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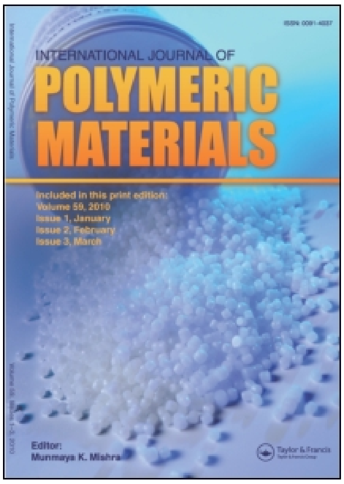

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Characterization of Short Glass Fiber-Reinforced Castor Oil-Based Polyurethane Polystyrene Interpenetrating Networks

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Characterization of Short Glass Fiber–Reinforced Castor Oil–Based Polyurethane Polystyrene Interpenetrating Networks

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Chopped strand glass fiber–reinforced particle-filled castor oil–based polyurethane polystyrene composites with varying weight fractions of glass fibers were investigated for morphology, tensile strength, and absorption of various chemicals. The short glass fiber fraction was varied from 1% to 16% (by wt.) of the total composite system. The tensile strength of these composites was much higher than that of unfilled IPNs for the same concentration of polystyrene. The tensile strength of the IPN composites increases with the increase in fiber content up to a fiber percentage of 9%. After that, there is a sharp decline in tensile modulus as well as elongation at break. The chemical absorption showed an increase with increasing glass fiber content.

Keywords: polyurethanes, castor oil, interpenetrating networks, chemical absorption, short glass fiber composites

INTRODUCTION

The kinds of composite material used in production technology and their use areas are continually increasing. Because of their good combinations of properties, fiber-reinforced-polymer composites are being used in the automotive and aircraft industries and the manufacture of spaceships and sea vehicles. There are two main characteristics that make these materials attractive compared to conventional metallic

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designs: They are of relatively low density and can be tailored to have stacking sequences to provide high strength and stiffness in directions of high loading [1] and the composite materials consist of a resin and reinforcement chosen according to desired mechanical properties and applications.

The mechanical properties of discontinuous fiber/polymer composites can vary tremendously depending on the process used to fabricate the test specimens. Fiber length and orientation directly affect the mechanical properties of a composite. The process used to fabricate test specimens can in turn directly affect the orientation and length of the fiber in the test specimen. The mechanical properties are also a function of the constituents, sizing, wetting, variability of bond, fiber resin distribution, and specimen/test design [2].

The use of discontinuous, short fiber thermoplastic composites is highly desirable for a wide variety of automotive and other applications that need high strength and impact resistance. Such applications are already increasing and expected to accelerate dramatically over the next several years. The three key factors that are required for commercial growth of these products are: (1) availability of high quality, low cost products, (2) high rate molding processes that maintain fiber length in the molded part, and (3) development of an understanding of the mechanics of these materials. In the lightweight applications, large specific stiffness and strength are attractive properties for a material. By combining short fibers with an appropriate polymer matrix and by controlling the production process, it is possible to make composite materials featuring strong specific properties. In addition, the constituents, that is, the polymer matrix and the glass fibers, are usually inexpensive and easily processed, for example, by injection molding. As a consequence of these technical and economical reasons, short fiber–reinforced polymer composites are finding increased industrial applications where high performance per unit weight at a reasonable price is required.

Short-fiber–reinforced polymer (SFRP) composites are very attractive because of their ease of fabrication, economy, and superior mechanical properties. In general, high fiber content is required in order to achieve a high performance SFRP composite. Therefore, the effect of fiber content on the mechanical properties of SFRP composites is of particular interest and significance. It is often observed that the increase in fiber content leads to the increase in the strength and modulus [3–9] and also in the toughness if the matrix has a low toughness [10]. The fiber content has an evident influence on the composite failure strain. It has been generally observed that the composite failure strain decreases with increase of fiber content [3–4,7,11]. The studies on failure mechanisms [11–12] has shown that with the loading of tensile stress, the cracks start at the fiber ends and propagate along the fiber–matrix interface or cross through the matrix and finally the failure takes place. Fiber ends have been shown to substantially concentrate the stress in the adjacent matrix [11], producing stress magnifications of ten or even higher. The failure is closely related to the number of fiber ends and thus to the parameters including fiber volume fraction, fiber length, and fiber radius, which determine the number of fiber ends. Consequently, there exists a relationship between composite failure strain and fiber volume fraction, mean fiber length, as well as fiber radius.

The focus of the current study was the characterization of the short glass fiber–reinforced interpenetrating polymer networks of polyurethane and polystyrene. The chemical and physical combination methods and the properties of polymer mixtures have been of commercial and academic interest, because they provide a convenient route for the modification of properties to meet specific needs. Among these methods, interpenetrating polymer networks (IPNs) represent a new approach to overcome the problem of mutual incompatibility of polymers. They possess excellent engineering properties because of the synergistic effect of individual polymers [13–16]. Some plastics, such as polystyrene (PS) and Polymethylmethacrylate (PMMA) are brittle and may be toughened by incorporation of small quantities of an elastomeric material. Polyurethane (PU) and polystyrene (PS) IPNs have been extensively studied [17–26]. To enhance the mechanical properties of these IPNs, they are reinforced with short glass fibers.

Castor oil, a renewable resource, has been a successful candidate in the formation of industrially useful materials [13–14,27,28] and has been extensively used for modification of polymers. A survey of the literature reveals that most of the properties like strength, resilience, resistance to chemicals, and hydrolysis of these PU/PS IPNs have been studied systematically for these IPNs [18,29–30]. Yet no work has been reported on short glass fiber–reinforced IPNs. In the present work, morphology, resistance to chemical reagents, and the mechanical properties of the short glass fiber–reinforced IPNs of PU/PS have been investigated.

EXPERIMENTAL

Material Used

Castor Oil (commercial grade) was purchased from the local market. It was dehydrated at 105°C in nitrogen atmosphere and was characterized for hydroxyl value (148), acid value (2), and moisture content (0.379%). Pyridine (Qualigens), dibutyl amine (E-Merck), diphenyl methane diisocyanate (MDI) (BASF, Korea) (isocyanate value 28.8%), xylene (E-Merck), and toluene (Qualigens), were used as such.

Synthesis of Polyurethane Prepolymer

The reactions were carried out in a 5-necked, 500 ml round bottom flask fitted with an agitator, temperature indicator, nitrogen inlet-out tubes, and sample withdrawal arrangement. This flask was kept in a water bath (Julabo, VC-5, with cooling as well as heating arrangements) maintained at 40°C temperature. Calculated amount of moisture-free castor oil was taken in the flask and the corresponding amount of MDI (for 1:1 ratio of NCO/OH) was added gradually so that complete addition of MDI took 5–10 min. When the MDI was uniformly mixed, samples were withdrawn at regular intervals to find the extent of reaction on the basis of isocyanate consumed as estimated by Stagg Method [31].

Preparation of Polyurethane/Polystyrene Interpenetrating Networks Sheets

Polyurethane pre-polymers (up to 60% conversion) were thoroughly mixed with styrene. Initiator MEKP (Methyl Ethyl Ketone Peroxide) and Cobalt Octoate as well as catalyst DBTL (dibutyl tin dilaurate) (1% each by weight of resin) were added. As the mixture became very viscous, it was poured into a mold, 300 × 30 × 50 mm, with polyvinyl alcohol film coating to facilitate demolding. The rest of the reaction was allowed to proceed in the mold. The polymer composites in the trays were compressed and cured at room temperature for 3–4 days. Post-curing was done at 80°C for 24 h. A series of IPNs were obtained with different compositions (ranging from 10 to 50% styrene) following the described procedure. The finished sheets were cut in desired shapes and sizes for further study. These sheets were tested for their tensile strength. The sheet, which has maximum strength, was reinforced with varying amount of short glass fibers.

Preparation of Short Glass Fiber–Reinforced Polyurethane/Polystyrene Interpenetrating Networks Sheets

Polyurethane pre-polymers up to 60% conversion were thoroughly mixed with styrene (to maintain 50 wt% styrene in the mixture). To this mixture, measured quantity of glass fibers were added so as to

TABLE 1 Data on Fiber Loading of Different Samples of Glass Fiber–Reinforced IPN Composites (All the IPNs Contain 50% Polystyrene)

Sample identification	Composition	Content of polyurethane/ polystyrene by weight (wt%)	Content of short glass fibers by weight (wt%)
S-1	1% glass fiber	99	1
S-2	2% glass fiber	98	2
S-3	4% glass fiber	96	4
S-4	6% glass fiber	94	6
S-5	7% glass fiber	93	7
S-6	9% glass fiber	91	9
S-7	12% glass fiber	88	12
S-8	14% glass fiber	86	14
S-9	16% glass fiber	84	16

vary the fiber content from 1–16% short glass fibers. This mixture was poured into a disposable container and mixed until the mixture became homogenous and viscous. The rest of the procedure was the same as in the previous section. A series of composite sheets (S1 to S9) of different glass fiber content were obtained following the described procedure (Table 1).

Characterization of Composite Sheets

Electron Microscopy

The scanning electron micrographs were obtained on a JSM 6100 CX (JEOL) electron microscope. The sample preparation technique used was based on Kato's osmium tetraoxide staining technique and Matsuo's two step sectioning method. The technique for taking micrographs was BSEI (back scattered electron image).

Mechanical Properties

For the mechanical strength, test specimen of IPN sheets were cut unto a dumb-bell shape, using a die. The stress strain properties were determined using an Instron universal testing machine Model 4466 according to ASTM D-527 procedure. The samples were dumb-bell shaped with span of 80 mm and overhead speed of 2 mm/min.

Chemical Absorption

The initial weight of the polymer samples was determined by weighing on a highly sensitive electronic balance having an accuracy of 0.0001 g. The samples were then kept immersed in penetrant taken in stoppered diffusion bottles at 30°C. The swollen samples were taken out after 48 h, wiped free of adhering solvents, and weighed on an electronic balance. Each weighing was completed within 30 s, so as to keep the error due to solvent escape from the surface to a minimum. The solvents used for chemical absorption study included toluene, xylene, HCl (conc.), DBA (dibutyl amine), NaOH (1.7 N), CCl_4, distilled water, ethanol, DMF (dibutyl formamide), formaldehyde, sulphuric acid, nitric acid, pyridine, and acetone.

RESULTS AND DISCUSSION

Morphology

The morphology of glass fiber–reinforced PU-PS IPNs is shown in Figure 1. Figure 1a–c show IPN sheets with pure polyurethane, 25% and 50% styrene, respectively. Figure 1d–f show short glass fiber–reinforced IPNs with 2%, 4%, and 7% glass fibers. The micrographs clearly show that at lower concentration of polystyrene, phase separation is very prominent and as the styrene content increases, polystyrene phase appears to be more uniformly dispersed throughout the PU matrix. The formation of IPN structure is vividly seen by the existence of finely mixed microstructure of polyurethane and polystyrene. The PU/PS IPNs (Figure 1b and c) show finer phase domain at high concentration of PS. Figure 1d, containing 2% glass fiber indicates an uneven distribution of fibers, voids in the polymer matrix, and poor impregnation of the fibers in the matrix. There is also clustering of the fibers at places, but as the fiber content increases (Figure 1f), there is more uniform distribution of fibers, and fibers align in the direction of load thereby increasing the tensile strength.

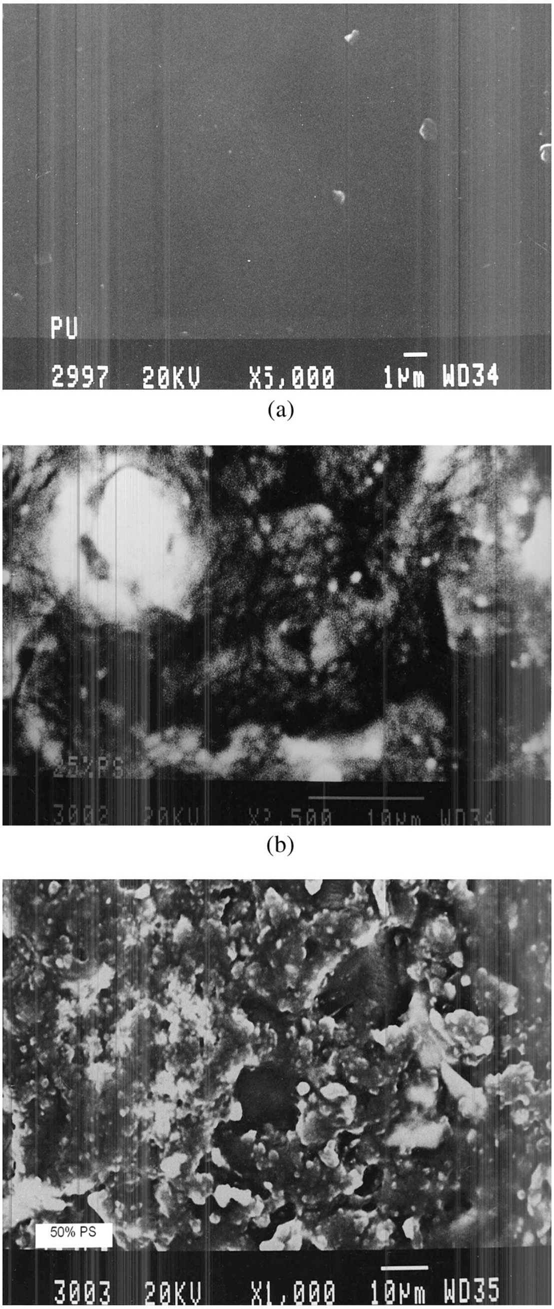
Chemical Absorption

The percent absorption was calculated using Eq. 1.

$$A = \frac{m_t - m_i}{m_i} \times 100 \tag{1}$$

where, m_t is the mass of sample at time t (48 h in this case) and m_i is the dry weight of sample.

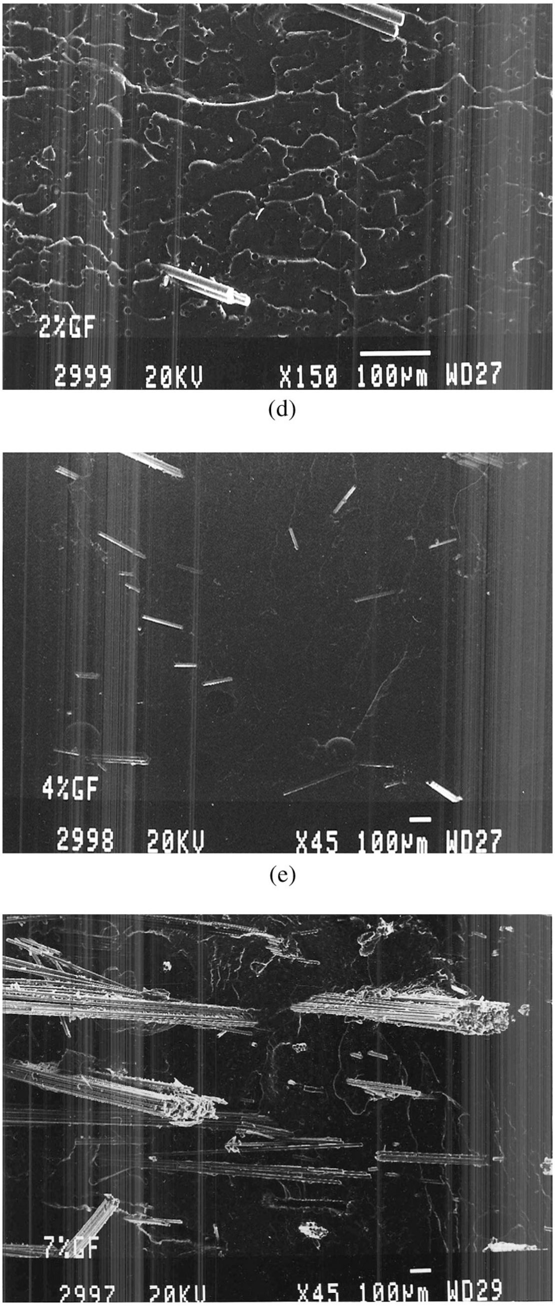
The chemical absorption of short glass fiber–reinforced IPN composites with different fiber content is being shown in Table 2. The pictorial representation is given in Figures 2 and 3 for high and low absorbing solvents, respectively. It is evident from Figures 2 and 3


PU
2997 20KV X5,000 1µm WD34
25%PS
3002 20KV X2,500 10µm WD34
50% PS
3003 20KV X1,000 10µm WD35

(a)

(b)

(c)


2%GF
2999 20KV X150 100μm WD27
4%GF
2998 20KV X45 100μm WD27
7%GF
2997 20KV X45 100μm WD29

(d)

(e)

(f)

that percentage absorption increased with the fiber content in IPN matrix and was maximum for S-9 containing 16 wt% glass fibers for all the solvents. The percent absorption was maximum for pyridine and varies from 221.46% to 341.12% for 1% to 16% fiber content, followed by carbon tetrachloride, dimethyl formamide (DMF), toluene, dibutylamine, and then xylene. For all the high absorbing solvents, that is, toluene, xylene, dibutyl amine, CCl_4, pyridine, ethanol, dimethyl formamide, and acetone, samples became brittle, lost their gloss, sheets lost elasticity but the embrittlement was only physical and no soluble fraction was observed. For the low absorbing solvents, that is, distilled water, HCl (conc.), formaldehyde, and NaOH (1.67 N), having absorption value less than 7%, the same trends were observed. The samples were stable and showed no embrittlement. The absorption was minimum for distilled water, varying from 0.475% to 2.69%, for 1% to 16% fiber content, respectively.

Mechanical Properties

Figure 4 illustrates the tensile strength of various IPNs with different styrene content. The results indicate that the tensile strength increases with styrene content and an almost linear relationship exists till 40% PS; after that there is a sudden increase in tensile modulus. IPNs containing 50% styrene shows the maximum tensile strength. Therefore, 50% styrene content was chosen for making short glass fiber–reinforced PU/PS composites.

Figure 5 shows the variation of tensile modulus for short glass fiber–reinforced PU/PS composites. Each sample was tested thrice. The short glass fiber–reinforced composites show a lot of dispersion in their behavior. This could be attributed to haphazard alignment of fibers. For each sample taken, fiber alignment may not be the same.

◄

FIGURE 1 Scanning Electron Micrographs (SEM) castor oil–based of PU/PS IPN composite sheets. (a) SEM of castor oil–based polyurethane sheet; (b) SEM of castor oil–based polyurethane/polystyrene sheet containing 25% polystyrene; (c) SEM of castor oil–based polyurethane/polystyrene sheet with 50% polystyrene; (d) SEM of castor oil–based polyurethane/polystyrene composite sheet with 50% polystyrene containing 2% short glass fibers; (e) SEM of castor oil–based polyurethane/polystyrene composite sheet with 50% polystyrene containing 4% short glass fibers; (f) SEM of castor oil–based polyurethane/polystyrene composite sheet with 50% polystyrene containing 7% short glass fibers.

TABLE 2 Percentage Absorption of Various Chemicals on Different IPN Samples Prepared

	Percentage absorption								
Solvent used	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Toluene	127.87	139.58	141.42	146.78	149.22	150.11	155.47	159.58	161.26
Xylene	119.02	121.057	127.56	134.78	139.21	143.44	147.67	153.87	156.23
HCl (conc.)[b]	1.486	1.578	1.752	1.967	2.054	2.168	2.212	2.248	2.298
DBA[a]	98.78	101.67	122.24	123.72	129.24	136.76	139.32	143.56	149.37
NaOH (1.67 N)	0.343	0.353	0.369	0.378	0.384	0.388	0.393	0.405	0.434
CCl_4	192.67	280.64	219.26	231.46	243.72	257.62	268.59	275.51	280.23
Distilled water	0.475	0.75	0.87	1.77	1.89	2.02	2.22	2.56	2.69
Ethanol	16.57	17.05	18.89	19.05	21.65	22.99	23.14	23.96	24.29
DMF	108.67	115.61	122.89	139.64	148.6	156.87	161.04	167.47	174.26
Formaldehyde	2.36	2.58	2.89	3.69	3.97	4.12	5.87	6.04	6.61
Sulphuric acid[b]	Samples completely destroyed								
Nitric acid[b]	15.67	17.08	18.08	19.87	21.67	24.56	25.04	25.53	25.88
Pyridine[a]	221.46	258.64	287.61	291.86	298.74	320.65	329.92	333.37	341.12
Acetone	70.648	79.02	81.04	98.47	103.56	106.47	110.97	115.23	122.57

[a] In solvents like DBA (dibutyl amine), Pyridine IPNs become brittle and film loses elasticity.

[b] In acids color of the sample changes and upper layer was solvated.

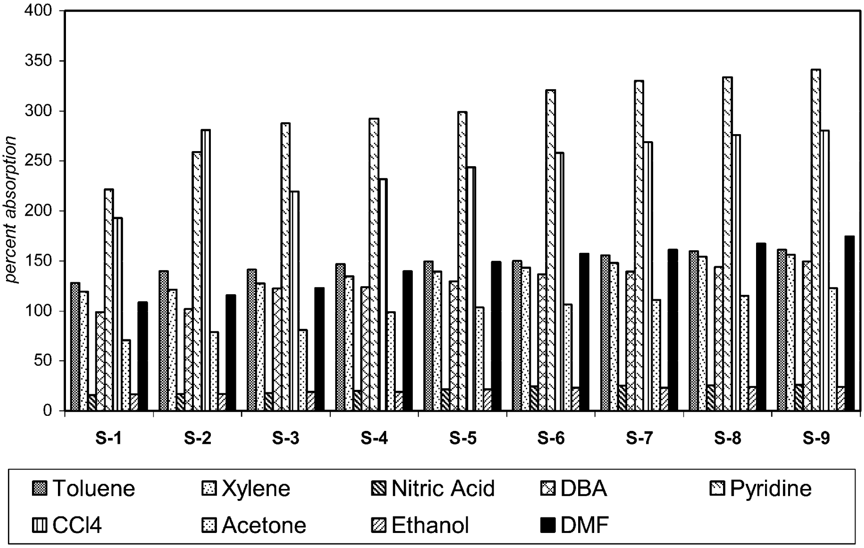


FIGURE 2 Chemical absorption of various chemicals in glass fiber reinforced castor oil–based PU/PS IPN composite sheets (high absorbing).

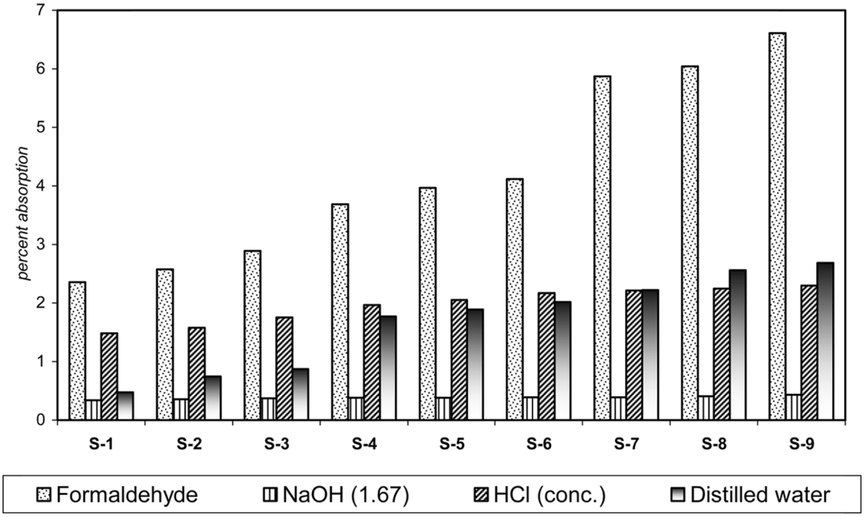


FIGURE 3 Chemical absorption of glass fiber–reinforced castor oil–based PU/PS IPNs composite sheets in various chemicals (low absorbing).

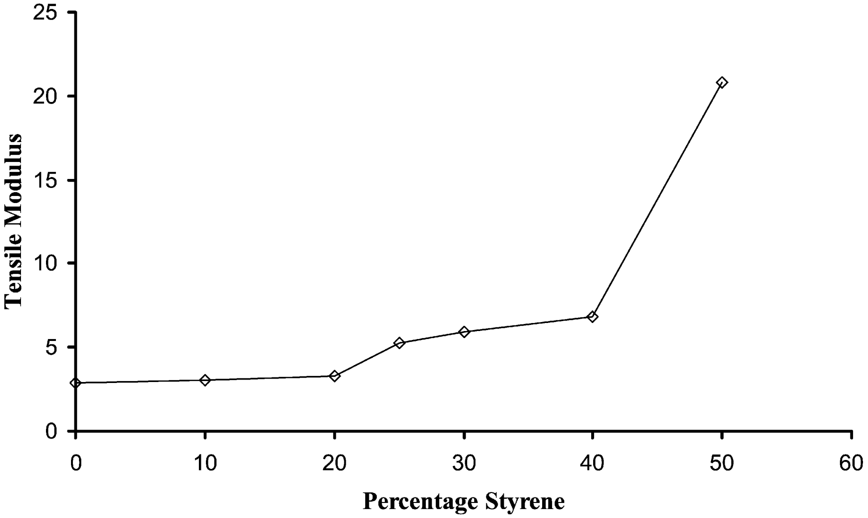


FIGURE 4 Variation of tensile modulus of castor oil–based PU/PS sheets with varying polystyrene content.

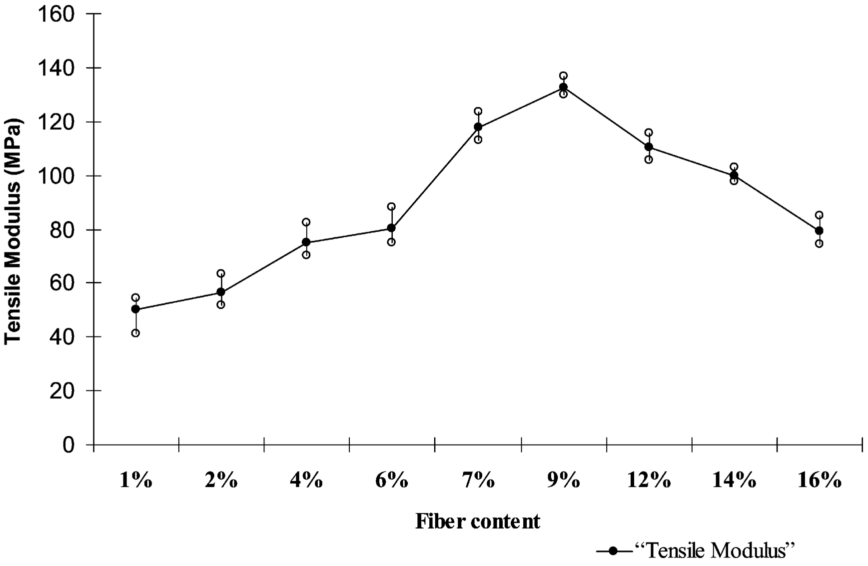


FIGURE 5 Variation of tensile modulus of short glass fiber–reinforced castor oil–based PU/PS sheets with varying glass fiber content.

A graph between tensile modulus and glass fiber content has been drawn taking the mean value of tensile modulus.

The tensile modulus increases till 9% glass fiber content, after which there is a sharp decline in the modulus. The reasons for this decrease may be:

- Uneven distribution and clustering of the fibers at certain places due to increase in viscosity in the polymer matrix.
- Voids at some places—poor impregnation of the fibers in the polymer-monomer dough. This can be due to relatively high viscosity of the dough.
- The voids of poorly impregnated fibers are oxygen reserves.
- Poor adhesion between the fibers and the IPN matrix because of the difference in properties of polymer matrix and glass fibers.
- Stress concentrations occur at regions around fiber ends. From this stress concentration, cracking initiates and propagates, thus causing premature failure.
- Non-homogenous mixing due to increase in the matrix viscosity.

CONCLUSIONS

- The overall mechanical strength of the castor oil–based polyurethane networks improved by the formation of IPNs with polystyrene.
- Scanning electron micrograph showed that the phase domains decrease in size with increasing polystyrene level. The phase separation was very prominent at a lower concentration of polystyrene. In 50/50 IPN, the extent of phase separation was minimal and the polystyrene phase structure was finer and exhibited a higher degree of continuity.
- Among the IPNs, the mechanical strength increased as the wt% of styrene increased and a linear relationship exists till 40 wt% styrene and there is a sudden increase in the tensile modulus at 50 wt% styrene.
- In chemical absorption, the samples were almost stable in acids and alkali but did completely deteriorate in conc. sulphuric acid. The percentage absorption was maximum for pyridine and minimum for distilled water and absorption increased with increased fiber content.
- The tensile modulus of IPNs increase with increase in fiber content up to 9% fiber, after which there was sharp decline in tensile modulus. This may be attributed to non-homogenous mixing, stress concentration, increased voids, or all the above.

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