Dynamic Mechanical Properties of SBR and EPDM Vulcanisates Filled with Cryogenically Pulverized Flexible Polyurethane Foam Particles

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ABSTRACT: The dynamic mechanical properties of rubber vulcanisates filled with cryogenically pulverized polyurethane foam particles, used as a reinforcing filler, were investigated with respect to storage modulus (E'), loss modulus, and the variation of glass transition temperature. Two rubbers were using styrene–butadiene rubber (SBR) and ethylene–propylene copolymer (EPDM). The effects of filler concentration and filler characteristics (such as particle size and moisture content) were also monitored. It was found that the optimum dynamic mechanical properties of the compounds were obtained when introducing the PU particles of 40–50 parts per hundred (pph) rubber in the SBR and 30 pph in the EPDM, the properties being affected by the size of PU particles and moisture content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1129–1139, 1999

Key words: dynamic mechanical properties; polymer recycling; flexible polyurethane foams; rubber vulcanisates

INTRODUCTION

Overview on Polymer Recycling

Considerable legislative pressures face the polymer industry to minimize the impact of polymeric waste on the environment. The cost of the polymeric waste resulting from landfill and transportation to be disposed of is anticipated to increase. Over the past decades, polymeric materials are increasingly in demand due to their applications and performances. This is one of the main reasons that higher quantities of the polymeric waste are produced. Packaging is found to be the most part of domestic wastes.[1] In this application, polyurethane foams are included. Polyurethane foams are isocyanate derived, and crosslinked materials and remelting or blending with virgin materials for reprocessing is extremely difficult. The commonly used methods for eliminating such materials include landfill and incineration, neither method being acceptable due to pollution as well as conservation of raw materials.[2] In addition, the volume of polyurethane (PU) scrap, produced by both manufacturers and consumers each year to be recycled is very large so that a number of alternative recycling technologies have become necessary. The recent status of recycling PU foam in the United States was reviewed[3] and found that the major recycled products from the PU scrap were rebonded carpet underlay, this being carried out by blending the granulated PU particles with an isocyanate-terminated prepolymer and then streaming in a mold under a degree of compression consistent with the desired final product density.[4] In this respect, the North American and European markets have one significant

difference. Large quantities of flexible PU scrap are used in the United States as rebonded carpet underlay, whereas this product is not acceptable in Europe, the latter being due to the cost of the energy requirement for curing and the amount of prepolymer necessary for adequate bonding. In 1990, it was estimated[4,5] that some 126,000 tons of US produced flexible PU scrap were used in this product, and approximately 50,000 tons were imported, presently allowing European manufacturers to export their problem. It appears that this market in the United States is almost saturated at the present time, and this implies that the recycling of PU foams will again become a problem. Another potential application for recycling flexible PU foam scrap is in the production of particles to feed back into foam formulations.[6]

Polyurethane recycling is the most advanced of thermoset recycling processes. An attempt to recycle the PU materials by grinding the foam into particles of suitable size to be incorporated into some other materials has been made.[6,7] Small-particle manufacture has been accomplished by a number of mechanical techniques including solid-state shear extrusion[8] and cryogenic pulverisation.[6,7] The most promising of these alternatives appeared to be the potential of PU particles to act as a filler/extender in rubber vulcanisates. Sombatsompop and Sims[9] conducted initial investigations into potential alternative uses of the PU particles (of an average size of 200 μm) as a filler into natural rubber vulcanisates, and the effect on tensile properties were studied. It was found that in the critical loading range from 25–30 parts per hundred rubber (pph), the mode of action of the PU particles appeared to change from one of a suitable NR extender to that of a reinforcing filler, which could potentially cheapen the product and improve certain properties (such as elongation set). It was postulated that the reinforcing mechanism was due to chemical and physical adsorption effects between carbonyl and NH groups of the PU particles and residual unsaturation in the rubber or double bonds oxidized during milling process, this being supported by the work of Ismael et al.[10] Similar behavior was observed while investigating such an effect on dynamic mechanical properties of the NR vulcanisates.[11] Later work[12] compared the reinforcing actions of the PU particles and carbon black in NR vulcanisates and the effect of blending the fillers was studied. It was found[12] that a relatively satisfactory level of reinforcement was obtained when loading PU filler particles and carbon black into NR formula-tions at the optimum loading for each filler individually, i.e., 30 pph PU and 60 pph carbon black. The addition of PU particles to carbon black reinforced rubber also offered potential cost savings. Recently, work has been carried out on the effect of PU particles on swelling characteristics of NR vulcanisates has been conducted.[13] The degree of solvent penetration into the PU-filled NR vulcanisates was generally found to be closely associated with the effectiveness of the chemical and physical adsorption and reinforcing mechanisms of the filler–rubber interaction.

Dynamic Mechanical Properties of Rubbers

The properties of a product made of vulcanized rubber depend on many factors, including the type and grade of polymer used and the selection of additives and the quantities used. The world's rubber markets are dominated by two rubbers—one being natural rubber and the other being SBR—which between them share about 70–75% of tonage consumption.[14] Due to its low price, the first rubber to be considered for manufacturing rubber products is SBR. In the United States, among synthetic rubbers, SBR is the largest volume of the total consumed, the main use being in automobile tires.[14] SBR has good mechanical properties, especially abrasion resistance, whereas NR shows good dynamic mechanical properties. An example of the use of NR is bridge bearings, and that of SBR is car tire treads. In the tire industry, SBR is used due to having a better wet grip rating. Another type of rubber that has become widely used as a nontire rubber is ethylene–propylene rubber (EPDM). This rubber does not require antioxidants and antiozonants during compounding, and the product has good heat resistance and electrical insulation properties.[14,15] Examples of use of EPDM are parts in washing machine, gaskets and driers, door and window seals, and waterproofing sheets. For many applications, the choice of a rubber has to be made before manufacturing, this usually being based on the fact that the engineer knows the requirements of the product in service. One means of selecting the right rubber is to investigate the relevant properties of the rubber. Most applications of rubbers for uses involve rapidly repeated deformations, these being well known as the dynamic mechanical properties of the rubbers, which are dependent on both the chemical and physical interactions of the fillers with the rubber.[15,16] Rubbers are known as viscoelastic materials, exhibiting both elastic and damping behavior. When they are deformed by a sinusoidal

stress, the resulting strain will be sinusoidal, but out of phase. Dynamic losses are usually associated with hysteresis and specific mechanisms of molecular or structural motions in polymer materials. The damping characteristics are extensively measured as "the tangent of the phase angle, (tan δ)" defined as the ratio of the loss modulus (E'') due to viscous dissipation in the materials to the storage modulus (E') representing the stored elastic energy.[16]

One method that has been used to evaluate the above parameters (E', E'', and tan δ) is Dynamic Mechanical Thermal Analysis (DMTA). This technique is particularly useful for nondestructive testing and for identifying the molecular mechanisms of polymer materials. A number of workers[17–21] utilized this technique to examine the molecular interactions between the fillers and the rubber materials. Pillai and Das[17] studied the effect of carbon black types on dynamic mechanical properties of polychloroprene rubber vulcanisates, this rubber being tested for the purpose of use of underwater electroacoustic transducer. It was found that dynamic moduli increased with addition of all types of carbon black. The carbon black having the smallest particle size showed the greatest reinforcing effect by an increase in storage modulus. Lower damping was observed as the fillers were added. Namboodiri and Tripathy[18] examined the dynamic mechanical properties of carbon black-filled EPDM vulcanisates for different vulcanization systems and deforming strain. The results showed that such parameters had a significant effect on the properties of the vulcanisates, the main reason being the interaggregate attractive forces in the vulcanisates. Neogi et al.[19] determined the dynamic mechanical properties of carbon black-filled NR and SBR vulcanisates under unswollen and swollen states. In the case of unswollen state, the loss tangent, loss modulus, and storage modulus increased with increasing carbon black content both at low- and high-strain amplitudes, the effect being less pronounced at the low-strain amplitude. They explained these results in terms of a breakdown of a large number of weaker bonds (reduced number of chains bearing the stress applied) and filler aggregates. Funt[20] indicated that the reinforcement in filled rubbers was caused by the hydrodynamic interaction and the increase in effective degree of crosslinking from entanglements formed between the bound and the bulk rubber. Varughese and Tripathy[21] studied the effect of various types of fillers on dynamic properties of epoxidized natural rubber, and suggested that the filler–rubber

reinforcement could be studied by considering the height of the damping peak and the spread of the peak. It was reported that with increasing filler content, the height of the damping maximum decreased, while simultaneously the damping peak was broadened, this indicating increased interaction between filler and rubber molecules in the system. This type of explanation was also used by Sombatsompop[11] while investigating the effect of PU foam particles, regarded as a new filler, in NR vulcanisates. It was recommended that PU filler at loading of 20–30 pph be used in NR vulcanisates to improve the level of dynamic mechanical properties.

The present work was part of an ongoing investigation of using PU foam particles as a filler in polymeric materials. Presently, it seemed logical to continue prior investigations by conducting a controlled series of experiments to incorporate PU particles as a filler into some other types of rubbers. In this work, the rubbers used were styrene–butadiene rubber (SBR) and ethylene–propylene rubber (EPDM). The effects of PU particle characteristics, including particle size and moisture content in the filler, were also examined. The results obtained were compared to those previously published on the effect of the PU filler on the dynamic mechanical properties of NR vulcanisates.[11,13] In this respect, it is hoped that the use of PU foam particles as a filler would show some remarkable properties, leading to newer applications in the rubber industry.

EXPERIMENTAL

Raw Materials

1. Materials used were styrene–butadiene–rubber (SBR-1502 23.5% styrene by weight, Goodyear Chemical Div.) and ethylene–propylene rubber (EPDM-501A, Channel Chemical Co, Lth).
2. Production of PU particles: PU particles used were based on flexible polyurethane foam grade 4200C of density 28 kg · m^{-3}, supplied by Caligen Foam Ltd. The PU particles were produced using cryogenic pulverisation, which has been shown elsewhere.[22] There were many problems previously noted in using the cryogenic pulverisation system to reduce the particle size of the PU foam, the usage of cryogen being large and thus uneconomic. These prob-

Table I   Particle Sizes of a PU Filler

Particle Designation	Size Range (μm)	Nominal Average Size (μm)
PU1	63–150	100
PU2	150–314	200
PU3	315–400	350
PU4	401–710	550

lems were minimized, in this work, by densifying the PU foam before loading into the cryogenic pulverization system.[22] The densification was carried out by compression molding the PU foam at 160°C for 45 min to obtain a semisolid of a density of approximately 800 kg · m^{-3} (from an initial density of 28 kg · m^{-3}).[23] This was then granulated using a 6-mm screen to produce reasonably uniform material of convenient size. Further size reduction was then achieved by precooling the material in a temperature-controlled freeze tunnel prior to feeding to the pulverisation system, the detail being previously described.[22] The size ranges studied are annotated in Table I. The concentration of PU particles filled into rubber compounds varies from 0–60 parts per hundred (pph) rubber.

Immediately after cryogenic pulverisation, the PU particles were noted to be free flowing, but after storage for several months the powder tended to aggregate and appeared somewhat damp, possibly due to atmospheric moisture pickup. It was, therefore, prudent to determine the moisture content and assess its effect on dynamic mechanical properties. PU particles, spread evenly on a metal tray, were subjected to heat treatment in an oven at 100°C from 90 to 450 min, determining weight loss and providing samples of varying moisture content for further study.[23] Moisture content was given by the average percentage moisture content of the particles when dried to constant weight loss. To prevent moisture regain, the dried PU particles were stored in a dessicator prior to compounding. In this case, PU2 (200 μm) and PU 4 (550 μm) were selected and loaded into an SBR compound with various concentration. Table II shows the moisture content obtained, each moisture content of PU particles being designated.

In all cases, sulphur vulcanization was prepared using the conventional system[24,25] consisting of 3 pph (parts per hundred rubber by weight) sulphur, 0.5 pph mercaptobenzthiazole (MBT), 4 pph zinc oxide, and 2 pph stearic acid. For the comparison purposes (with NR vulcanisates[11]), the rubber vulcanisates loaded by various concentrations of PU filler, using PU2 (200 μm) unless indicated otherwise.

Compounding and Sample Preparation

Each type of rubber was mixed with the addition of the quantities of zinc oxide and stearic acid according previous work,[11] in batches of 275 g in a two-roll mill, the mill rolls being cooled using chilled water at 15°C. The temperature of blending on the two-roll mill measured using a temperature probe was between 40–50°C. This was carried out for 10 min. The compound was produced in stages to ensure the uniformity of the materials used throughout the work, while ensuring that the compound did not scorch prior to use.[26] Where appropriate, PU particles with the required proportions, the amount of sulphur and the accelerator (MBT) were added for a further 5 min. Cutting and folding processes were carried out for a further 5 min to ensure the uniform and homogeneous mixing of the compounds. From the resulting compounds of each mix, vulcanisate sheets of approximately 1.5-mm thick were produced by the use of compression molding at a pressure of 5000 kPa and a temperature of 160°C.[9,11,13] Cure time used was 30 min. Test pieces were obtained using a square cutting punch 40 × 10 mm, and the test pieces were kept and tested throughout the work under controlled environmental conditions of 25°C and 50% relative humidity for 24 h.

Dynamic Mechanical Properties

The dynamic mechanical properties of samples of PU particle-filled vulcanisates were determined

Table II   Rubber Vulcanisates with Various Moisture Contents

Designation	Average Size (μm)	Average Moisture Content (%)
WT-1	200	40
WT-2	200	10
WT-3	200	1
WT-4	550	41
WT-5	550	14
WT-6	550	3

Table III   Effect of PU Particle Size on the Dynamic Mechanical Properties of SBR Vulcanisates Filled with 0, 20, and 40 pph PU Filler Loadings

	Properties								
	E' 25°C (*10^6 N/m^2)			tan δ_{max}			T_g (°C)		
Mix	0 pph	20 pph	40 pph	0 pph	20 pph	40 pph	0 pph	20 pph	40 pph
PU1	0.87	1.19	3.94	1.92	1.58	1.46	−48.0	−46.5	−44.5
PU2	0.87	1.07	3.84	1.92	1.62	1.50	−48.0	−46.5	−45.0
PU3	0.87	1.05	3.26	1.92	1.69	1.52	−48.0	−47.5	−45.0
PU4	0.87	0.93	3.01	1.92	1.71	1.58	−48.0	−47.5	−46.0

using Dynamic Mechanical Thermal Analyzer (DMTA), supplied by Polymers Laboratories Ltd., which is comprised of a temperature programmer and a controller. The dual cantilever mode of deformation geometry known as three-point bending was used in the temperature range of −90–80°C at a heating rate of 10°C/min, with a strain amplitude of 0.2% and at a frequency of 1 Hz.[11] The cooling process was achieved by the use of liquid nitrogen. Details of the test procedure and equipment are explained elsewhere.[27] The results were presented in terms of storage modulus (E'), loss tangent (tan δ) and glass-transition temperature (T_g) for the temperature range of −90–80°C. The loss tangent (tan δ) is measured as the ratio of loss modulus (E'') to the storage modulus (E'), as shown earlier, whereas the T_g value is obtained from the peak of the E''.[11,28] The average value of experimental results, based on at least four determinations, had error in the range of ±2.5%. These variations could be caused by two possible reasons; first, there are variations in PU filler dispersion in the rubber compounds, and second, the PU particles that impede the flow of the rubber during processing generates a small amount of orientation in the rubber compound. However, these variations are considered to be small enough to be neglected in this work.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of PU-Filled SBR Vulcanisates

Effect of PU Loading

Figure 1 shows the dynamic mechanical properties of the SBR vulcanisates added with PU foam

particles as a function of temperature, various concentrations of PU particles being introduced. It was found that the storage modulus (E') decreases with increasing temperature, and this trend is very pronounced around temperature range of −50−−40°C, this temperature range being the transition region. The sharp decrease of the storage modulus in the transition region was due to the mobility of polymer chains that increases with temperature. It is widely known that the state of a polymer below the transition region is glassy, whereas that above the transition is rubbery. It can be seen from the figure that the dependence of the storage modulus on PU loading is more pronounced around the rubbery region. There were no major differences in the modulus observed in the glassy and transition regions due to the small strain amplitude used in this work.[11]
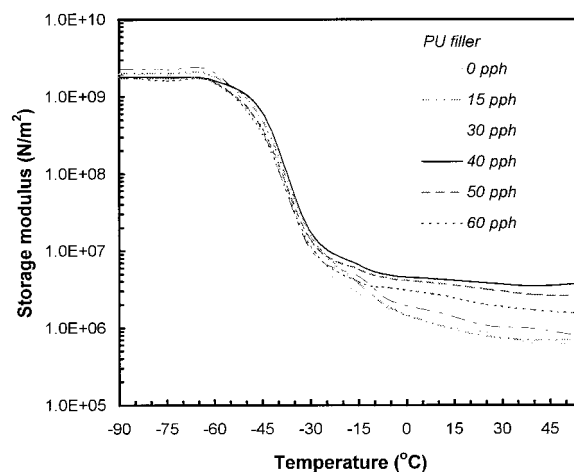

Figure 1   Storage modulus vs. temperature plots for SBR vulcanisates filled with PU foam filler at various concentrations.
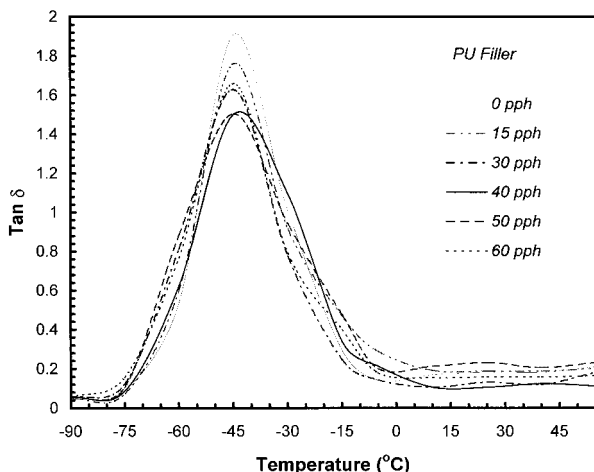
Figure 2 Effect of PU concentration on tan δ as a function of temperature for SBR vulcanisates.

A variation of E' with PU loading in the rubbery state is of interest here. The E' value increases with increasing PU particles up to 40–50 pph and reduces at the higher PU content (60 pph). The increase in the modulus due to the presence of PU filler was thought to caused by an interaction between crosslinks of the rubber and functional groups present the PU particles. It was evident from previous investigations[9] (PU particle-reinforced NR vulcanisates) that polyurethane containing the C=O and NH functional groups in diamine salts of carboxylic acids (C=O and NH groups in the urethane and urea hard segments and C=O in the polyester soft segments) increased the mechanical properties of PU filled rubber compounds. This may also result from a dipole–dipole molecular interaction between the C=O group and sulphur crosslinks and hydrogen bonding between NH groups in the rubber compounds. However, it should be noted that at the loading of 60 pph the reinforcement of the PU–SBR vulcanisates reduces, this being due to the fact that the packing of PU filler has reached a critical point where the filler is no longer separated by the polymer matrices.[29] It seems that the optimum loading of PU particles filled in the SBR vulcanisates with respect to the dynamic mechanical properties is 40–50 pph.

These results can be substantiated by considering the tangent loss (tan δ) and the variations in glass transition temperature (T_g) of the SBR compounds added with various contents of PU particles, the results being shown in Figures 2 and 3, respectively. In the case tan δ, the maximum values (tan δ_{max}) were observed around the transition temperature, this being associated with the large change in the modulus, as indicated earlier. The higher the tan δ_{max}, the greater the mechanical loss in the system. These losses were related to high energy input required for the motion of the polymer chains as the transition is approached.[11] It can be observed that the magnitude of tan δ_{max} reduces as the concentration of PU particles increases up to 40–50 pph and starts to increase again at the higher concentration, corresponding to the E' results explained earlier. When considering the variation of glass transition temperature (T_g), it is found that the higher the PU loading, the higher the glass transition temperature, showing the maximum at 40–50 pph PU loadings. The decrease in the height of tan δ peak and the increase in T_g indicate greater molecular interactions of the filler and rubber molecules.[11] Therefore, it can be concluded that the optimum loading of PU particles added into the SBR vulcanisates, with respect to dynamic mechanical properties was 40–50 pph.

Effect of Particle Size and Moisture Content

Table III shows the effect of PU particle size on dynamic mechanical properties of the SBR vulcanisates containing 0, 20, and 40 pph PU filler. The storage modulus at 21°C, the value of tan δ_{max}, and the variation of T_g are of interest here. It is clearly seen that as the PU particle size is increased, the modulus, T_g, and tan δ_{max} are only marginally changed. Comparing the three PU concentrations, the vulcanisates with 40 pph PU filler gives the highest reinforcement, this being the case for all particle sizes used. The increase in
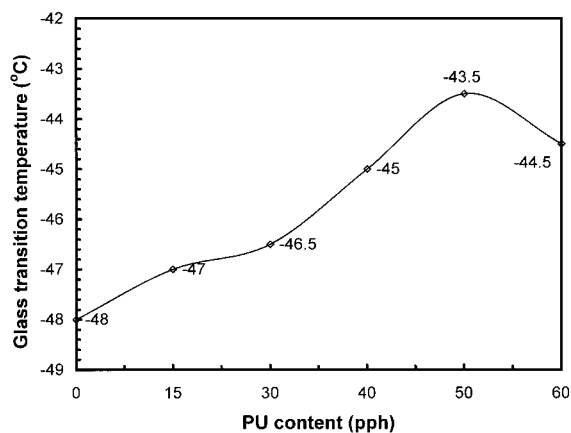

Figure 3 Variations in glass transition temperature (T_g) of SBR/PU compounds.

Table IV Effect of Moisture Content on the Dynamic Mechanical Properties of SBR Vulcanisates Filled with 0, 30, and 40 pph PU Filler Loadings

	Properties								
	E' 25°C ($*10^6$ N/m^2)			tan δ_{max}			T_g (°C)		
Mix No.	0 pph	30 pph	40 pph	0 pph	30 pph	40 pph	0 pph	30 pph	40 pph
WT-1	0.87	1.07	3.84	1.92	1.62	1.50	−48.0	−46.5	−45.0
WT-2	0.88	1.09	3.92	1.92	1.61	1.52	−48.0	−46.0	−44.5
WT-3	0.87	1.08	3.91	1.92	1.52	1.56	−48.0	−46.0	−44.5
	0 pph	30 pph	40 pph	0 pph	30 pph	40 pph	0 pph	30 pph	40 pph
WT-4	0.87	0.93	3.01	1.92	1.71	1.58	−48.0	−47.5	−46.0
WT-5	0.87	0.91	3.06	1.92	1.71	1.56	−48.0	−47.0	−45.5
WT-6	0.87	0.93	2.98	1.92	1.71	1.56	−48.0	−47.0	−46.0

reinforcing action of PU filler–rubber vulcanisates as the particle size reduces was caused by increased surface interaction due to increasing the surface area to volume ratio and a decrease in the inherent flaw size.[17]

In a previous work on the dynamic mechanical properties of PU particle-filled NR vulcanisates,[11] there was a critical point of moisture content that could be allowed in the PU filler for maintaining the optimum dynamic mechanical properties, this value being less than 1%. Above this value, the properties worsened considerably. However, it can be seen that with SBR vulcanisates, it was not the case (see Table IV). Unlike in the case of NR vulcanisates,[23] moisture content does not seem to have any significant effect on the dynamic mechanical properties of the compounds. This may probably be related to differences in absorbing the moistures of SBR and NR vulcanisates, the SBR being more impermeable to moisture than the NR vulcanisates.[30] The differences in the results were only caused by the variations of PU loading for a given moisture content.

Dynamic Mechanical Properties of PU-Filled EPDM Vulcanisates

Effect of PU Loading

Figure 4 shows the dynamic mechanical properties of the EPDM vulcanisates filled with PU particles from 0−60 pph. The trend of the E' is found to be very similar to that observed in PU-filled SBR vulcanisates, the E' values decreasing with increasing temperature, and around the glassy and transition regions the effect of PU concentration on the change in the modulus E' was relatively small. In the rubbery region, the effect of PU concentration in the EPDM vulcanisates on the modulus became very significant, the modulus changing considerably with PU concentration. The PU loadings from 0 to 30 pph result in a progressive increase in the modulus. Above these concentrations, the modulus in this region decreased considerably. It should be noted that in the case of using PU particles as a filler in the EPDM, the optimum dynamic mechanical proper-
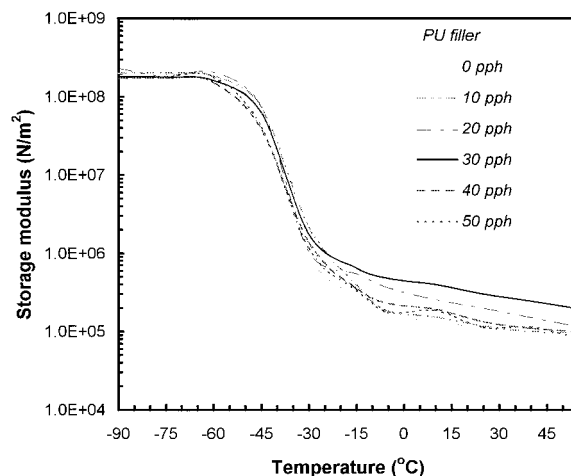

Figure 4 Storage modulus and temperature for EPDM vulcanisates filled with PU filler at various concentrations.
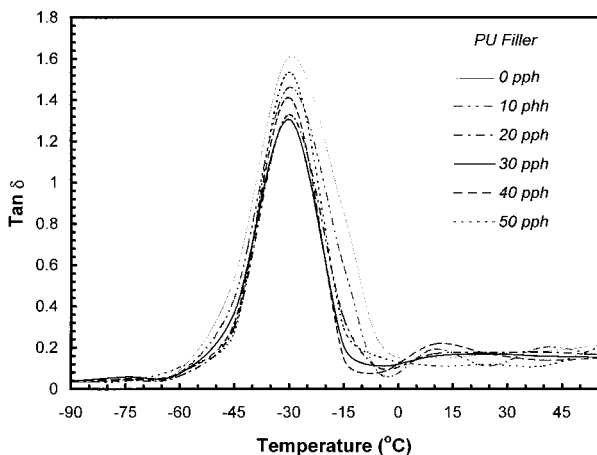
Figure 5 Effect of PU concentration on tan δ as a function of temperature for EPDM vulcanisates.

ties were obtained at the filler loading of 30 pph. The reasoning mechanism was thought to be the same as that given in the case of PU filled SBR vulcanisates.

Figure 5 shows the effect of PU particles on the loss tangent-temperature behavior of EPDM vulcanisates. The results correspond to those suggested by the use of values of the storage modulus, that is the optimum loading was 30 pph. At this concentration, the lowest values of tan δ_{max} and the maximum T_g were obtained. Another feature to consider was the overall width of the loss tangent peaks. It can be seen that with the presence of PU particles, the peaks became clearly narrower, indicating lower dynamic mechanical

losses occurring in the compounds. This may be caused by the fact that the mobility of the polymer networks becomes restricted when the PU particles were introduced in the compounds. When comparing with PU filler SBR vulcansates, it was observed that the overall widths of the loss tangent peaks of the PU/EPDM vulcanisates were less than those observed in the PU/SBR vulcanisates. This indicated that for, a given PU loading, the mechanical losses in the SBR compounds were greater than those in the EPDM compounds.

Effect of Particle Size and Moisture Content

It has been postulated that the moisture interferes with adsorption effects potentially acting as a lubricant between filler surface (functional groups) and rubber molecules, and this causes a marginal reduction in mechanical properties of rubber vulcanisates.[13,23] This is found to be true in the case of PU-reinforced EPDM vulcanisates because the dynamic mechanical properties marginally decrease as the moisture content in the filler is increased. The results are tabulated in Table V. In all cases, it was clearly seen that as the moisture content is reduced, the modulus and T_g values are marginally changed, with a decreased value of tan δ_{max}, this indicating an increase in filler–rubber reinforcement.

In the case of particle size effect, it was found that the finer the particle size the better the mechanical properties, the results being shown in Table VI. This is the case for PU contents from 0 to 30 pph. At 50 pph PU loading, the effect is very

Table V   Effect of Moisture Content on the Dynamic Mechanical Properties of EPDM Vulcanisates Filled with 0, 30, and 50 pph PU Filler Loadings

	Properties								
	E' 25°C ($*10^6$ N/m^2)			tan δ_{max}			T_g (°C)		
Mix No.	0 pph	30 pph	50 pph	0 pph	30 pph	50 pph	0 pph	30 pph	50 pph
WT-1	1.12	3.02	1.14	1.61	1.33	1.53	−32.0	−30.0	−31.0
WT-2	1.12	3.12	1.18	1.61	1.30	1.48	−32.0	−29.5	−30.5
WT-3	1.02	3.31	1.20	1.61	1.26	1.44	−32.0	−28.5	−30.0
	0 pph	30 pph	50 pph	0 pph	30 pph	50 pph	0 pph	30 pph	50 pph
WT-4	1.12	2.83	0.98	1.61	1.41	1.56	−32.0	−31.5	−31.5
WT-5	1.12	2.91	1.01	1.61	1.30	1.52	−32.0	−30.0	−31.0
WT-6	1.12	3.07	1.02	1.61	1.28	1.50	−32.0	−29.5	−30.5

Table VI Effect of PU Particle Size on the Dynamic Mechanical Properties of EPDM Vulcanisates Filled with 0, 30, and 50 pph PU Filler Loadings

	Properties								
	E' 25°C (*10^6 N/m^2)			tan δ_{max}			T_g (°C)		
Mix No.	0 pph	30 pph	50 pph	0 pph	30 pph	50 pph	0 pph	30 pph	50 pph
PU1	1.12	3.41	1.23	1.61	1.26	1.49	−32.0	−29.5	−30.5
PU2	1.12	3.02	1.14	1.61	1.33	1.53	−32.0	−30.5	−31.0
PU3	1.12	2.94	1.03	1.61	1.38	1.55	−32.0	−30.5	−31.0
PU4	1.12	2.83	0.98	1.61	1.41	1.56	−32.0	−31.5	−31.5

small. The reasonings and reinforcing mechanism were thought to be the same as those used for PU particles filled SBR vulcanisates.

Comments on the Dynamic Mechanical Properties of PU-Filled SBR and EPDM Vulcanisates Compared with Those of PU-Filled NR Vulcanisates

It was interesting to compare and discuss the effects of pulverised flexible polyurethane foam particles as a filler in various types of rubber vulcanisates, the rubbers including NR, SBR, and EPDM, upon the dynamic mechanical properties. The readers are encouraged to seek the detail of PU particle-reinforced natural rubber compounds regarding the dynamic mechanical properties elsewhere.[11] A number of comparisons were made in terms of the effects of temperature, filler concentration, and filler characteristics (particle size and moisture content) on the properties of the rubber compounds. The following are noted:

- The optimum loading of PU particles: the optimum concentration of PU particles was found to vary with the type of rubbers. For an economical use of the filler and satisfactory reinforcing purposes, it was recommended in this work that the optimum loading of PU foam particles filled in the SBR and EPDM vulcanisates regarding their dynamic mechanical properties are 40–50 pph and 30 pph, respectively. In the case of natural rubber,[11] the recommended concentration of PU particles was 20 pph.
- Excess filler concentration: there was a similarity between the three rubber vulcanisates (SBR, EPDM, and NR) in terms of addition of

a PU filler above the optimum loading in each case. Addition of a PU filler above the optimum results in a slight reduction of the mechanical strength of the vulcanisates. The had practical implications. PU particles added above the optimum loading result in an increase in the volume of the raw material, and this gave some benefits to the rubber manufacturing including (1) reduction of use of raw rubbers, (2) exploitation of the recycled polyurethane foams, leading to many other benefits as listed in the section of Introduction, and (3) cheapening the product price.
- Modulus of the compounds: at the optimum PU loadings of the three rubber vulcanisates for a given filler characteristic (particle size of 200 μm with 40% moisture content) their storage moduli were found to be slightly different. At 25°C, the values of the storage modulus at the optimum PU loading decrease in the order of NR–SBR–EPDM (NR: 4.10 MPa,[11] SBR: 3.84 MPa and EPDM: 3.02 MPa).
- The glass-transition temperature: according to previous work,[11] the PU filler has a T_g of 5.5°C, but when it was introduced into the NR vulcanisates its T_g was not seen. The introduction of PU particles in the NR vulcanisates resulted in a shift of the transition temperature of the rubber. This behavior was also seen in the case of SBR and EPDM vulcanisates. The reasons for these were probably related to the small amount of PU filler dispersed in the test sample, and the reinforcements of rubbers and PU filler in the compounds.

Table VII   Crosslink Densities of NR, SBR, and EPDM Vulcanisates Containing Various Concentrations of PU Particles

Rubber	PU Content (pph)	Crosslink Density (mol/m^3)
NR	0	56.8
	10	59.2
	20	60.5
	30	63.1
	40	64.3
SBR	0	45.9
	15	53.7
	30	62.2
	40	75.2
	50	84.4
	60	89.1
EPDM	0	60.5
	15	65.2
	30	69.1
	40	74.2
	50	77.9
	60	80.6

- Crosslink characteristics: it was very difficult to directly compare the strength (modulus) of the three vulcanisates because this parameter is strongly affected not only by the nature of the polymers, but also by crosslink characteristics (such as crosslink density and type), the former varying in the presence of a filler. Table VII shows the crosslink densities of the three rubbers at various PU contents. The crosslink densities were determined by the stress–strain measurement based on the Mooney-Rilvin equation, which has been detailed elsewhere.[25] It can be seen that for a given PU loading, different rubbers (using the same curing conditions) give different crosslink densities.

It should be noted that the use of PU foam had practical implications and very important advantages, especially in the case of SBR vulcansates. As stated, in automobile tire industry, SBR is the largest volume of total consumed. The improvement of the properties of the rubber vulcanisates by the presence of PU particles and, hence, increased properties of the finished rubber articles. As a result, it is hoped that the use of PU filler will show some remarkable applications in the rubber industry.

- Effect of moisture content: this part of the investigations had practical implications in that measures to reduce moisture pickup in the PU foam particles would be beneficial, and pulverised particles should preferably be stored in sealed containers. It would also be preferable to introduce hopper drying prior to compounding. The results in this article indicate that this is necessary in the case of EPDM vulcanisates, not SBR vulcanisates. Previous investigations showed that the moisture in the PU filler had a significant effect on the properties of filled NR compounds.[13,23]

- Particle size effect: the results indicated that minimum particle size of a PU filler may be used for reinforcement purposes in rubber vulcanisates.

CONCLUSION

The use of pulverised flexible polyurethane foam particles as a reinforcing filler in SBR and EPDM rubber vulcanisates was investigated. It was found that the optimum concentration of PU particles vary with the type of rubbers. In the case of SBR vulcanisates, it was recommended that 40–50 pph PU particles is the optimum concentration to be added into the compounds to obtain a satisfactory level of reinforcement, whereas in the case of EPDM, the optimum PU content is 30 pph. The reinforcements were mainly associated with the physical and chemical adsorption between the functional groups in the filler and rubber molecules. It was also observed that the smaller the particle size, the better the properties obtained, this involving increased surface interaction due to increasing the surface area-to-volume ratio. Moisture content is observed to have an effect on the properties in the case of EPDM vulcanisates, but not SBR vulcanisates.

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