Chapter 4

Dynamic Mechanical Properties: Effects of Blend Ratio, Reactive Compatibilisation and Dynamic Vulcanisation

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4.1 Introduction

Miscibility between two polymers is usually characterised by dynamic mechanical analysis or viscoelastic data. The viscoelastic properties like storage modulus, loss modulus and loss tangent of polymer depend on structure, crystallinity, extent of crosslinking, etc. Karger-Kocsis and Kiss have investigated the effect of morphology on the dynamic mechanical properties of PP/EPDM blends. The presence of two phase morphology and two separate damping peaks for blend components remaining at their original positions in the dynamic mechanical spectrum indicated the incompatibility of the system. Influence of microstructure on the viscoelastic behaviour of polycarbonate/styrene acrylonitrile copolymer (PC/SAN) blend has been studied by McLaughlin and Guest and Daly. The compatibility of polycarbonate with polystyrene and polyester was investigated by Li et al. using dynamic mechanical and DSC measurements. Their investigations indicated that the PS/PC system is partially miscible since the Tg values corresponding to PC and PS are composition dependent. Wippler reported on the dynamic mechanical properties of PC/PE blends. They have used Takayanagi model to predict the behaviour of experimental storage modulus.
The effect of polychloroprene (CR) content on the storage moduli of ABS was reported by Kang et al. They found that the storage moduli of the blends increase with increase in CR content. Recently, the influence of blend composition on the viscoelastic properties of NR-EVA and NBR-EVA blends has been investigated. The damping factors of these blends are found to increase with increase in rubber content, and this behaviour has been correlated with the phase morphology of the system.

The miscibility of poly(vinyl chloride) (PVC) with 50% epoxidised natural rubber (ENR) was investigated by Varughese et al. using dynamic mechanical and DSC measurements. These blends showed a single Tg lying between the Tg's of pure components, which indicated the miscibility of the system. They also found that a moderate level of broadening of glass transition temperature region occurs with increasing PVC concentration.

The effect of compatibilisation on the dynamic mechanical properties of various polymer blends has been reported. The investigations of Brahim et al. indicated that the addition of pure and tapered diblock copolymers into PE/PS blends enhances the phase dispersion and interphase interactions of these blends and that the addition of excess copolymer create micelles. Ramesh and De investigated the effect of carboxylated nitrile rubber as a reactive compatibiliser in PVC/ENR blends in terms of dynamic mechanical data. The DMA results indicated that an immiscible composition of PVC/ENR blends becomes progressively miscible by the addition of XNBR. The addition of ethylene-methyl acrylate copolymer as a compatibiliser in LDPE/PDMS blends was found to shift the Tg values corresponding to the homopolymers. Cohen and Ramos have used the mechanical model of Takayanagi to describe the viscoelastic behaviour of binary
and ternary blends of cis-1,4-polyisoprene, 1,4-polybutadiene and the polyisoprene-polybutadiene block copolymer.

The effect of static and dynamic vulcanisation on the dynamic mechanical properties of polymer blends has been reported. Kuriakose et al. investigated the effect of dynamic vulcanisation of PP/NR blends on the viscoelastic properties. They found that the increase in storage modulus and decrease in loss modulus becomes more remarkable as extent of crosslinking increases. Thomas et al. investigated the effect of dynamic vulcanisation on the dynamic mechanical properties of NR/EVA blends. Liao et al. reported that the damping characteristics of the dynamically cured IIR/PP blend depend on blend composition and the curative level. PVC/ENR blends upon dimaleimide vulcanisation showed a lowering in storage and loss moduli in the glassy zone. The damping peak became narrow upon dynamic vulcanisation.

In many practical applications, since the materials usually undergo cyclic stressing, the study of viscoelastic properties are very important. In this chapter the effect of blend composition and morphology on dynamic mechanical properties of PP/NBR blends have been investigated. The effect of compatibiliser concentration and dynamic vulcanisation was also investigated. The dynamic mechanical properties have been correlated with the morphology of the blend. Attempts have also been made to predict the experimental dynamic mechanical properties using existing theoretical models.

4.2 Results and discussion

4.2.1 Binary blends

The dynamic mechanical properties such as storage modulus (E'), loss modulus (E'') and damping (tan δ) of the pure components and the blends were
evaluated from -50 to 150°C. Figures 4.1–4.3 show the variation of tan δ, E'' and E' Vs temperature for the homopolymers. The tan δ curve of nitrile rubber shows a peak at -16°C due to the α-transition arising from the segmental motion. This corresponds to the glass transition temperature (Tg) of nitrile rubber. Polypropylene shows glass transition temperature at 25°C, as shown by a tan δ peak at 25°C in the tan δ Vs temperature curve. Nitrile rubber has higher damping than polypropylene because of its rubbery nature. The loss modulus (E'') curve also shows the presence of loss maxima for NBR and PP at -20 and 25°C, respectively (Figure 4.2).

![Graph showing variation of tan δ of PP and NBR with temperature.](image)

**Figure 4.1.** Variation of tan δ of PP and NBR with temperature.
Figure 4.2. Variation of loss modulus ($E''$) of PP and NBR with temperature.

Figure 4.3. Variation of storage modulus ($E'$) of PP and NBR with temperature.
Nitrile rubber has higher storage modulus than polypropylene below the Tg region and the trend is reversed beyond the relaxation stage. In the case of nitrile rubber, the storage modulus shows a drastic fall around Tg while for polypropylene, because of its crystalline nature, the modulus drop is at a slower rate. The higher modulus of NBR compared to PP below the transition region is due to the fact that at this stage the entire molecular chains of amorphous NBR is frozen to form a fully glassy state. As NBR undergoes transition from the fully formed glassy state to the rubbery state, the storage modulus decreases considerably. In crystalline materials, during transition, only the amorphous part undergoes segmental motion, while the crystalline region remains as solid until its temperature of melting (Tm). Hence in the case of polypropylene, due to its crystalline nature, the storage modulus drops only at a lesser extent than that in NBR during the relaxation process.

Dynamic mechanical data was used to predict the miscibility of the system by various researchers.\textsuperscript{10,19-21} If two polymers are not compatible, the tan δ vs. temperature curve shows the presence of two separate damping peaks corresponding to the glass transition temperatures of individual polymers.\textsuperscript{19} For a highly compatible blend the curve will show only a single peak\textsuperscript{10} lying between the Tgs of the component polymers, whereas in partially compatible system a broadening of Tg is noticed.\textsuperscript{21} In the case of compatible and partially compatible blends the Tgs are shifted to higher or lower temperatures as a function of composition. The variation of tan δ with temperature of PP/NBR blends is shown in Figure 4.4. The blends show two tan δ peaks around -20°C and +20°C, which correspond to the Tgs of nitrile rubber and polypropylene, respectively. Two separate peaks corresponding to the Tgs of PP and NBR indicate that the blends are not compatible. The Tg corresponding to PP component is shifted to lower
temperature on the addition of NBR. This may be due to the plasticizing effect of NBR, by which the chain mobility of PP is increased. The damping of the blends increases with increase in concentration of nitrile rubber. The variation of $\tan \delta_{\text{max}}$ of the blends as a function of NBR content is shown in Figure 4.5. The increase in the damping and $\tan \delta_{\text{max}}$ with increase in NBR content is due to the reduction in the crystalline volume of the system on increasing the concentration of NBR whose damping is always higher than PP. The variation of $\tan \delta_{\text{max}}$ is more pronounced above 50 wt% of NBR. This behaviour can be explained in terms of the morphology of the blends. In $P_{70}$ and $P_{50}$, the NBR phase is dispersed as domains in the continuous PP matrix. In $P_{30}$, the NBR phase also forms a continuous phase resulting in a co-continuous morphology (Figure 3.2). Since above 50 wt% of NBR, it forms continuous phase, the $\tan \delta_{\text{max}}$ shows a pronounced variation due to the higher contribution of $\tan \delta_{\text{max}}$ from NBR phase.

**Figure 4.4.** Variation of $\tan \delta$ of PP/NBR binary blends with temperature.
The variation of storage modulus $E'$ of various blends as a function of temperature is shown in Figure 4.6. As in the case of blend components the modulus of the blends decreases with increase in temperature. It is seen from this figure that the modulus of the blends decreases with increase in NBR content. At the glassy region, $E'$ becomes higher for high NBR blends and its value drops down several decades faster above $T_g$. This behaviour can be attributed to the better glass forming characteristics of NBR with a higher degree of modulus value. Thus, $P_{30}$ in which NBR is also distributed as continuous phase, has the higher storage modulus below the transition region than the other ones in which NBR is in the form of dispersed phase only. Above the transition region, $E'$ is higher for low NBR blends due to the influence of crystalline PP.
Figure 4.6. Variation of storage modulus (E') of binary PP/NBR blends with temperature.

Figure 4.7 shows the variation of storage modulus at 30°C as a function of NBR content. As we have already discussed the modulus decreases with increase in rubber concentration and the curve shows a negative deviation from the additivity line. This negative deviation is due to the lack of interfacial interaction and adhesion between the non-polar crystalline PP and polar nitrile rubber phases. The curve shows a slope change from P30 to P30 due to the phase inversion of NBR from dispersed to continuous phase.

The variation of loss modulus with temperature (Figure 4.8) also shows the same trend as that of tan δ, i.e., the curves show two maxima corresponding to the glass transition temperatures of polypropylene and nitrile rubber. The loss modulus also increases with increase in NBR content.
Figure 4.7. Variation of storage modulus (E') of binary PP/NBR blends with wt % of NBR at 30°C.

Figure 4.8. Variation of loss modulus (E'') of binary PP/NBR blends with temperature.
4.2.2 Modelling of viscoelastic properties

Various composite models such as parallel, series, Halpin-Tsai, Coran's and Takayanagi's models have been applied to predict the viscoelastic behaviour of the binary blends. The storage modulus of PP/NBR blends was calculated for parallel, series, Halpin-Tsai and Coran's model using equations (3.2–3.6).

The viscoelastic behaviour of heterogeneous polymer blends can be predicted using Takayanagi's model. The Takayanagi model is given by

\[ E^* = (1-\lambda)E^*_M + \left[ \left(1 - \phi \right)/E^*_M \right] + \left(\phi/E^*_N\right) \]  

(4.1)

where \( E^* \) is the complex modulus of blend; \( E^*_M \), the complex modulus of matrix phase; \( E^*_N \), the complex modulus of the dispersed phase; and \( \lambda \phi \), the volume fraction of the dispersed phase and the values of \( \lambda \) and \( \phi \) related to the degree of series-parallel coupling.

As suggested by Cohen and Ramos, degree of parallel coupling of the model can be expressed by

\[ \% \text{parallel} = \left[ \phi(1-\lambda)/(1-\phi\lambda) \right] \times 100 \]  

(4.2)

Figure 4.9 shows the experimental and theoretical curves of storage modulus of PP/NBR blends as a function of NBR volume fraction. As expected the storage modulus values of these blends lie in between those of parallel and series models. The experimental values are close to Halpin-Tsai and Coran model \((n = 2.2)\) up to 50 wt% NBR. In the case of Takayanagi model, which is widely used for the prediction of viscoelastic data, the experimental values can be described with 20% parallel coupling. However for the P30 blend the experimental values are higher than those obtained from any other theoretical models. This may be due to the fact that all theoretical values are calculated, based on the assumption that NBR phase is dispersed in the continuous PP matrix. But in the case of P30,
the NBR also forms a continuous phase leading to a co-continuous morphology of
the blend (Figure 3.2c).

**Figure 4.9.** Experimental and theoretical curves of storage modulus of binary
PP/NBR blends as a function of wt % of NBR at 30°C.

### 4.2.3 Effect of compatibilisation

The variation of storage modulus as a function of temperature of 70/30
PP/NBR blends compatibilised with different concentrations of phenolic modified
polypropylene is shown in Figure 4.10. With the addition of 3% Ph-PP the
modulus of the unmodified blend is increased at lower temperatures i.e., below
glass transition temperature. However with further addition of compatibiliser (7.5
and 10 wt % Ph-PP) the storage modulus is decreased from the levels of P70
containing 3% Ph-PP. The increase in the modulus with the addition of 3% Ph-PP
is due to the increase in the interfacial adhesion caused by the emulsifying effect of
the block copolymer formed by the interaction between the phenolic modified
polypropylene and nitrile rubber (Figure 3.16). The better interaction between PP and NBR in presence of Ph-PP is evident from the morphology observed in SEM micrographs (Figure 3.8). At lower concentration of compatibiliser, the average domain size of NBR particles decreased due to interfacial tension reduction and high interfacial interaction. The decrease in modulus at higher concentration of the copolymer is due to the formation of micelles of the compatibiliser in the polypropylene matrix. As the micelle formation starts some of the copolymer already at the interface leaves the interface. This increases the domain size. Similar behaviour has been reported in the compatibilisation of PS/PE blends by PS-b-PE copolymers.\textsuperscript{11} Brahimi \textit{et al.}\textsuperscript{11} reported that the modulus of PE/PS blend increased by compatibilisation using PS-PE block copolymers up to interface saturation concentration and after that the modulus decreased. At higher temperatures all the blends of PP/NBR showed approximately the same modulus.

![Figure 4.10. Variation of storage modulus ($E'$) of Ph-PP compatibilised PP/NBR blends with temperature.](image-url)
Figure 4.11 depicts the variation of storage modulus $E'$ of 70/30 PP/NBR blend compatibilised with maleic anhydride modified polypropylene. In this case also the addition of 1% maleic anhydride modified polypropylene increases the modulus of the blend as compared to the unmodified one at lower temperatures i.e., below glass transition temperature of PP. At high temperatures the values are lower than the P$_{70}$ blend. When the concentration of MA-PP is increased to 10% the modulus shows lower values than that of P$_{70}$. At higher temperatures it shows values higher than that of the blend modified with 1% MA-PP. At temperatures above 50°C all the blends show nearly the same values of $E'$. In the modification of PP/NBR with maleic anhydride modified polypropylene (MA-PP), the MA-PP increases the interfacial interaction between PP and NBR by the dipolar interaction between polar maleic anhydride groups of MA-PP and polar NBR. The increased interaction at the interface may be the reason for the increase in the modulus upon the addition of 1% MA-PP. The further decrease in $E'$ by the addition of 10% MA-PP indicates the formation of micelles in the PP matrix. Here also, the increased interfacial interaction is evident from the small and uniform dispersion of NBR particles upon the addition of MA-PP. Above 1% MA-PP the domain size levelled off due to interfacial saturation (Figure 3.9).

![Figure 4.11. Variation of modulus ($E'$) of MA-PP compatibilised PP/NBR blends](image)
The variation of tan δ as a function of temperature of Ph-PP compatibilised blends is shown in Figure 4.12. The compatibilised blends also show the same behaviour for the tan δ curve as that of unmodified blend, i.e., the compatibilised blends show the presence of two maxima corresponding to the glass transition temperature of polypropylene and nitrile rubber. This indicates that the compatibilisation does not alter the level of miscibility. In other words, presence of a compatibiliser does not promote molecular level miscibility. This is in agreement with the conclusions made by Paul\textsuperscript{22} who suggested that if two polymers are far from being miscible, then no copolymer is likely to make one phase system. In a completely immiscible system, the main role of the compatibiliser is to act as an interfacial agent. At lower temperatures the tan δ values show an increase for 3 and 7.5% of Ph-PP. However, at intermediate temperatures the tan δ values of these blends are lower than that of unmodified blend. When the concentration of Ph-PP is increased to 10% the tan δ values decrease and the values are lower than those of P\textsubscript{70}. All the compatibilised systems show higher values of tan δ than unmodified blend at higher temperatures. This increase in tan δ indicates that the interfacial interaction caused by the presence of Ph-PP in PP/NBR blend may be weakened at higher temperatures. The decrease in interfacial interaction at higher temperature will decrease the interfacial adhesion and hence leads to increased segmental motion. The glass transition temperature corresponding to NBR remains unaltered by the incorporation of Ph-PP. However, Tg values corresponding to PP changes slightly with the incorporation of Ph-PP. On the addition of 3% Ph-PP, the Tg value remains the same as that of P\textsubscript{70}. However, in the case of 7.5 and 10% Ph-PP incorporation, the Tg values shift to a slightly higher temperatures.
Figure 4.12. Variation of $\tan \delta$ of Ph-PP compatibilised PP/NBR blends as a function of temperature.

The variation of $\tan \delta$ of MA-PP compatibilised PP/NBR blends is shown in Figure 4.13. By the incorporation of 1% MA-PP, the $\tan \delta$ values increase for the whole temperature range. When the concentration of MA-PP is increased to 10 wt% the $\tan \delta$ shows an increase at lower temperature and at intermediate temperature it decreases. In this case also, the decrease in $\tan \delta$ is due to the increase in interfacial interaction caused by the presence of MA-PP. The compatibilised blends have higher $\tan \delta$ than the uncompatibilised system at higher temperatures.
Figure 4.13. Variation of tan δ of MA-PP compatibilised PP/NBR blends as a function of temperature.

Figure 4.14 depicts the variation of loss modulus (E") as a function of temperature of Ph-PP compatibilised blends. The loss modulus shows a similar trend as that of tan δ curves. The E" curves show the presence of two peaks corresponding to the glass transition temperature of PP and NBR. Similar to tan δ curves, here also the addition of 3 and 7.5% Ph-PP increases the E". The values are lower than those of P70 at lower temperatures. At intermediate temperatures all the compatibilised blends show slightly lower E" values than P70.

In MA-PP compatibilised blends, the variation of loss modulus is shown in Figure 4.15. The behaviour is similar to tan δ curves. It shows the presence of two peaks corresponding to NBR and PP. At lower temperatures, 1 and 10% MA-PP modified blends show higher values of E" than those of the unmodified blend. At intermediate temperature the values of E" lie below that of unmodified blend. Here also at higher temperatures the compatibilised blends show higher values of E".
Figure 4.14. Variation of loss modulus ($E''$) of Ph-PP compatibilised PP/NBR blends as a function of temperature.

Figure 4.15. Variation of loss modulus ($E''$) of MA-PP compatibilised blends as a function of temperature.
4.2.4 Effect of dynamic vulcanisation

The variation of $E'$, $E''$ and $\tan \delta$ of P70 blend crosslinked with sulphur, dicumyl peroxide and mixed systems are shown in Figures 4.16–4.18. The modulus of the blends vulcanised with DCP and mixed systems shows higher values than the uncrosslinked system, while the sulphur crosslinked system shows the lowest value. In PP/NBR blends, on peroxide vulcanisation, there is a possibility of degradation of PP phase in the presence of DCP. However, the results from the figure indicates that the crosslinking reaction predominates over degradation reactions in the case of DCP vulcanisation. The increase in modulus for DCP system is also due to the crosslinking of NBR phase. In the case of sulphur system, sulphur crosslinks only the NBR phase and so shows the lowest modulus value. As expected the mixed system shows an intermediate behaviour.

![Graph showing variation of storage modulus (E') with temperature](image)

**Figure 4.16.** Variation of storage modulus (E') of sulphur, DCP and mixed (DCP + sulphur) vulcanised 70/30 PP/NBR blends with temperature.
Figure 4.17. Variation of loss modulus ($E''$) of sulphur, DCP and mixed (DCP + sulphur) vulcanised PP/NBR blends with temperature.

Figure 4.18. Variation of $\tan \delta$ of sulphur, DCP and mixed (DCP + sulphur) vulcanised PP/NBR blends with temperature.
The loss modulus values of the vulcanised systems shown in Figure 4.17 indicate that the loss modulus increases upon vulcanisation. Here also DCP system shows the lowest $E''$ and sulphur system shows the highest $E''$ values. The mixed system shows intermediate behaviour.

The variation of $\tan \delta$ with temperature (Figure 4.18) also shows the same trend as that of loss modulus i.e., among the crosslinked samples, the DCP crosslinked system shows the lowest $\tan \delta$ values and sulphur system the highest value. The mixed system shows intermediate values. In all cases the introduction of crosslinks increases the $\tan \delta$ values.

The morphology obtained from scanning electron micrographs (Figure 3.21) indicates that the crosslinking is more effective in DCP vulcanised system as proved by the presence of fine and uniform distribution of rubber particles in this case. However, this effect of crosslinking is not so predominant on the properties of the peroxide vulcanised system due to the degradation of PP phase in presence of DCP.

### 4.3 References