reduced tan δ values. In fact, an overall effect of nearly 50% reduction is observed. The higher damping value of SF-01 neat resin system is due to the aliphatic nature of the molecular chain that is more flexible. The tan $\delta_{\max}$ values of the foams are also lower than those of the neat resin materials, giving an idea about the overall flexibility and interaction of the constituents in these materials.

4. Conclusions

Three-phase epoxy syntactic foams of density value of 0.45 g/cc were fabricated from glass microballoons and three different binder matrix formulations. The viscoelastic property values E', E'', and tan δ were recorded over a temperature range using DMA. The studies could give the following conclusions that are useful in material development, quality control and design of composites involving them.

1. Composition of syntactic foams of similar density values, differs within a close range of percentage volume of constituents.
2. The T_g of syntactic foams were found to be 130.7°C, 151°C and 202.4°C respectively for SF-01, SF-02 and SF-03. Generally the T_g values for the foams are higher than those of neat resins. The maximum use-temperatures ($T_{\max}$) of these foams were interpreted to be 106°C, 125°C and 175°C respectively, which serves as a useful design input.
3. The reduction in the storage modulus values of the foams with increasing temperature is less in the foams in comparison to the neat resins. In fact, in the foams the reduction at maximum use temperature is within 25%.
4. The damping factor tan δ was found to be greater for the cycloaliphatic amine based system SF–01.
5. The various results of DMA experiments are interpreted in terms of softening of matrix, chain flexibility and hindrance of molecular motion in the interphase region between the binder matrix and reinforcement.

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