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Influence of hygrothermally degraded polyester-urethane on physical and mechanical properties of chloroprene rubber ☆

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Abstract

The influence of hygrothermally-degraded polyester urethane (HD-PUR) waste on chloroprene rubber (CR) has been studied giving special attention to curing behaviour, mechanical properties and dynamic mechanical behaviour. The presence of primary and secondary amines in HD-PUR, did not increase the cure rate of CR. The mechanical properties of chloroprene vulcanizates were improved upon HD-PUR addition. The strain-induced crystallisation of CR did not show any deviation upon the addition of HD-PUR. Crosslink densities calculated from swelling studies, stress–strain behaviour, and modulus measurements are found to increase upon HD-PUR addition and showed similar trend. The glass transition temperature (T_g) did not show any significant change, with the addition of HD-PUR. Scanning electron microscopic studies have been done in order to have an insight into fracture behaviour of the samples and to analyse the microstructure of the blends.

Keywords: Chloroprene rubber; Polymeric wastes; Recycling

1. Introduction

Polymeric wastes, which include plastic and rubber wastes, have caused immense pollution problems to the entire world. These include the plastic and rubber wastes. Used tires are a major threat to the environment. Due to these problems, recycling of polymeric wastes has emerged as a thrust area of applied research. Several methods like mechanical degradation, incineration and land filling have been tried for the past few decades. Open burning of the wastes is prohibited due to emission of toxic gases. Recycling by blending of plastics and scrap rubbers have been done by several researchers. Mathew et al. [1] have studied the use of latex rejects as potential filler in rubbers. Devulcanization of waste tires is done by several methods. It includes the ultrasonic irradiation as reported by Isayev et al. [2]. The resulting devulcanized rubber could be reprocessed, shaped and revulcanized just like a virgin rubber.

Recycling of polyester-urethane wastes has gained much importance due to the increasing amount of PUR in consumer wastes. Polyurethane footwear wastes can be degraded by different methods. Karger Kocsis et al. [3] reported on the hygrothermal degradation of polyester-urethane (HD-PUR). Hygrothermally degraded PUR could be a suitable polymeric ingredient in rubber recipes. It has been used as filler in natural rubber, styrene–butadiene rubber and nitrile rubber [4–6] in order to improve their cure characteristics, physical and mechanical properties. HD-PUR can also be used

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for toughness improvement in thermosets and rubber stocks.

Chloroprene is a synthetic rubber substitute, which is used for solvent resistant high performance applications. In the present work attempts have been made to study the influence of HD-PUR on the curing behaviour, mechanical and dynamic-mechanical properties and swelling characteristics of chloroprene rubber. The mechanical performance of the compounds is correlated with the morphology of the fracture surfaces.

2. Experimental

2.1. Materials

Chloroprene rubber (CR) (Bayprene 1501) used was supplied by BAYER AG-Germany. The accelerator ethylene thiourea (ETU) and mercaptobenzthiazyldisulphide (MBTS) were also obtained from Bayer-AG, Germany. Other rubber chemicals, zinc oxide, magnesium, oxide, stearic acid were all commercial grades obtained from Ranbaxy Ltd., Bombay, India. Hygrothermally degraded PUR was produced as described in earlier papers by Karger Kocsis et al. [3,4].

2.2. Compounding

Compounding of CR was carried out on a two-roll open mill according to ASTM-D-16-627. The formulation of the mixes is given in Table 1. The mixes K_0, K_1, K_2, K_3, K_4 correspond to an HD-PUR loading of 0, 10, 20, 30, and 40 phr. The rheograph of the mixes and their cure characteristics were obtained using Monsanto Rheometer R-100 at 150 °C (Fig. 1). The rubber compounds were cured in a hydraulic press at 150 °C for the optimum cure time.

2.3. Tensile tests

The tensile properties and tear resistance of the compounds were measured on an Instron tensile testing machine at a crosshead speed of 500 mm/min according to ASTM D 412-98a and ASTM-D 624-98 respectively.

Table 1
Formulation of the mixes

	Composition				
	K_0	K_1	K_2	K_3	K_4
CR	100	100	100	100	100
ZnO (phr)	5	5	5	5	5
MgO (phr)	4	4	4	4	4
Stearic acid (phr)	1.0	1.0	1.0	1.0	1.0
MBTS (phr)	0.2	0.2	0.2	0.2	0.2
ETU (phr)	0.5	0.5	0.5	0.5	0.5
HD-PUR (phr)	0	10	20	30	40

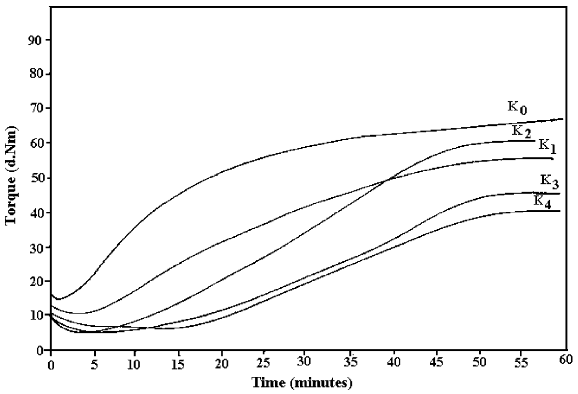


Fig. 1. Rheograph of the mixes cured at 150 °C.

2.4. Swelling studies

A test piece weighing about 0.2 g was cut from the compression-molded rubber sample. The sample was immersed in pure toluene at room temperature for five days to allow the swelling to reach diffusion equilibrium. At the end of this period the test piece was taken out and the adhered liquid was rapidly removed by blotting with filter paper. Afterwards the swollen weight was immediately measured. The sample was dried in vacuum to constant weight and the desorbed weight was taken. The swelling ratio is defined as

$$R = (W_1 - W_0)/W_0 \tag{1}$$

where W_0 is the weight of the test piece before swelling and W_1 is the weight of the swollen test piece after time 't' of immersion. The swelling ratio is a direct measurement of the degree of crosslinking. The concentration of the crosslinks was determined using the equilibrium swelling data [7]. The volume fraction of rubber (V_{rf}) in the swollen network was then calculated by the method reported by Ellis and Welding [8] using the following equation:

$$V_{\mathrm{rf}} = [(D - fW)\rho_{\mathrm{p}}^{-1}]/[(D - fW)\rho_{\mathrm{p}}^{-1} + A_0\rho_{\mathrm{s}}^{-1}] \tag{2}$$

where D is the deswollen weight of the test specimen, A_0 is the weight of the solvent absorbed, f is the volume fraction of the filler, W is the initial weight of the sample. ρ_{p} and ρ_{s} are the density of the polymer (1.32 g/cm^3) and solvent (0.858 g/cm^3) respectively. The crosslink density was determined using the Flory–Rehner equation [9].

$$M_{\mathrm{c}} = \frac{-\rho_{\mathrm{p}} V_{\mathrm{s}} (V_{\mathrm{rf}})^{1/3}}{[\ln(1 - V_{\mathrm{rf}}) + V_{\mathrm{rf}} + \chi V_{\mathrm{rf}}^2]} \tag{3}$$

where V_s is the molar volume of the solvent and χ the interaction parameter, which is given by the equation proposed by Hildebrand [10],

$$\chi = \beta + (V_s/RT)(\delta_s - \delta_p)^2 \tag{4}$$

where β is the lattice constant which was taken as 0.38, R is the universal gas constant, T the absolute temperature, δ_s, δ_p are the solubility parameter of the solvent and polymer (17.6×10^{-3} and 18.2×10^{-3}) $(\mathrm{J/m^3})^{1/2}$ respectively.

2.5. Dynamic-mechanical measurements

Dynamic-mechanical thermal analysis (DMTA) tests were conducted on an Eplexor™ 150 N (Gabo Qualimeter, Ahlden, Germany) device. Viscoelastic material parameters such as mechanical loss factor, loss modulus and storage modulus ($\tan\delta$, E'' and E' respectively) were measured over a broad temperature range (−110 to +60 °C) at a heating rate of 0.8 °C/min. Rectangular specimens 60 mm × 10 mm × 6 mm (length × width × thickness) were subjected to tensile loading consisting of a static preload of 3 ± 1 N on which a sinusoidal wave of 1.5 ± 0.5 N at 10 Hz frequency was superimposed.

2.6. Scanning electron microscopy studies

In order to study the dispersion of HD-PUR on chrloroprene rubber scanning electron microscopic (SEM) studies were done on a Joel (Tokyo, Japan) scanning electron microscope (SEM). The failure behaviour was also analysed using SEM. The samples were broken in liquid nitrogen and the phase morphology was examined.

3. Results and discussion

3.1. Cure characteristics

The cure characteristics of HD-PUR loaded chloroprene rubber are shown in Table 2. The difference in maximum and minimum torques (Mh − Mn) is a measure of the modulus of the compound. It is seen that the Mh − Mn values decrease with the addition of HD-PUR. This indicates a decrease in modulus, which in turn is a measure of crosslinking. It may also be noted that the mix with 20 phr of the filler shows the highest torque (modulus) values. This composition could be considered as the optimum concentration as far as modulus values are concerned.

Table 2
Cure characteristics

	K_0	K_1	K_2	K_3	K_4
Mh − Mn (d Nm)	46	44	55	39	32
Optimum cure time (min)	35	39	43	45	48
Scorch time (min)	7.5	7	8	9	11
Cure rate index (min^{-1})	3.64	3.13	2.85	2.77	2.70

As far as the cure activation is concerned, it is seen that HD-PUR deactivates the cure process. With PUR loading, the optimum cure time (t_{90}) increases. Fourier transform infrared spectroscopy studies made earlier [2,5] revealed the presence of primary as well as secondary amine groups in HD-PUR. These amines may interact with chloroprene rubber and there is a possibility of hydrogen bonding between the amines and chloroprene. A schematic representation of the possible interactions is shown in Scheme 1. It is known that organic compounds containing nitrogen atoms are capable of forming complexes with curatives. Since the amines in HD-PUR can form hydrogen bonds with CR, the nitrogen present in amines is not free to form complexes with curatives. The complex forming capability of amines depends on the availability of lone electron pairs on nitrogen atom. The greater this availability the more will be the complex forming ability. Since the amines are in strong interaction with chloroprene molecules, the availability of lone pairs of electrons become difficult and consequently the relative concentration of amine-curative complexes decreases remarkably.

This may be the reason for cure retardation is observed in this system. At the same time scorch time is found to increase with HD-PUR addition. HD-PUR acts as inhibitor for cure initiation. This clearly shows that HD-PUR does not influence the cure initiation and on the other hand scorch safety of the mixes increases. This is advantageous as far the processing safety is concerned. Cure rate index, which is a measure of the rate of the cure reaction, is given by

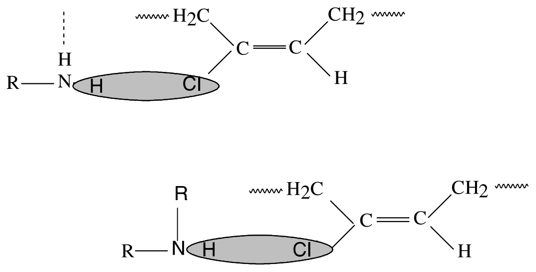
$$\mathrm{CRI} = 100/(t_{90} - t_{10})$$

It is seen that cure rate index decreases with HD-PUR addition and it supports the deactivation of cure reaction shown by the HD-PUR.

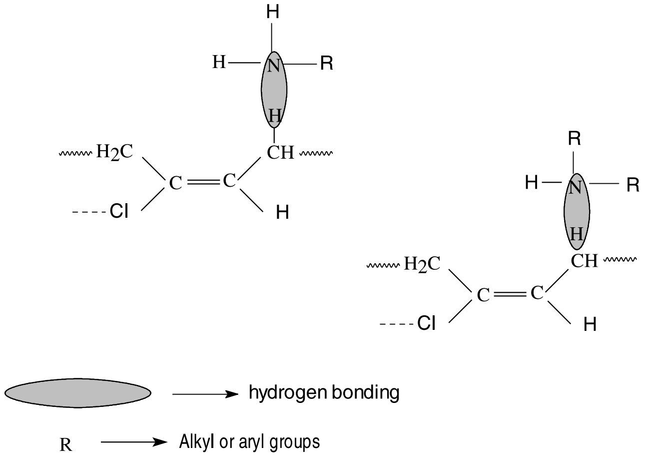
3.2. Phase morphology

In order to get a clear idea of the HD-PUR distribution the cured samples were cryogenically fractured and morphology was studied (Fig. 2). Two phases could be seen so that HD-PUR is dispersed in CR matrix. Absence of vacuoles indicates high level of interaction between CR and HD-PUR, from which an improved strength for the CR filled with HD-PUR can be predicted.

Polar interactions between Cl of chloroprene rubber and H of primary and secondary amines



Hydrogen bonding between N of primary and secondary amines and H of chloroprene.



Scheme 1.

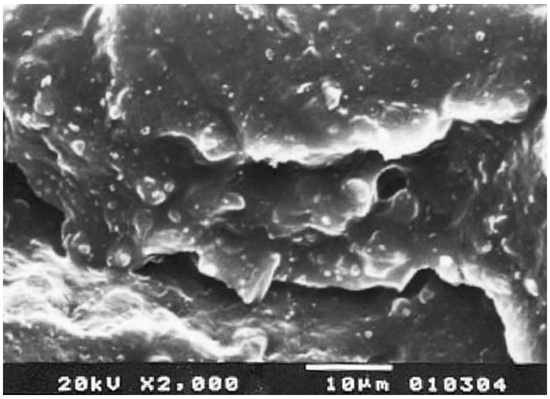


Fig. 2. Phase morphology of cryogenically fractured chloroprene rubber filled with HD-PUR.

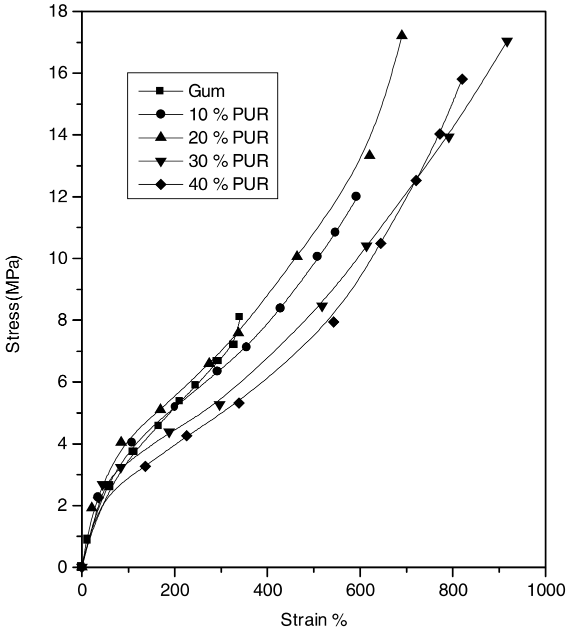


Fig. 3. Stress–strain graphs of the vulcanizates.

3.3. Tensile properties

Characteristic stress–strain graphs of the vulcanizates are shown in Fig. 3. It is seen that with the addition of HD-PUR, stress values show an increase along with the strain values. The strain at break is less for the reference compound. As the concentration of HD-PUR increases the strain at break also increases. At the same time the strength of the vulcanizates also increases as strain increases. It is clear from this figure that CR shows strain crystallising behaviour. Addition of HD-PUR does not hinder the strain crystallising nature of CR. This is because the structural regularity is not hindered with HD-PUR. It is important to note that HD-PUR in CR does not inhibit the strain-induced crystallisation of CR. This may be explained by considering the hydrogen bonding interaction between the CR and HD-PUR. Usually polar interactions such as hydrogen bonding will not affect the strain-induced crystallinity, otherwise it may enhance the crystallinity to a certain extent. Also these interactions resulted in an increase in tensile strength. Table 3 shows the influence of HD-PUR on tensile properties of CR. It is seen that the modulus at 300% elongation first decreases with filler loading, then increases and reaches a maximum at 20 phr and after that a decrease is observed. The Young's modulus values also show more or less a similar trend. The maximum value is shown at 20 phr filler and after that a regular decrease is observed. The elongation at break values showed an increase with HD-PUR addition. The strain crystallising nature of HD-PUR/CR vulcanizates is clear from the shape of the tensile stress–strain curves. Due to the interaction of the amine group (primary and secondary) in HD-PUR with chloroprene a better stress transfer occurs between the CR and HD-PUR and this leads to increased mechanical properties. Characteristic tear curves are given in Fig. 4. It is clear from this figure that the addition of HD-PUR increases the tear strength of the mixes. The strength and the modulus values of HD-PUR loaded CR samples could be explained by two factors. (1) At lower loadings polar interactions help effective stress transfer between the filler and the matrix. After an optimum loading, the primary and secondary amine groups may form hydrogen bond between them and as a result agglomeration occurs between the PUR domains. This prohibits an effective stress transfer between the matrix and the PUR phase. (2) Another explanation is given by considering the fact that at lower loading there is not enough PUR particles to give adequate reinforcement and at higher loading there is a shortage of rubber to fill all the voids in the filler. At optimum loading the bonding capacity of HD-PUR is fully exhausted and the vulcanizates are likely to exhibit the highest mechanical properties.

Table 3
Mechanical properties

	K_0	K_1	K_2	K_3	K_4
Tensile strength (MPa)	8.1	12.0	17.2	16.0	15.8
Tear strength (N/mm)	13.8	15.9	18.8	18.3	11.9
Modulus at 300% elongation (MPa)	6.8	6.4	7.06	5.5	4.9
Young's modulus (MPa)	1.32	1.33	2.21	1.53	1.31
% Elongation at break	341	577	690	916	820

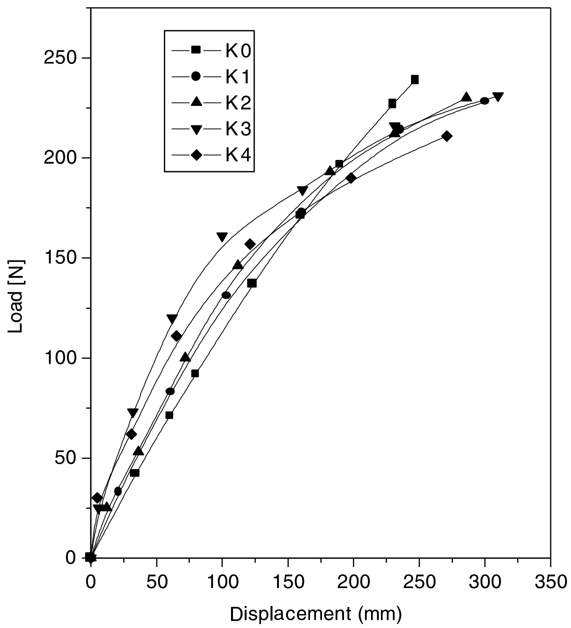


Fig. 4. Tear curves of the vulcanizates.

3.4. Failure surface morphology

The morphology of tensile fractured gum samples is shown in Fig. 5a and b. The SEM pictures clearly reveal the morphology changes on the addition of HD-PUR samples. Catastrophic failure is observed in neat CR compounds, which indicates a low strength. The stick slip failure of CR is clear from the SEM pictures of the gum compound. Fig. 5c and d show the fracture surface morphology of CR containing 30% HD-PUR filled samples. Though this type of failure is also shown in 30% HD-PUR/CR compound here it is less prominent. It is seen that HD-PUR loaded sample shows improved mechanical properties. From the SEM, figures, extensively deviated fracture path could be seen. Accordingly, the HD-PUR filler particles increase the resistance to the crack propagation via a crack tip deflection mechanism. This supports the high strength obtained for the HD-PUR filled compound.

3.5. Dynamic-mechanical studies

The variation of storage modulus (E') with temperature of gum and HD-PUR loaded CR is shown in Fig. 6. Three distinct regions are visible in the graph, viz, the

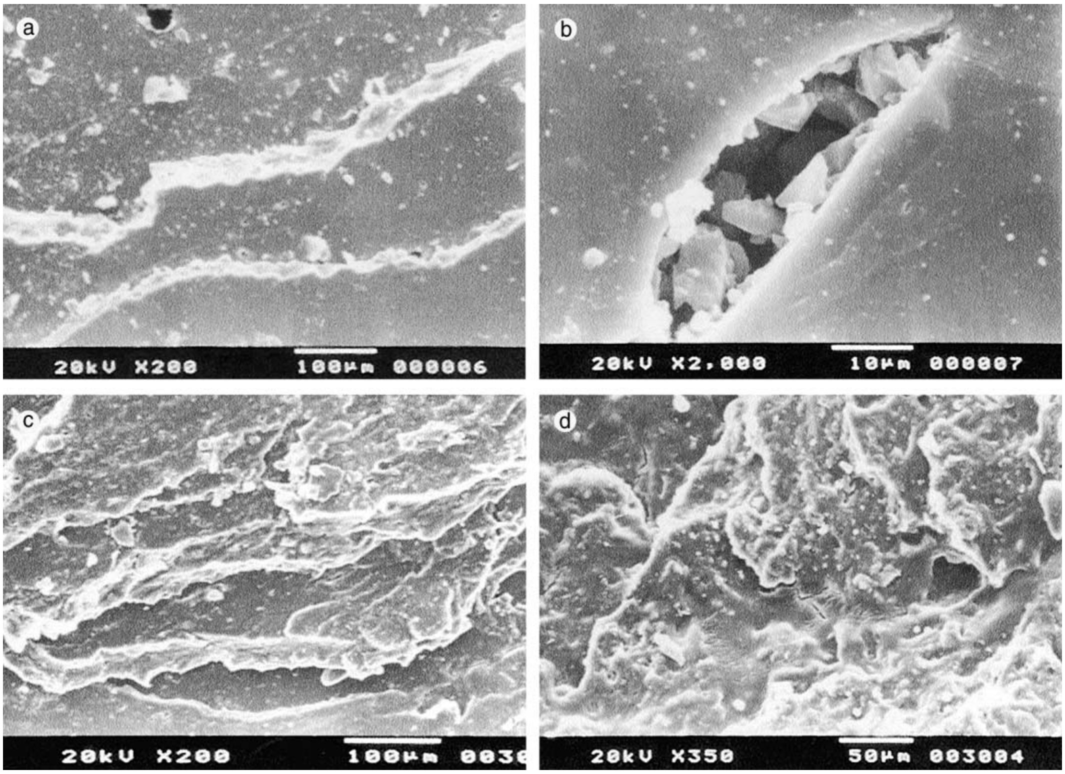


Fig. 5. Failure surface morphology of unfilled (a,b) and HD-PUR filled (c,d) samples.

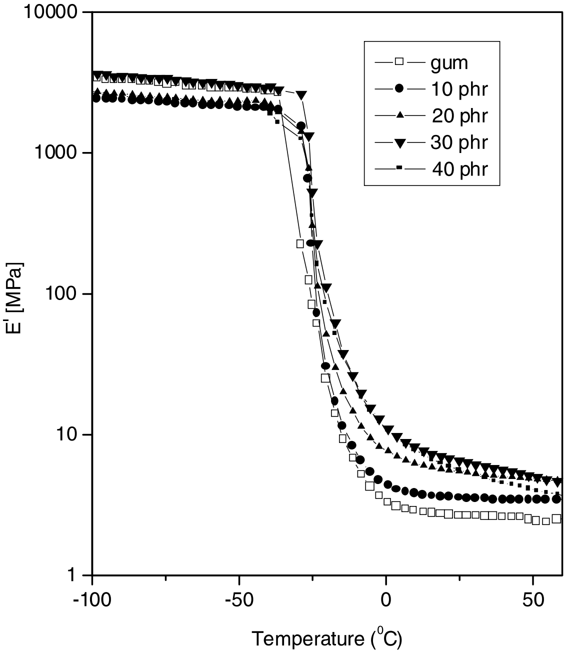


Fig. 6. Variation of storage modulus with temperature of HD-PUR loaded CR vulcanizates.

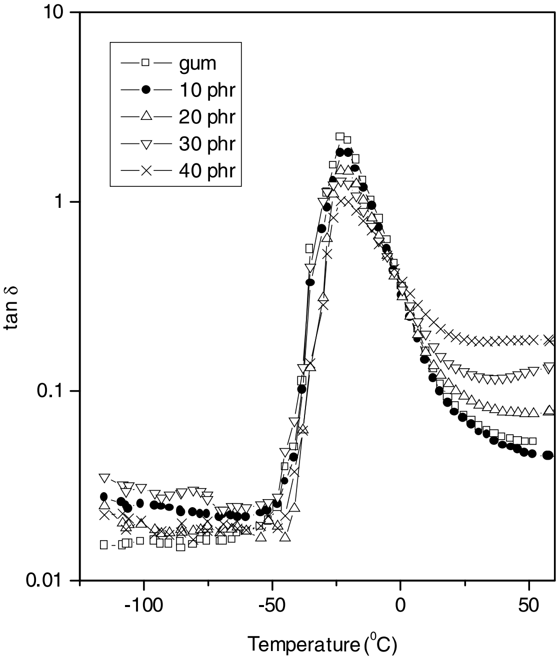


Fig. 7. Variation of loss factor with temperature of HD-PUR loaded CR vulcanizates.

glassy region, transition region and the rubbery region. No systematic change is observed in the modulus in the glassy region. But in the rubbery region with HD-PUR addition higher modulus is observed for 20 and 30 phr HD-PUR loaded samples. This is interesting as it correlates well with observation in mechanical properties. This clearly indicates the reinforcing action of HD-PUR.

The influence of filler addition on loss factor (tan δ) and loss modulus (E'') for a wide range of temperatures is given in Figs. 7 and 8. A sharp peak is observed at the T_g region of the CR phase. The height of the peak is generally a measure of damping nature of the compound. From the loss modulus and loss factor curve it is observed that the height of the peak reduced with HD-PUR addition. This indicates lower damping. This is disadvantageous as far as damping applications are concerned. But it is known that lower damping indicates for improved strength. The tan δ peak and E'' peak are an indication of crosslinking. It is seen from both the figures that the tan δ peak and E'' peak corresponding to CR are shifted to a positive region slightly with increasing HD-PUR concentration. This indicates an increase in the extent of crosslinking. This may be the reason for improved strength of the materials.

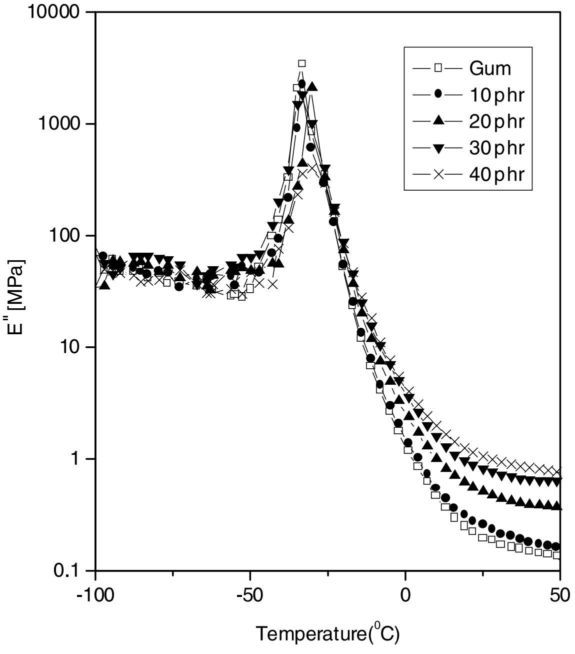


Fig. 8. Variation of loss modulus with temperature of HD-PUR loaded CR vulcanizates.

3.6. Crosslink density measurements

The swelling ratio of the samples gives a direct measure of the crosslink density. As the swelling ratio decreases the degree of crosslinking increases. The swelling ratio values are given in Table 4. This value decreases with increasing HD-PUR. It is in agreement with the observed crosslink density. In order to study the effect of HD-PUR on crosslink density of the CR vulcanizates, HD-PUR was considered as filler and calculations were made accordingly.

Mooney–Rivlin [11] equation was used for calculating the amount of crosslinks from stress–strain measurements. According to this equation,

$$v = \frac{F}{2A_0\rho RT(\alpha - \alpha^{-2})} \tag{5}$$

'v' is the physically effective crosslink density, F is the force, A_0 is the area of cross section, R is the universal gas constant, T is the absolute temperature and 'α' is the extension ratio of the sample. In this method the crosslink density is related to the extension ratio of the samples, which is subjected to tension. It can be seen that the crosslink density values follow similar trends in both types of measurements. The highest values are shown by the stress–strain measurements. The physically effective crosslink density contains a contribution due to the chemical crosslinks, chain entanglements and loose chain ends acting as crosslinks in rubber. The physically effective crosslink density is in general higher than estimated, because the estimates are based on the concentrations of purely chemical crosslinks without contributions of chain ends and entanglements [12].

According to the statistical theory of rubber elasticity, the crosslink density for a tetra functional network can be calculated according to the equation

$$v = E'/6dRT \tag{6}$$

where E' is the dynamic storage modulus measured from the rubbery plateau region. The calculated crosslink

Table 4
Network characterisation

Crosslink densities from	K_0	K_1	K_2	K_3	K_4
Swelling $v \times 10^5$ (mol/g)	1.69	2.14	2.34	1.72	1.15
Stress–strain $v \times 10^4$ (mol/g)	1.01	0.983	1.84	0.98	0.92
Modulus $v \times 10^4$ (mol/m^3)	2.42	3.46	4.92	4.92	3.97
Swelling ratio	2.52	2.32	2.27	2.31	2.30

density values are given in Table 4. All the mixes follow the same trend in crosslink density. The higher values are shown by K2 and K3 mixes with a loading of 20 and 30 phr HD-PUR respectively, which is in accordance with the observed crosslink density values from swelling and stress–strain measurements.

4. Conclusions

The influence of hygrothermally degraded polyesterurethane HD-PUR on cure characteristics, mechanical, dynamic-mechanical and morphological characteristics of CR has been studied in detail. The addition of HD-PUR was accompanied with a decrease in cure rate of CR. This may be due to the inability of nitrogen present in primary and secondary amine groups to form complexes with the curatives. The strain-induced crystallisation of chloroprene rubber is not affected by the HD-PUR addition. Properties like tear strength, Young's modulus and modulus at 300% elongation increased with PUR addition and a maximum value is shown by 20 and 30 phr. The improvement in mechanical properties is explained on the basis of interaction between amine groups, present in the HD-PUR, with the polar chloroprene rubber. The crosslink density of CR increased with HD-PUR addition, which is evidenced by the values obtained from swelling, stress–strain and dynamic modulus measurements. Dynamic mechanical studies proved the ability of HD-PUR to impart higher modulus in chloroprene rubber. Even if damping is decreased appreciable values are shown by 20 and 30 phr loading. A slight shift in glass transition temperature, obtained from the loss modulus curves indicated increase in crosslink density with HD-PUR. The study of the specimen morphology supported the observed improvement in mechanical properties with the addition of HD-PUR. Based on the present study it is concluded that HD-PUR could be effectively used as filler in chloroprene rubber and in order to get best properties an optimum loading of 20–30 phr is suggested.

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References

[1] Mathew G, Sing RP, Laxminarayanan R, Thomas S. J Appl Polym Sci 1996;61:2035.

[2] Isayev AI, Chen J, Tukachinsky A. Rubber Chem Technol 1995;68:267.

[3] Karger Kocsis J, Gremmels J, Mousa A, Ishiaku US, Mohd Ishak ZA. Kautsch Gummi Kunstst 2000;53(9):528.

[4] Mousa A, Karger Kocsis J. Plast Rubber Compos 2001; 30(7):309.

[5] Gremmels J, Karger Kocsis J. Kunststoffe 2000;90(5):112.

[6] Karger Kocsis J, Gremmels J. SPE-ANTEC 2000;46:840.

[7] Gorton ADT, Pendle TD. N R Technol 1976;7(4):77.

[8] Ellis B, Welding GW. Rubber Chem Technol 1964;37:571.

[9] Flory J, Rhener J. J Chem Phys 1943;11:5120.

[10] Hildebrand JH, Scott RL. The solubility of non-electrolyte. 3rd ed. New York: Van Nostrand Reinhold; 1950.

[11] Rivlin RS. Rubber Chem Technol 1992;65:G51.

[12] Campbell DS, Chapman AV. J Rubber Res 1990;5(4):246.